PRACTICAL APPLICATIONS OF SPECTRUM ANALYSIS

by

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PREFACE

The purpose of this book is to provide a trustworthy guide, as complete and self-contained as is possible in a single volume, for the practical spectroscopist engaged in analytical work connected with any field of study whatever. The necessary complementary volumes are tables of wave-lengths—*The Massachusetts Institute of Technology Wave-Length Tables* (John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London) certainly, and if possible the Kayser/Ritschl *Tabelle der Hauptlinien der Linienspektra aller Elemente nach Wellenlange geordnet* (Julius Springer, Berlin; Adam Hilger, London; 1939) as well. Pearse and Gaydon's *The Identification of Molecular Spectra* (Chapman & Hall) is also very desirable. Those engaged in industrial work in which saving of time is important should also keep in constant touch with the catalogues of instrument makers in order to acquaint themselves with the latest devices for particular parts of the process. No attempt has been made here to describe more than the essentials of the various forms of apparatus for producing luminosity, forming an image of the source, etc., embodied in simple but adequate equipment for all purposes except that of producing the greatest number of results in the shortest time. New devices are constantly being produced, and it would have been foolish to occupy space with descriptions of those current at the moment, which would probably have been superseded before publication.

The book is essentially a record of personal experience rather than a general conspectus of all the methods that have been used. It is an appropriate time for such a record, since I am now leaving this work after having been engaged in it for nearly thirty years, during the first half of which I was in the closest association with the late Professor A. Fowler, F.R.S., to whom I owe the foundations of my knowledge of the subject. An almost unlimited variety of problems have been presented to us at the Imperial College, nearly all of which have been parts of some wider biological, agricultural, geological, metallurgical or other investigation, and the solutions have not been separately published. It would be a pity, therefore, not to make available for others, as far as may be, the general experience gained.

The small amount of space given to quantitative spectrum analysis properly reflects, I believe, the present state of achievement in this field, but not the promise for the future. I have not thought it desirable to give more than the general principle of the many *ad hoc* methods used in particular industries—lack of space alone would have prohibited this

—but I have given what I believe must be the foundation of any practicable general method for such work. The principles of the production of spectra are now sufficiently well understood to make a theoretical approach possible, and it is most desirable that the problem should now be dealt with in this way rather than by narrowly empirical methods which, however useful they may be for their own special purposes, have no trustworthy wider application. I do not know of any previous attempt at a theoretical approach to the general problem.

While the book is in no sense a theoretical account of spectroscopy, I have tried to give sufficient theory, both of the mechanism of radiation and of the optical principles exemplified in the spectrograph, to enable the worker to form a mental picture of what is happening and to readjust his instrument for any desired end. The book should therefore be useful not only for the fortunate worker who can obtain fresh apparatus for each special purpose, but also for him who has to use the same instrument for all purposes and even to construct that instrument from parts separately acquired.

I am glad to record my thanks to various students and colleagues at the Imperial College for help with the illustrations. They are too numerous to mention personally, and of the source of some of the earlier plates I have no record. Except where special acknowledgement has been made, the illustrations were all produced at the Imperial College or have been associated with it so long that they have come to be regarded as such. For all inadvertent omissions of acknowledgement I express my regret. My thanks are also gratefully accorded to Dr. G. R. Harrison for permission to include the M.I.T. list of *raies ultimes* in Table V; to the Director of the Lick Observatory and Dr. K. Burns for permission to include Table II; to the Physical Society and Drs. A. Hunter and R. W. B. Pearse for permission to include the Table on p. 58; to the Institute of Physics and Dr. R. W. B. Pearse for permission to include Fig. 9; and to Messrs. Hilger & Watts, Ltd., for permission to include Plate XVIIIA, their list of *raies ultimes* in Table V, and the portions of the iron arc spectrum in Plates X and XI.

H. D.

London,
June 1949

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CHAPTER

1

GENERAL PRINCIPLES

THE FUNDAMENTAL PRINCIPLE of spectrum analysis is very simple. If any substance is made hot enough to become luminous and (if it is not already so) gaseous, the light which it emits is characteristic of the chemical nature of the substance. If, then, the radiations of all kinds of known substances are examined and recorded, the nature of any unidentified substance can be determined by subjecting it to the appropriate treatment and comparing its radiations with the record.

The application of this principle is obviously attended by certain difficulties, which are, however, not insuperable. In the first place, the characteristics of the radiation which are most distinctive must be determined. These are found to be (using everyday language) the particular individual colours, with their relative intensities, which make up the total light emitted. Any particular combination of colours can be emitted by one substance and one substance only. When, by a suitable arrangement, the total radiation is analysed into its component colours, arranged side by side, the result is known as the *spectrum* of the substance, and the fundamental principle of spectrum analysis may therefore be expressed by the statement that each substance can be made to yield a characteristic spectrum by which it can be identified.

Secondly, there are an indefinitely large number of substances, and it is a practical impossibility to record the spectrum of every kind. This difficulty can be partly overcome by making them so hot that they are dissociated into their elements. The resulting spectrum is then made up of the spectra of the various elements in the substance examined, and since there are only 92 natural elements in the chemist's table, their spectra can be recorded without undue labour. This solution of the problem, of course, gives us no knowledge of the state of combination of the elements in the original substance. That can be determined spectroscopically only comparatively rarely. Compounds, like elements, yield characteristic spectra which sometimes serve to identify them, but more often the process of making the substance gaseous and luminous necessarily breaks it up into simpler compounds or into elements, or may cause it to form new compounds by combination with the gases of the atmosphere or by internal chemical reaction.

For this reason spectrum analysis is chiefly applied to the determination of the elementary constituents of the substances examined, although in certain special cases it is applicable to compounds also.

The greater proportion of such cases are those of semi-transparent compounds—especially gases and solutions—which may be identified not by the colours of the light they emit but by those of the light which they absorb when a beam containing light of all colours is passed through them. The issuing light is analysed, and the colours which are missing or weakened constitute the "absorption spectrum" of the substance. To yield an absorption spectrum the substance need not be heated; it is usually placed, in its existing state, in the path of the light, and it survives the ordeal unchanged. The absorption spectrum is not, however, even in these circumstances necessarily that of the complete substance, since certain groupings of atoms in the molecules may absorb colours characteristic of those groupings and not of the larger molecules of which they are a part. This is a particularly frequent occurrence with organic molecules. Nevertheless, the comparatively inactive part of the molecule does usually cause some slight modification of the absorption which serves as a clue to the nature of the whole substance.

The third complication is that although no two substances can give the same spectrum, the same substance may give several different spectra according to the physical conditions under which it is made to emit its light. In the wider applications of spectroscopy this is a most fortunate circumstance, for the spectrum of a single element—calcium, for example—while remaining recognisably the spectrum of that element, may show modifications which reveal the state of motion of the radiating body and the temperature, pressure and intensity of electric, magnetic and gravitational fields at the place of emission of the light. In spectrum analysis, however, it is on the whole an inconvenience, though not a serious or unrelieved one. The chief modifications of a particular spectrum arising from other than chemical causes are two. First, as the amount of an element diminishes, the number of colours in the spectrum gradually diminishes until, for very small amounts, only very few persist. These are known, after de Gramont, as *raies ultimes*, and it is necessary to know them for each element in order that an analysis shall be trustworthy: if, for instance, certain colours in a spectrum appear to be present but the *raies ultimes* are absent, then a mistake has been made and the colours in question must proceed from another substance. The second modification depends on the fact that every element can emit a number of distinct spectra as the energy which causes emission is gradually increased (e.g. as the temperature in the source is gradually raised). Thus we speak of the various calcium spectra as CaI, CaII, CaIII, etc., in the order of increasing stimulus. For a given means of excitation—for example, if the substance is made luminous in an electric arc—the complete spectrum obtained for an element Z may consist only of Zɪ, or of a mixture of Zɪ and Zɪɪ, or of Zɪ, Zɪɪ and Zɪɪɪ, and so on, according to the energy available and the ease with which the successive spectra are produced for the element Z. No ambiguity can arise from this fact if one keeps it in mind, but it requires that in comparing any particular spectrum with tables of standard spectra the character of the source of light shall be taken into account.

The net result, then, is that if practical difficulties can be overcome it is always possible to determine the elements present in a given substance by producing and examining its spectrum under controlled conditions: it is sometimes possible to determine the compounds present in the substance. The procedure is known as *qualitative spectrum analysis.*

To determine how much of a particular substance is present is a much more difficult problem which, up to the present, can be solved only in particular cases. This is the problem of *quantitative spectrum analysis.* All effective methods so far devised depend on the fact that if the amount of a substance in the source of light is increased, everything else remaining unchanged, the amount of light of any particular colour in its spectrum emitted in a given time is also increased, provided that the substance is not already present in excessive amount. It is therefore theoretically possible to determine the amount of substance by measuring the intensity of the light Other principles of quantitative analysis are conceivable. For example, the completeness of the spectrum may be used as an index, for, as we have already seen, when the amount of substance is reduced the colours gradually disappear; or since, as we shall see later, the amount of a particular element in a mixture has an effect on the spectrum of another constituent of the mixture, the measure of that effect might serve as a criterion. Neither of these phenomena, however, has yet provided a basis for practicable quantitative analysis, and we have therefore only to consider the problem of correlating the intensity of light of a particular colour with the amount of substance from which it proceeds. The great difficulty in doing this is to eliminate or satisfactorily allow for the numerous factors other than the amount of substance which influence the intensity of the light.

The Nature of Radiation. In order to form a clear idea of what is taking place when a spectrum is produced it is necessary to know something of the physical character of radiation and of the process by which it is emitted from matter. This is one of the most fundamental of physical problems, and it may be said at once that the account which we shall give is not to be taken as the last word of the physicist on the matter. Ideas of radiation are in a process of transition, and the particular theory which is dominant at any moment in a limited field of study is to be thought of more as a symbol or an analogy or a metaphor than as a statement of absolute truth. Fortunately there is a particular view, comparatively easy to grasp, which is adequate for all the purposes of spectrum analysis. We may therefore describe it as though it were finally established, and the reader may use it with absolute confidence, remembering only that if he goes beyond spectrum analysis into more recondite problems of physics he will not necessarily find it suitable for his purpose.

According to this view, light consists of transverse waves in a medium called the ether, in which it travels at a speed of 3×10^{10} cm. (about 186,000 miles) a second in empty space.* The speed in transparent matter (air, glass, etc.) is slightly less than this and varies with the medium concerned. All light travels with the same speed in empty space, and different colours differ in *wave-length* (the distance between consecutive crests in the wave train) or *frequency* (the number of waves emitted from the source in a second). If c is the velocity, λ the wave-length, and n the frequency, then the fundamental equation of wave motion is

$$c = \lambda n.$$

This is obvious, for if n waves are emitted in a second and each occupies a length λ, then the total length occupied by the waves emitted in a second must be $n\lambda$, and this length is clearly the velocity of the waves.

It follows that since, in empty space, c is the same for all colours, λ must be inversely proportional to n. In a material medium c depends not only on the medium but also on the wave-length. A particular colour is therefore uniquely characterised by the frequency, and not by the wave-length or the velocity, for as the light of that colour passes from air into glass, say, both the velocity and the wave-length change, but their ratio, n, remains the same. It would therefore seem desirable, when speaking of colours in theoretical terms, to speak of them as "frequencies" rather than as "wave-lengths." The latter term is, nevertheless, most often used, because it represents a quantity which we can more directly measure. If light of a particular colour is given us we can measure its wave-length and also its velocity, but we can determine its frequency only by dividing the latter by the former; no direct method is possible. Hence, notwithstanding its indefinite character, tables for spectrum analysis invariably indicate each colour in a spectrum by its wave-length. The values given are generally those in air under ordinary conditions of temperature and pressure, for it is in air under such conditions that most of the measurements are made. It follows that if we wish to determine the frequency we must either divide the tabulated wave-length into the velocity of light of that colour in air, or else correct the wave-length to what it would have been if the light had been in a vacuum and divide the result into the velocity of light *in vacuo*. The latter is the alternative usually adopted.

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* The accepted value at the present time is $2{\cdot}99776 \times 10^{10}$ cm. a second.

As a particular example let us take the element mercury, which emits, among other colours, a green light whose wave-length in normal air is $5460{\cdot}740 \times 10^{-8}$ cm. The wave-length is always less in a material medium than in empty space, and to obtain the wave-length of this light in a vacuum we must add $1{\cdot}514 \times 10^{-8}$, giving $5462{\cdot}254 \times 10^{-8}$ cm. Dividing this into the velocity of light *in vacuo* given above, we obtain for the frequency, $5488{\cdot}188 \times 10^{11}$ waves per second. This is an inconveniently large number, and it is therefore customary to substitute for the frequency the *wave-number*, i.e. the number of waves per cm. of the wave train instead of the number of waves emitted from the source per second. This is evidently obtained by dividing the frequency by the velocity of light, giving 18,307·46. Obviously, therefore, the process of obtaining a wave-number is equivalent to finding the reciprocal of the corrected wave-length in cm. It is rarely necessary in analytical work to deal with frequencies or wave-numbers, the wave-length in air being the usual identifying characteristic of a colour, but it is nevertheless important to understand what the terms mean and to know how to obtain the corresponding measures if necessary.

The example just given shows that wave-lengths are very small quantities judged by ordinary standards. For this reason a special unit of length is chosen, known as the *angstrom*. It is approximately equal to 10^{-8} cm. A unit of this size was originally chosen by the Swedish physicist Ångstrom about the middle of the last century, and was then known as the *Ångstrom unit* or *tenth-metre*, since its value was 10^{-10} metre. To measure a wave-length in tenth-metres it was therefore necessary to compare it either with the standard metre or with another wave-length which had already been compared with the standard metre. For reasons of practical convenience the latter alternative was chosen, but it was subject to the disadvantage that if the measurement of the wave-length directly compared with the standard metre was erroneous (and to some extent, becoming increasingly important as the accuracy of measurement improved, it must inevitably have been so) all other measurements of wave-length necessarily partook of the error also. To obviate this the following device has been adopted. A chosen wave-length (that of a particular red colour emitted by the element cadmium), produced in a specified type of tube under definite controlled conditions, has been measured with the utmost attainable accuracy in terms of the standard metre at Paris: the result is $6438{\cdot}4696 \times 10^{-10}$ metre. A unit of length is then defined as follows:

$$\frac{\text{Wave-length of Cd red light in dry air at 15° C. and 760 mm pressure, where } g = 980{\cdot}67 \text{ C G S units}}{6438{\cdot}4696}$$

and called the *angstrom*. If, then, the measurement of this line should be absolutely accurate, the value of the angstrom is 10^{-10} metre. If there is a slight error in the measurement the value of the angstrom is slightly different from 10^{-10} metre. In either case, however, the measurements of other wave-lengths, obtained by comparison with red cadmium light, are unaffected; the mercury light mentioned above has still a wave-length of 5460·740 angstroms, but the value of the angstrom in terms of the metre is slightly uncertain. The measurement of the cadmium light, however, was one of the most accurate measurements ever made, so that we may regard the angstrom as 10^{-10} metre without qualification in all ordinary work. No error that may be discovered in the future can have any importance for spectrum analysis.

In view of a practice which is still far too common it is worth while to emphasise that the name of the unit is the *angstrom* and not the *Ångstrom unit*, and a wave-length should be written as 5460·740 A. and not 5460·740 Å.U. Not only is this officially correct (see *Trans. Int. Ast. Union*, vol. VI, pp. 338, 378, 1938) but also it is desirable for two other reasons. First, the cost of printing the small circle over the A when the symbol occurs frequently is by no means negligible in most countries. Secondly, the names of units are in general derived from but not necessarily identical with those of scientists associated with the measurements to which they refer; thus we speak of the *volt* and the *farad*, but not of the *Volta unit* or the *Faraday unit*; it would therefore be anomalous to choose *Ångstrom unit* instead of *angstrom* for wave-length measurement.

When a beam of light of all colours is passed through a material medium the velocity is reduced, as we have already seen, by an amount which varies with the colour. This fact may be used (the method will be described later) to separate the colours and set them out side by side in order of wave-length, thus making the spectrum susceptible of convenient inspection. When this is done it is found that the colours appear in the order shown by the rainbow—which is, in fact, the spectrum of sunlight—the wave-length decreasing regularly from the red end through orange, yellow, green, blue, indigo to violet. This corresponds to a range of wave-length from about 7600 to 3900 A. These figures are, of course, approximate only, since the colours are not sharply bounded and, moreover, the range of sensitivity of the eye varies from person to person.

The instrument for analysing the light is, in laboratory operations, always so constructed that each colour appears as a narrow line and the whole spectrum as a set of such lines arranged side by side (see, for example, Plate VI). For this reason the colours are usually referred to as "spectrum lines," but the use of this term should not lead us to forget that the linear form of the colour is an entirely artificial construction and may in certain circumstances be discarded. In astronomy, for example, the colours emitted by certain nebulae are often shown in the spectrum in the shape of the nebulae themselves, and it is sometimes convenient in laboratory observations also to modify the instrument so as to produce a similar result—for example, when small flames are being examined.

Beyond the visible spectrum at each end waves exist identical except in wave-length and frequency with light waves. Those at the violet end are known as *ultra-violet* and those at the red end as *infra-red* waves. Their existence may be demonstrated in various ways—the ultra-violet waves chiefly by their power of impressing a photographic plate or of exciting fluorescence in various materials, and the infra-red waves chiefly by their heating effect. The evidence up to the present is that there is no definite limit at either end to the wave-lengths that are possible, and that waves exist filling the range from a small fraction of an angstrom up to many kilometres in length. Out of this enormous array, spectrum analysis is concerned only with the range from about 2000 to 10,000 A. This includes the visible spectrum, a considerable stretch of ultra-violet and a little infra-red. The reason for this particular selection is two-fold. First, the most easily produced spectra of the elements—i.e. those earliest in the series earlier exemplified by ZI, ZII, . . .—fall mainly in this range; and secondly, those wave-lengths are the easiest to examine, for below 2000 A. the air becomes opaque and all work has to be conducted *in vacuo*, while above 10,000 A. photographic plates, if effective at all, are very insensitive.

The problem of spectrum analysis may thus be conveniently summarised as follows. First, the substance must be made to emit its characteristic waves; secondly, those waves within a limited range of wave-length must be separated and displayed as an array of separate radiations; thirdly, the wave-lengths of the radiations in the spectrum thus formed must be ascertained; and fourthly, the spectrum must be interpreted so as to yield the required information about the substance. In the ensuing pages, Chap. 2 will be concerned with the first of these stages, Chap. 3 and 4 with the second, Chap. 5 with the third, and Chap. 6, 7 and 8 with the fourth. First of all, however, it is necessary to consider in some detail the physical process of emission of light, for only thus can the problem be approached with a reasonable prospect of its mastery. The remainder of this Chapter, therefore, is devoted to an account of the view of this process which is now universally adopted in analytical work. Like the account of radiation just given, it is not a final description appropriate to all circumstances, but we shall present it as though it were, for it is entirely adequate for all the applications with which we are concerned.

Atomic Structure. Since the spectrum of a substance is characteristic of that substance and of no other, it must proceed from the ultimate units, for only there are various substances absolutely distinguished from one another. The ultimate units of an element are its atoms, and those of a compound its molecules. We must therefore look for the origin of spectrum emission in atoms and molecules. This leads us to expect that the spectrum of a mixture of substances will be a mixture of the spectra of the separate substances, for the respective atoms or molecules in a gas will each radiate more or less independently of the others. This expectation is realised, and is, indeed, a *sine qua non* for the spectroscopic analysis of a mixture. It is clearly necessary, therefore, in order to understand the process of spectrum emission, that we have some idea of the structure of atoms and molecules. We begin with atoms.

The atom of an element consists of a number of electric charges. At the centre is a "nucleus"—a "particle" whose exact structure is uncertain and is in any case immaterial for our purpose but which has always a positive electric charge, E, which is an exact multiple of a unit, e, whose value is $4{\cdot}8 \times 10^{-10}$ e.s.u. The various elements are distinguished by the particular multiple of this unit; thus the nucleus of the hydrogen atom has charge e, that of helium $2e$, and so on, through the periodic table, up to uranium, $92e$.* The coefficient of e in this series is called the *atomic number* of the element, and its value uniquely identifies the element to which it refers; thus, "helium", "He", "2" are three synonymous symbols for the element helium.

Outside the nucleus and revolving round it, like the planets round the Sun, are a number of *electrons*—unit negative charges each having a value $-e$. In the atom of every element the number of electrons is equal to the atomic number; the atom, of whatever element it may be, is therefore on the whole electrically neutral, for if its nucleus has a charge ne it is surrounded by a total electronic charge of $-ne$.

The unit, e, of positive charge, though electrically equal in magnitude to the unit negative charge, exists as a particle (called the *proton*) which is about 1836 times as massive as the electron. It follows that the nucleus of an atom must be at least 1836 times as massive as all the electrons which revolve round it taken together, for an atom of atomic number n must have at least n protons in its nucleus. It may have more, for if a proton and an electron, or any number of such pairs, could be added to the nucleus, the net charge, and therefore the atomic number, would be unaltered and we should therefore have the same element with a more massive nucleus. The same result would follow if a *neutron* (a particle with the mass of a proton but without electric charge), or any number of neutrons, were added to the nucleus. The mass of the atom of any element is therefore indefinite, for the element is characterised by the nuclear *charge*, which may conceivably be associated with nuclei having various masses above a certain minimum. It has been found, in fact, that the atoms of most elements have nuclei whose masses are not all the same, the variations arising probably from differences in the numbers of neutrons in the nuclei. Atoms with the same nuclear charge and different nuclear masses are called *isotopes*

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* A few elements beyond uranium have been formed artificially.

of the element to which they belong. Thus hydrogen has at least two isotopes, one (containing one proton) with a nuclear mass of one unit, and another (containing one proton and one neutron) with a nuclear mass of two units. In an ordinary sample of hydrogen, nuclei of the former type greatly outnumber those of the latter type, and the chemical "atomic weight," which represents the *average* weight of the atoms, is therefore slightly greater than 1, viz. 1·008. In Table I in the Appendix the elements are listed with their atomic numbers and atomic weights: it will be noticed that the latter are always greater than the former.

In their chemical properties and (except for refinements which lie beyond our present interest) their spectroscopic properties also the isotopes of an element are identical; only in their masses are the atoms distinguishable. This is because chemical and spectroscopic properties are associated almost entirely with the outer electrons and not with the nucleus. The number of outer electrons is determined by the nuclear charge and not by its mass, and since the electrostatic attraction between the nucleus and electron is overwhelmingly greater than the gravitational attraction, the orbit also of an electron is determined almost wholly by the nuclear charge. The isotopic composition of an element has therefore a negligible effect on its spectrum.

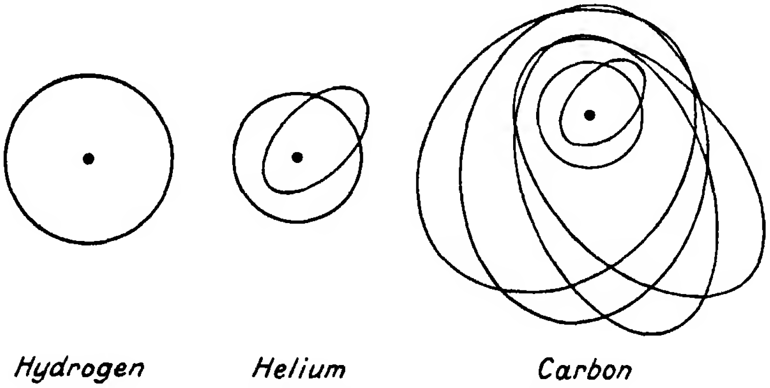

FIG 1.—Diagrams of electron orbits in atoms.

In atoms undisturbed by any outside agency the electrons revolve perpetually each in its own orbit round the nucleus. The orbits are to a first approximation circular or elliptical, and no two electrons share the same orbit. All atoms of the same element are identical with respect to their electronic orbits. Each electron in its revolution possesses a certain definite amount of energy, arising partly from its motion (kinetic energy) and partly from its position with respect to the attracting nucleus (potential energy). Fig. 1 shows, in purely diagrammatic form, the atoms of a few typical elements.

The Emission of Radiation. We are now in a position to understand what happens when an element radiates light. In order to do so it must be supplied with energy; it may be heated, or an electric current may be passed through it, or it may be bombarded by swiftly moving particles or stimulated in some other way, but in one form or another energy must be supplied. The atoms absorb this energy and then re-emit it as radiation (i.e. light or infra-red or ultra-violet radiation—we use the general term "radiation" to denote any of these forms of energy). The process by which this is done is as follows.

Although, in an undisturbed atom, each electron keeps to the same orbit always, it can, in certain circumstances, revolve in any of a number of larger ones. In each of these possible orbits it would have a definite amount of energy, which increases with the size of the orbit. When energy is available from an outside source, therefore, the electrons can absorb it by moving out to larger orbits: the atom is then said to be *excited*. They do not remain there, however, for it is only in their normal, smallest orbits that they are permanently stable. They therefore return inwards, giving out *as a beam of radiation* the energy they had absorbed for the outward journey. Any or all of the electrons in an atom may, in appropriate circumstances, be excited, but in general only one is so perturbed, and we shall suppose, in order to rid the description of unnecessary complications, that this always happens. The atom in the process of radiation thus behaves as a machine for transforming and scattering energy of various kinds into radiation: the energy, however it is supplied, is first changed into energy of electronic revolution in a larger orbit and then, through the inward movement of the electron, into radiation which is broadcast into space.

The larger orbits which our electron can temporarily occupy are definitely fixed for each kind of atom, and the amount of energy required to enable it to revolve in each of them is also definitely fixed. Thus, if the energy in the normal orbit is E_1, the electron has a choice of orbits requiring energy E_2, E_3, . . ., all larger than E_1, but it cannot revolve in intermediate orbits requiring amounts of energy lying between E_1 and E_2, or E_2 and E_3, etc. A certain minimum amount of energy (namely, E_2-E_1) must therefore be supplied before the atom can radiate at all. If less is available the atom cannot absorb it. Similarly, if energy greater than E_2-E_1 but less than E_3-E_1 is available, the atom can accept the amount E_2-E_1 but must leave the balance unabsorbed. It is just possible, if E_3-E_2 is not greater than the available energy, that an atom whose electron has moved out to orbit 2 might manage to pick up this amount before returning to its normal orbit, and so reach orbit 3 although there is not enough energy to take it direct from 1 to 3. This, however, is a comparatively rare occurrence, for the length of time an electron remains in one of the larger orbits is exceedingly small—something like 10^{-8} sec.—and it has therefore very little chance of absorbing energy before it starts to move inwards again. An electron may, however, on an inward journey stop at any of its possible orbits which it happens to meet; thus an electron moved from orbit 1 out to orbit 4 may return to orbit 3, 2 or 1 (there are certain exceptions to this, certain transitions which are said to be *forbidden*, but we may ignore these here). While in any of these orbits it may absorb more energy and move out to a more distant orbit, or it may take another jump inwards. We may thus picture the electrons, when there is a plentiful supply of energy continuously available, as constantly moving to and fro between orbits, each outward transition requiring the absorption of a definite amount of energy and each inward transition being accompanied by the radiation of a definite amount of energy outwards into space. In a furnace, for example, the kinetic energy of the rapidly moving and colliding atoms is absorbed by the electrons, which move out to larger orbits and in returning give out the light which comes from the furnace. Fig. 2 shows, again in purely diagrammatic form, some of the orbits in the hydrogen atom. This atom is chosen for simplicity, since it has only one electron, but the figure can represent any atom at all if it is understood that the central black dot represents all the quiescent part of the atom, i.e. the nucleus plus all the electrons except the one engaged in absorption and radiation.

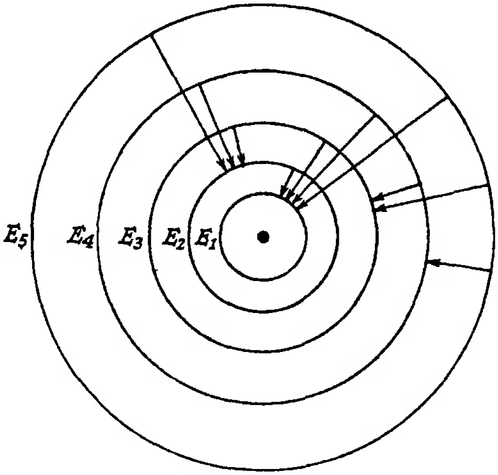

FIG. 2.—Electron orbits in the hydrogen atom.

The various amounts of energy, E_2-E_1, E_4-E_3, etc.—represented in general by $E_{n+a}-E_n$—which an atom can absorb are known as *quanta*, and it follows from the description just given that radiation is always emitted in quanta. It is a fundamental characteristic of the process that each quantum has a single frequency, given by dividing the amount of energy by a very small quantity known as *Planck's constant* and usually written h, which has the value $6{\cdot}624\times10^{-27}$ erg seconds. Thus the energy radiated by the transition from orbit 4 to orbit 3 has the frequency $(E_4-E_3)/h$. The radiation from the atoms of a given element, then, consists of a number of beams having definite frequencies. Together they constitute the spectrum of the element. At any instant one atom in the source of light will be radiating one possible frequency, another will be radiating a second possible frequency, another will be absorbing a quantum of energy, and so on; but since there are billions of atoms in even the smallest amount of substance of practical importance, we can be sure that at each instant there will be a large number radiating each frequency and so maintaining the spectrum constant. Moreover, the values of E_1, E_2, etc., though the same for all the atoms of any one element, differ from one element to another because the energies are determined by the electric field of the nucleus and the electrons. Hence each element will have its own characteristic spectrum.

The atom may absorb sufficient energy to remove its electron out of the sphere of influence of the atom altogether. It is then lost to the atom, which consequently has a resultant charge of $+e$ and is said to be *ionised*. The energy necessary for this varies from one element to another, but it is not excessively large and is often attained in the ordinary means of producing luminosity. At each ionisation, of course, the atom is split into an *ion*, as it is called, and a free electron, but if many atoms are so broken up recombination becomes frequent also, for the electrostatic attraction between an ion and an electron tends to bring this about when the two approach one another. For a given average rate of energy supply, therefore, we tend to establish a sort of equilibrium condition in which a fairly constant proportion of the atoms of each element are ionised and a certain proportion are neutral, i.e. have their full complement of electrons. Both kinds of atoms, neutral and ionised, are then subjected to the applied energy, and the ionised atoms respond to it in essentially the same way as the neutral ones, by the movement of one of the remaining electrons between possible orbits. The orbits, however, are not the same as those of the neutral atom because the electric field of the ion is not the same as that of the full atom. Hence the energies, and therefore the frequencies of the light emitted, are different—i.e. the ionised atom has a different spectrum from the neutral one.

The process of ionisation may be repeated if enough energy is available. An atom may become doubly, trebly, . . . ionised, emitting a fresh spectrum at each stage. An element has therefore a series of spectra—the series already referred to and symbolised, for an element Z, by Zɪ, Zɪɪ, ... Each of these spectra, as we have seen, is quite characteristic of the element Z and serves to identify it. With the means of excitation ordinarily used, only the first two members of the series, Zɪ and Zɪɪ, corresponding respectively to the neutral and singly ionised atoms, occur in any strength with most elements. The spectrograms with which we are concerned here may therefore be expected to contain, for each element, lines of each of these spectra, their relative prominence varying with the element and with the method used for making the substance luminous. Clearly, however, an element has theoretically a number of spectra equal to its atomic number.

Structure and Radiation of Molecules. A molecule is a group of atoms in which the satellite electrons are shared by the whole system of nuclei. In the simplest case—that of a diatomic molecule—for example, we have two nuclei surrounded by a double system of electrons which arrange themselves so that the whole configuration is in equilibrium. We may, if we wish, think of the natural repulsion of the similarly charged nuclei as being counteracted by the attraction of the electrons so that the system remains integrated. Although, in molecules composed of atoms of fairly high atomic number, some of the electrons may revolve round a single nucleus, the outermost ones must be regarded as belonging to the whole system rather than to the individual nuclei. A diatomic molecule (and the same applies *a fortiori* to a polyatomic molecule) is therefore not merely two atoms in close proximity but a single organisation in which the individuality of the constituent atoms is at least partly lost. Fig. 8 gives an imaginary picture of the atoms H and F and the molecule HF. It could, of course, correspond at best only to instantaneous states of the systems since the electrons are in rapid revolution, and in fact it is not to be regarded at all as an actual but only as a symbolic representation. It does indicate, however, that the electrons must be assigned primarily to the whole molecule, and not to the nuclei separately.

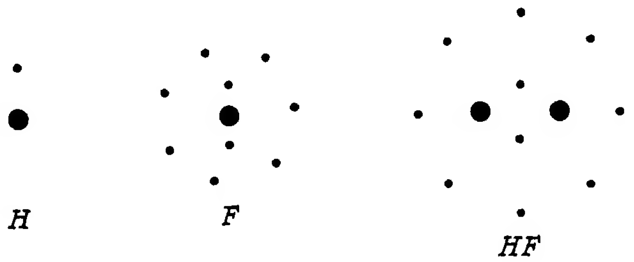

FIG. 8.—Diagrams of instantaneous states of atoms of hydrogen and fluorine and of molecule of hydrogen fluoride.

Radiation by molecules resembles radiation by atoms in that it occurs in discrete quanta characteristic of the particular molecule concerned. The molecule changes from one "energy level," as it is called, to a higher one by the absorption of energy in some form, and then returns to a lower energy level by the emission of the appropriate quantum of radiation of a single frequency. The difference is that the energy levels are determined not merely by the orbital energy of an electron but also by the energies of rotation and vibration of the system of nuclei. In a given state—say the undisturbed state, when the molecule is not radiating—the whole system (again, for simplicity, we consider only a diatomic molecule) is rotating with a certain definite frequency round an axis perpendicular to a line joining the nuclei. At the same time the nuclei are vibrating to and fro, again with a certain definite frequency, along the line joining them, so that they alternately approach and recede from one another many times a second. And, of course, the electrons are revolving, each in its own orbit and with its own energy. The process of absorption by the molecule may then consist of: (a) an increase of energy of rotation; (b) an increase of energy of vibration; or (c) an increase of electronic energy by a transition to an outer orbit. In each case if energy is absorbed it is absorbed in definite finite amounts; it cannot be taken up continuously or in amounts indefinitely small. Further, the absorbed energy, when re-emitted as radiation, is again sent out in finite amounts, each with its own definite frequency. The result is that the spectrum of a molecule is much more complicated than that of an atom: it is known as a *band spectrum*, in contrast to the *line spectrum* of the atom. An example is shown in Plate XIVB, which represents the spectrum of CN—a very familiar spectrum, since it is readily produced in a carbon arc in air.

It will be noticed that the spectrum consists of a number of groups of bands (or "flutings," as they used to be called), which appear to be sharply bounded on one side (the "head") and to fade away gradually on the other. Magnification shows that each band actually consists of a regular arrangement of close lines which get further apart as we recede from the head, and so give the appearance of fading out. Each group of bands is known as a "sequence" and a set of groups, such as that comprising Plate XIVB, is called a "band system." The reader will have no difficulty in identifying the single bands, the sequences of bands, and the system, of which the spectrum in the Plate shows only a part.

In terms of molecular changes the structure of a band system is interpreted as follows. *Each separate line* in the whole system corresponds in general to the resultant of three changes—of rotational, vibrational and electronic energy. (In particular cases it may happen that one of these changes does not occur, but that does not affect the general description.) In *each single band* the electronic and vibrational changes are the same, and the difference between the lines is therefore only in the rotational changes to which they correspond. In *a band sequence* the electronic change is the same for all the bands, but they differ in the vibrational changes. Nevertheless all the bands in a sequence arise from vibrational changes of the same *number* of quanta; it is the particular vibrational levels differing by that constant number that distinguish one band of a sequence from another. The ***different sequences in a system*** correspond to the same electronic energy change but to different numbers of quanta in the vibrational energy changes. We may sum this up by saying that the common characteristic of a system is the electronic energy change; that of a sequence is the electronic energy change plus the number of quanta in the vibrational energy change; and that of a band is the electronic energy change plus the actual vibrational energy change. The ***complete spectrum*** of a molecule may, of course, include several systems.

These somewhat complex considerations will not concern us to any appreciable extent in what follows. They are mentioned merely in order not to leave a common feature of spectra as though it were a complete mystery.

CHAPTER

2

SOURCES OF LUMINOSITY

It has been said in the former chapter that in order that a substance shall emit its characteristic spectrum it must be made gaseous as well as luminous. The reason is that only in a gas are the atoms and molecules far enough from their neighbours to radiate without interference. In a solid or liquid the atoms are practically in contact with one another. The energy of an electron in an orbit is therefore constantly undergoing violent changes as the electron approaches or recedes from an electron in an adjacent atom, and so no definite value can be assigned to it. If, therefore, the electron has moved to an outer orbit, the excess of energy which it radiates on its return (and therefore the frequency of the radiation, since that is proportional to the energy excess) may have various values, depending on the amount of the disturbance. Taking into account the very large number of atoms which the substance contains, we can easily see that light of all frequencies between certain rather vague limits will be emitted; we have, in fact, what is called a *continuous spectrum*, in which the whole of the visible spectrum appears as a continuous band of colour shading gradually from red at one end to violet at the other. The spectrum of the filament of an incandescent electric lamp affords an example. Such a spectrum is given by any glowing solid or liquid, and is therefore useless for distinguishing one substance chemically from another.*

In order that spectrum analysis shall be possible, therefore, the means employed for making the substance luminous must be capable of vaporising it also if it is not already in the gaseous state. Since substances have a wide range of boiling-points it follows that a source of luminosity suitable for one may not be so for another. We shall consider first the simplest forms of luminosity—namely, flames—in which this limitation is particularly marked. Few flames are hot enough to vaporise the most refractory substances but, to counteract this disadvantage, their comparatively gentle stimulus enables us to study the spectra of many molecules which in the hotter and more vigorous sources are dissociated into their component atoms.

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* For a possible partial exception to this, see p. 29.

Flame Spectra. An ordinary Bunsen or Meker burner flame readily vaporises a number of metals—e.g. Li, Na, K, Mg, Ca, Sr, Ba, Tl, etc.—and provides the readiest means of detecting the presence of those substances in a mixture. The procedure is extremely simple. The powder is moistened with a little HCl and held in the flame at the end of a piece of iron wire or the charred end of a match-stick, and the spectrum is examined. The lines are easily recognisable after a very little experience. It should, of course, be ascertained that the supporting wire or match-stick is not itself contaminated by the element in question; this is done by moistening it with HCl and looking at its spectrum before the substance is introduced. Sodium, for example, is sure to appear, since it is a constituent of the air in any laboratory, and a considerable intensification of its lines must be observed when the powder is placed in the flame before its presence in the powder is established.

A method of this kind, though it may easily be unduly neglected, is clearly of very limited application. It can be used only when few elements are of interest and when one needs to know only whether they are present or absent. It is applicable to liquids, including solutions, but not with confidence to refractory solids which are suspected of containing one of the elements in question. For example, one would not use it to ascertain whether a sample of tungsten contained a trace of strontium. It should be noted (and this applies in lesser degree to all flames, including the hotter ones to be mentioned presently) that the colour of the flame is a very unsafe guide to the spectrum, and the "flame tests" of elementary chemical analysis are not at all a simplified form of spectrum analysis. A strontium salt, for example, when placed in the Bunsen flame gives a bright red colour, but the only line of strontium which is emitted is a bluish-violet one. The colour is due to the much more copious radiation from an undissociated compound of strontium—all halogen compounds of this element give strong red radiation—and not to that of the metal itself. Often a metal, dissociated from its original partner, will form an oxide in a flame burning in air, and give the spectrum of the oxide. There are always, however, in such cases enough free atoms to permit an identification by the atomic spectrum alone.

Although, in such a compound as NaCl, for instance, dissociation of the sodium implies dissociation of the chlorine also, the spectrum of chlorine does not appear; it is, in fact, a general rule that a dissociated salt shows in the flame only the spectrum of the metallic constituent. The reason may be either that the energy in the flame is insufficient to raise the electrons of the non-metals to larger orbits in enough atoms to make visible radiation possible (in general metals are easier to excite than non-metals) or else that the radiation from the non-metals is in the ultra-violet or infra-red region where it is less readily observed.

Owing to the small range of applicability of the Bunsen flame spectrum, it is not often that one needs to maintain it for any appreciable length of time; a glance is usually sufficient to settle the question at issue. Occasionally, however, longer inspection is necessary, and from among the various devices which have been adopted for feeding the flame with the substance—suitable methods will occur to anyone who needs them—we select for description one of the neatest, which is due to Merton. A solution of the substance is placed with a little dilute HCl in the bottom of a small wide-necked flask, and a Meker burner made of glass (except the grid, which is made of quartz, to prevent melting) is inserted in it as shown in Fig. 4. Coal gas is supplied at the side, and the necessary air goes up through the open end of the vertical tube in the flask. When the observations are to begin a rod of zinc or magnesium is placed in the flask. It reacts with the HCl causing evolution of hydrogen, and in the resulting effervescence particles of the substance are thrown up into the air with which the flame is supplied. They therefore go into the flame and emit their spectrum, and the process continues until the HCl or zinc is used up. The substance is in such a finely divided state that no contamination of the burner occurs, and within a minute or so after removing the zinc all trace of the spectrum has disappeared from the flame and the burner is ready for a new observation.

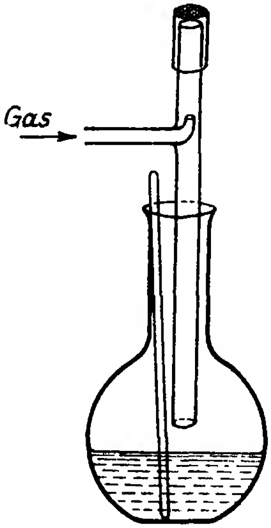

Fig. 4.—Merton's method of feeding flame with salt for spectroscopic purposes.

The oxy-coal gas or oxy-hydrogen flame gives a hotter source than the Bunsen, and accordingly has a wider range of applicability. It is necessary, in prolonged observation, to make allowance for the spectrum of the flame itself. This is shown for the oxy-coal gas flame (the spectrum of the Bunsen or Meker burner is identical with this) in Plate XVIA. It must be understood that the rather complicated spectrum shown in the figure was photographed with a much longer exposure than would be necessary for an ordinary observation, and the spectrum of the substance of interest is usually so much brighter than that of the flame that the latter does not have the obscuring effect that might be feared. The oxy-hydrogen flame spectrum is much simpler, consisting only of bands in the ultra-violet arising from the molecule HO: these are shown on the left in Plate XVIA, since they occur in the oxy-coal gas spectrum also.

Flame spectra have been used for quantitative work by some investigators because the conditions can be kept steady more easily in them than in the more vigorous sources of luminosity. Within their range of usefulness their simplicity and the ease with which they are controlled are strong points in their favour, but when, as is often the case, the substance has an unknown composition or contains elements refractory to the flame, the difficulties of the more universally applicable sources must be faced.

There is an important class of investigations in which the source of luminosity is not at one's disposal. Astronomy offers by far the most prominent example of this class, but in terrestrial matters also we frequently wish to study processes of combustion or other chemical action involving the emission of radiation, in order better to understand the details of the processes. The glow of phosphorus, various forms of fluorescence, as well as violent chemical combination accompanied by light are examples which readily come to mind.* In these investigations the spectrum represents always the molecules which emit it, not necessarily the original or final forms which the reacting substances take. It is therefore sometimes indispensable in showing what course the reaction has taken and what combinations of atoms have temporarily existed while it has been going on. It frequently—one might say usually—happens, not only in the processes we are now considering but also in the ordinary processes of emission by a means voluntarily chosen, that the emitter of a spectrum is something that could not exist in the undisturbed state. Thus the luminosity of the oxy-hydrogen flame already referred to arises from the molecule HO, not H_2O which is the final product of the chemical action, and the atoms which emit line spectra are often incapable of permanent existence as single atoms.

Arc Spectra. The commonest and most generally useful source of luminosity is the electric arc. This discharge is usually passed between rods of some conducting material at a voltage of 100 or 200 (the difference in the resulting spectra is usually one of brightness only) A variable resistance should be included in the circuit, to be adjusted according to experience. If the substance to be examined is obtainable in the appropriate form and is a conductor of electricity it can itself conveniently form the electrodes, and this has the great advantage that we thus obtain a spectrum completely free from lines of any extraneous substances (the air, if reasonably clean, contributes nothing except in the infra-red, where a few lines of oxygen may possibly be emitted from the region of the poles of the arc). If, however, as usually happens, the substance is in powder form or in small fragments, rods of some other material may be chosen, held collinearly in a vertical position, and the substance placed in a small cavity made in the lower one.

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* The reader interested in this aspect of spectroscopy is referred to *Spectroscopy and Combustion Theory*, by A. G. Gaydon.

The arc is struck by bringing the two electrodes, between which the requisite potential difference exists, together for a moment and then slightly separating them. The current, usually of the order of 10 amperes or less, persists through a length of vapour of the material of the electrodes, which becomes intensely hot and emits a bright spectrum. All known solids are vaporised at the temperature of the arc, so that, unlike the flame, it is universally applicable except to substances normally gaseous. Special stands are used for holding the electrodes, providing for a raising or lowering of both together, an approach or separation of the electrodes, and a lateral movement of one of them so as to bring them into line with one another. (See Fig. 5.) It is convenient to have the upper electrode shaped to a blunt point, and the lower with its upper surface flat or, if it has to hold a powder, slightly scooped out to form a receptacle. A liquid may be examined by steeping the lower pole in it for a day or two, but it is usually better to evaporate the liquid to dryness and treat it as a powder.

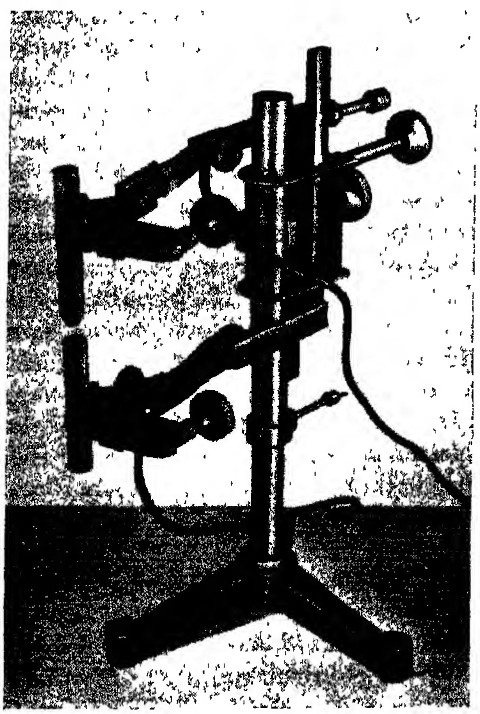

Fig. 5.—Electrodes in stand for electric arc.

During the passage of the current, the positive pole (the anode) becomes hotter than the negative (the cathode), though both are sufficiently hot to vaporise all solids. The material of the poles is gradually transferred from the cathode to the anode, so that the latter tends to grow at the expense of the former, although, of course, much of the vapour escapes into the air and condenses on the stand and elsewhere in the neighbourhood. The direction of the current is accordingly chosen to suit the circumstances. If only a small amount of material is available, and it is therefore desired to get as much radiation as possible, the cathode is placed at the bottom so that the powder vaporises comparatively slowly. If, on the other hand, refractory constituents are suspected and it is desired to obtain their spectra with the same prominence as those of the easily vaporised materials, the powder is placed on the anode. This applies only to qualitative work. In quantitative analysis the procedure has usually to be standardised in every detail, and a single direction of current, depending on the particular technique used, must then invariably be chosen.

The auxiliary electrodes, which are necessary when the specimen to be examined cannot be used alone, may be of any convenient conducting material, but by far the commonest choice is carbon, generally in the form of graphite. There are a number of reasons for this. In the first place, graphite can be obtained without undue expense in a reasonably pure state. Secondly, its spectrum is very simple except in a restricted region. Thirdly, although it conducts electricity it has a greater resistance than the metallic vapours, and so its own spectrum usually tends to disappear when there is a good supply of the material under test. Fourthly, being soft it is easily made into any desired shape. There is a little to be said on some of these points.

The impurities in graphite vary with the source from which it is obtained, but for a given source they are fairly constant. It is therefore desirable as far as possible always to work with the same kind of graphite and to become familiar with its impurities. In the specimens with which the writer is most familiar the chief ones are titanium, vanadium, iron, silicon, boron, calcium, magnesium and copper, but, except for the first two, only the *raies ultimes* appear. The determination of impurities in the electrodes is not so simple as might be, and often is, imagined (see p. 79).

The spectrum of the carbon atom in the pure graphite arc in air in the ordinary region of observation contains little if anything more than a line at 2478·5 and a pair at 2837·6, 2836·7.* The greater part of the spectrum, however, is not that of the carbon atom but that of cyanogen (CN) and, somewhat less prominently, bands of the carbon molecule, C_2. CN is formed by the union of the carbon vapour with the nitrogen of the atmosphere; this is an instance of a compound formed, and not broken up, at the high temperature of the arc. The extent of this spectrum is shown in Plate XIVA. It is clear that lines of the spectrum under examination which happen to fall in the region of the CN bands are apt to be obscured, and certain elements may have to be tested for by other lines which are more favourably situated. This occurrence, however, is less frequent than might be feared, since the bands can be almost completely eliminated if the lower pole is well covered by the specimen. This effect is shown in Plates IV and V, which give the spectrum of a powder on graphite poles in the same region as the strong CN bands. (It might be noted here that if the lower pole is *completely* covered it might not be possible to strike the arc, as the solid powder often fails to conduct the current. It is well, therefore, to leave a small

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* Throughout the book, whenever a spectrum line is indicated by a number, that number stands for the wave-length in angstroms.

space uncovered directly opposite the tip of the other pole. When the substance is fused it spreads over the surface and produces the effect desired.)

For certain purposes carbon is not a suitable material for electrodes. For example, one might wish to examine a spectrum for small traces of an element which exists as an impurity in graphite, or even for carbon itself. The electrodes in such cases are chosen according to the particular problem. Thus, if only a single element is of interest, any electrodes will do, no matter how impure, whose spectrum contains no lines that might be mistaken for the *raies ultimes* of that element. When several elements are to be looked for, however, electrodes with a simple spectrum are desirable. Silver is usually the most suitable material for them, as it fulfils this condition and has the additional advantage that it can be obtained in a high state of purity. Its cost is against its common use, and copper is often a satisfactory substitute. It is important, however, that one's practice in this respect should not become too stereotyped, and the whole range of available electrodes should, if necessary, be considered in relation to the specific problem in hand.

In order to excite the substance to radiate, the following procedure is generally suitable. The electrodes are inserted in the arc stand, the upper one first. The reason for this is that the stand is inevitably coated to some extent with the condensed vapours of previous arcs and any deposit disturbed by the insertion of the electrode will then not be able to contaminate the lower pole. If the electrodes are to be used again, the lower one is removed first for the same reason. The electrodes having been aligned, the arc is struck between them and allowed to run for about a minute so that they become hot enough to fuse at least some of the powder. The arc is then broken, a supply of powder is placed on the lower pole, and the arc is struck again. If the supply is short the spectrum is photographed after the arc has been running for 10 seconds or so; otherwise, the arc is allowed to run for about half a minute and then a second supply is added and photography begun some 10 seconds after that. The length of exposure will depend on whether one is seeking only the main constituents of the powder or the presence of minute traces; it must in either case be determined by experience with the particular apparatus used. In general it is about a minute or less, so that, except in special cases, it is not necessary to recharge the arc with powder during the exposure.

Spark Spectra. A spark spectrum is obtained by passing a discharge from an induction coil or transformer between two fragments of the specimen. In order to intensify the discharge it is customary to place a condenser (say a Leyden jar) in parallel, and a short air gap (about ⅛ inch) in series, with the spark. The pieces of specimen are held in an insulated stand somewhat similar in principle to that for the arc but usually less robust (Fig. 6). A primary voltage of 12 V. or so is sufficient, with an ordinary small size coil, to give a sufficiently bright spark.

The advantage of the spark as a form of discharge is that it is very economical in its use of the material: two small fragments can be used for several hours without having perceptibly diminished in size at the end. Its disadvantages are that it gives much less total light, and therefore requires longer exposure, than the arc; the spectrum is only that of the small regions near the points between which the discharge passes, so that if the constituents are not homogeneously distributed an untrustworthy result is obtained; and the spectrum contains lines of the air or other gas in which the spark is passed. For these reasons the spark is in general a much less suitable source of luminosity for ordinary work. It should be added, however, that, owing to the comparative ease with which it can be controlled and kept steady, it has been preferred to the arc by some workers in quantitative analysis.

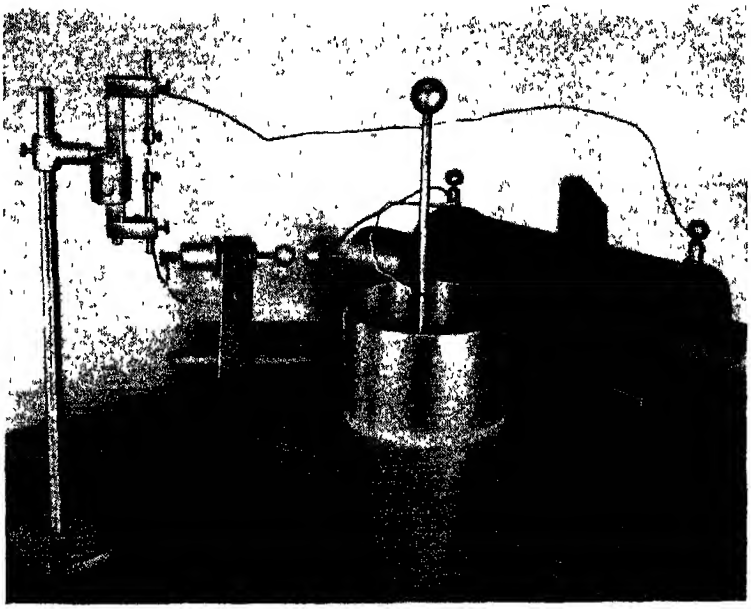

FIG 6.—Arrangement for producing electric spark

The numerous air lines which appear can be distinguished by the fact that they are common to the spectra of two or more sparks with different electrodes. It is occasionally advisable to pass the spark in hydrogen,* which has a very simple spectrum, instead of air, but as a rule the result is not worth the trouble. Provided the lines required

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* It may not be superfluous to add a reminder that a slight leak in the sparking chamber will lead to an explosion when sufficient air has got in.

are obtained, free from overlapping by others, there is no harm in the presence of additional ones. For this reason it is generally hardly worth while to include a coil having appreciable self-inductance in series with the spark, although this, if carefully regulated, eliminates the air lines and leaves the spark lines of the electrodes. Too much self-inductance eliminates some of the lines of the electrodes as well.

The spark spectrum of a non-inflammable liquid or solution is most conveniently obtained by means of the apparatus shown in Fig. 7. The electrodes are of platinum wire; the lower is fused into the bottom of a test-tube and a piece of capillary glass tubing is placed over it. The liquid in the test-tube rises to the top of the capillary through the effects of surface tension, and so remains at a constant height as the liquid is gradually evaporated by the heat of the spark. A hole in the side of the tube allows the shorter ultra-violet radiations, which are absorbed by glass, to pass to the spectrograph.

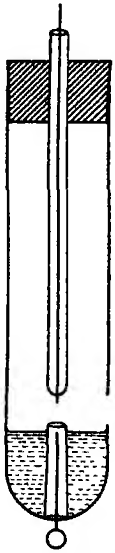

Fig. 7.—Apparatus for obtaining spark spectrum of a liquid.

The spark spectrum of a powder can be obtained by a method described by de Gramont. The lower electrode is a horizontal piece of platinum foil, and the upper a short piece of platinum wire held vertical about ¼ inch above it. The powder is mixed with four or five times its bulk of sodium carbonate or fusion mixture, and placed on the foil. A Meker burner underneath melts it and the spark is then passed. It is important to melt the substance before beginning the discharge, or it will be scattered away. The spectrum will contain, in addition to the lines of the powder, those of platinum, the fusion mixture, the air, and the flame. It is necessary, therefore, to take a preliminary photograph in which everything but the powder is present, and consider only the additional lines which appear when the powder is added.

Differences between Flame, Arc and Spark Spectra. In general the arc spectrum of an element Z contains the Zɪ spectrum (sometimes called the "arc spectrum") fully developed, with perhaps a few lines of the Zɪɪ spectrum. The flame spectrum contains a portion only of the Zɪ spectrum, and the spark shows Zɪ weaker and Zɪɪ considerably stronger than in the arc. It is therefore common to speak of Zɪɪ lines as "spark lines." The reason for these differences is that in the flame the energy available is only sufficient to move the electron to a few of its possible orbits, and therefore only a few inward transitions are possible. The arc provides enough energy to bring them all into play, and with some elements it can ionise sufficient atoms to give visible lines of the ionised atom (Zɪɪ). An older name, due to Lockyer, for these Zn II lines is "enhanced lines": without knowing so clearly as we do now the origin of the lines, he distinguished them as those which were strengthened, or appeared for the first time, in passing from the arc to the spark. In the spark the energy is much more intense, and many atoms are ionised, giving the Zn II spectrum equal prominence with Zn I. Plate XIII shows the three spectra for thallium. Here no Tl II lines appear in the arc, and all the arc lines are weakened in the spark. The new lines which appear in the spark are partly air lines (these are mainly in the longer wave-length region) and partly Tl II lines.

Spectra of Gases. The flame, arc and spark are suitable sources of luminosity for solids and liquids but, with the partial exception of the spark, not for gases. To obtain the spectrum of a gas the commonest method is to reduce its pressure to a few millimetres of mercury and pass through it an electric discharge from an induction coil. At low pressures gases conduct electricity, and the discharge passes readily over considerable distances. Different spectra are obtained from a "condensed" (i.e. a discharge with a condenser in parallel with the discharge tube) and an "uncondensed" discharge. The latter corresponds roughly to the arc and the former to the spark spectrum of a solid. Spectra of gases have usually to be obtained where the gas is produced, and one has therefore less freedom than with solids and liquids in the arrangements made. For this reason it is impossible to describe a standard procedure, and only the most general remarks can be given.

Impurities are much commoner, and their lines are much more prominent, with gases than with solids and liquids, since they are unavoidably introduced from the electrodes (from which occluded gases may be released when the pressure is reduced), from mercury or oil used in pumps, from tap grease, from various sources of moisture, and from other sources peculiar to the problem in hand. The commonest and most troublesome of these unwanted gases are oxides of carbon, which have a large variety of spectra * depending on the temperature, pressure and conditions of discharge. Owing to the ease with which chemical reaction may take place in gases under the influence of an electrical discharge, the utmost care is needed in deducing from the spectrum what gas was originally in the vessel. Here again the variety of possibilities precludes any satisfactory attempt at their enumeration.

If for any reason it is undesirable to insert electrodes in the gas, an "electrodeless" discharge may be used. This, in its simplest form, is produced by wrapping round the tube or bulb containing the gas a number of turns of wire which form part of the secondary circuit of an induction coil in which a small air gap is included. A condenser is placed across the secondary terminals, and the vigour of the discharge is adjusted by varying the capacity of the condenser or, more simply,

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* See *The Identification of Molecular Spectra*, by Pearse and Gaydon, pp. 77–86.

the length of the air gap until the maximum intensity of radiation is produced in the tube. The spectrum obtained under these conditions varies with the character of the discharge, and may be different in different parts of the tube. It is usually much fainter than that yielded by a discharge with internal electrodes, but the sources of impurities are somewhat reduced.

Light as a Stimulus—Absorption Spectra. When an atomic electron falls from an outer to an inner orbit a wave of light of a particular frequency is radiated. Correspondingly, when light of that frequency is made to fall on an atom with its electron in the inner orbit, the electron absorbs the light and moves out. This applies to every transition of which the electron is capable, and there is a complete reciprocity between emission and absorption. There is this difference, however. When an electron moves inwards and radiates light it does not move out again unless forced to do so by some externally applied agency, but when it absorbs light and moves outwards it has a natural tendency to return, and does so, radiating light of the same frequency as that which it absorbs if it returns direct, or a succession of smaller frequencies if it returns by way of intermediate orbits. The incident light may therefore be grouped with the flame, arc, spark and other exciting agencies as one of the means by which *a substance can be made to emit its spectrum.* The most expeditious procedure is to allow a beam containing all colours within the range of interest to fall on the substance whose spectrum is required. Its atoms select only those colours which correspond to their natural transitions, absorb them, and radiate them again.

It is the almost universal practice, however, when light is the stimulating agency, to ignore the re-radiation and allow the earlier absorption to indicate the nature of the absorbing substance. This is done in the following way. The incident light is made to pass through the substance, and on emergence is analysed into its constituents. The wave-lengths which are missing from the spectrum are those which the substance has absorbed. The fact that it re-emits them offers no difficulty, for while the incident light is travelling all in one direction through the substance, that which is absorbed is re-emitted in all directions—according, presumably, to the various orientations of the billions of atoms in which the absorption occurs. The absorbed wave-lengths are therefore, in effect, scattered by the substance while the unabsorbed ones pass straight through. The spectrum seen in the line of incidence is therefore so deficient in the former that they appear as though they were absent altogether. It is called an *absorption spectrum* of the substance; an example is shown in Plate XVIB.

Line or band absorption spectra, characteristic of the absorbing substance, are commonest with gases, but substances in dilute solution or impregnated in glass may have their atoms or molecules so far apart that they act independently of one another and give characteristic absorption spectra. Light can be the gentlest of all stimuli, and generally leaves the substance, after absorption and re-emission, in its original state. An absorption spectrum therefore often affords the best means of determining the nature of a substance which it is desired not to destroy by the process. The absorption spectrum of blood, for instance, tells one a great deal about the molecular forms existing in it; venous and arterial blood give different and characteristic spectra, and poisoning by carbon monoxide and other substances causes changes which the absorption spectrum readily shows. It is a very good rule, whenever one has a gas or liquid to analyse, to take its absorption spectrum before treating it in any other way. The results may be negative—the substance may be completely transparent in the ordinary spectrum region or may show only continuous absorption—but no harm can possibly be done since, if the substance had been destructible by light, it would already have been destroyed by the sunlight to which it has presumably been exposed.

Although a substance can absorb only those wave-lengths which it is able to emit, the emission and absorption spectra are not identical, the latter being only a portion of the former. This is because, when a substance at ordinary temperatures is placed in the path of the light, all its atoms or molecules are in their lowest energy state—the electrons are in their innermost orbits and, in molecules, the energy of vibration and rotation is the least possible. Accordingly the only frequencies which can be absorbed are those in which that state takes part. For example, denoting the orbits in the atom by E_1, E_2, E_3, . . . as before, the only frequencies which can be absorbed are those corresponding to energy differences E_2-E_1, E_3-E_1, E_4-E_1, etc. In emission not only these frequencies but also those corresponding to such transitions as E_4-E_3, E_3-E_2, etc., may occur. These could be absorbed only if the incident light could catch the atoms in the states E_3, E_2, ... There is a remote chance of this, but the electrons remain for so short a time in the excited orbits that it is in practice negligible, and the absorption spectrum reveals only those transitions in which the smallest orbit, E_1, plays a part. The case is different when the absorbing substance is itself luminous, as in the atmospheres of the Sun and stars for example. Here some of the atoms have their electrons in the outer orbits before the light from the interior of the body falls on them, and accordingly absorption of the whole spectrum may occur.

To obtain an absorption spectrum the substance, if a solid, is simply cut to an appropriate thickness and held in the path of the light, the transmitted light being examined by the spectrograph. A fluid substance must be placed in a suitable container which, with a gas, usually takes the form of a tube whose ends are made of quartz so that the whole of the ultra-violet down to 2000 A. can pass through it; glass is opaque below about 3800 A. or so. The ends may be attached to the tube by sealing wax, cooled by a continuous stream of water if the tube has to be heated. Liquids can be held in a similar container, usually with a device for varying and measuring the length of the light-path through them. Wedge-shaped cells (see Fig. 8) placed as in the figure are often convenient containers for liquids. A single such cell would act as a prism and deviate the light, but with a pair the path of absorption can be varied by sliding one member along the other so that the outside faces remain always parallel to one another.

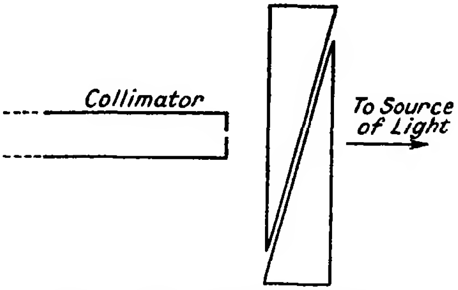

FIG. 8.—Cells for obtaining absorption spectra of liquids.

The light source should give a spectrum continuous over the range to be examined. For the visible and infra-red, and at least part of the ultra-violet, a glowing solid, such as the filament of an incandescent lamp or the pole of a carbon arc, will serve the purpose. A more universally applicable source, however, is a discharge tube containing hydrogen which, though a gas, can under certain conditions yield a continuous spectrum of more uniform intensity throughout the whole range of practical interest than that of any heated solid. A convenient form of such a tube has been described by Hunter and Pearse*; it is shown in section in Fig. 9. The central feature is a "capillary" tube EE′, 50 cm. long and 0·7 cm. in internal diameter, made of quartz. At the ends are attached, by wax seals, pyrex tubes AA′ containing

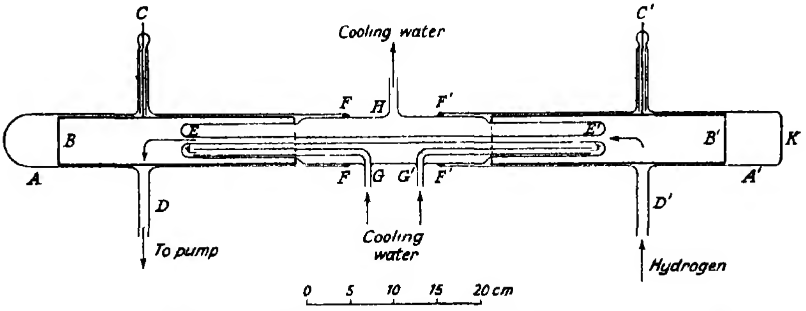

FIG. 9.—Discharge tube for obtaining continuous spectrum of hydrogen.

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* *Journ. Sci. Inst.*, **13**, 408 (1936).

hollow cylindrical aluminium electrodes which may be connected through tungsten leads CC′ with the source of electrical supply, A.C. or D.C. The system is exhausted, and a stream of hydrogen from a commercial cylinder passes through a needle valve into the tube at D′ and leaves it at D, the pressure being maintained at about 3 mm. of mercury. Water is kept circulating during the passage of the current, being admitted at the bottom and withdrawn at the top as shown. Direct current from a rotary converter with a maximum output of 2 A. at 3500 V. may be used, but the tube keeps cooler with A.C., for which a 7 kVA. transformer delivering 2500 or 5000 V. as required, for medium pressures, or a 5 kVA. transformer delivering 10, 20 or 40 kV. for higher pressures, is used The discharge starts when the voltage across the electrodes reaches about 3000 V., and then runs at about 1500 V. The current, regulated by an adjustable resistance, should not exceed about 0·7 A., which corresponds to a dissipation of more than a kilowatt and a current density in the capillary of 2 A. per sq. cm. Both current density and light intensity (which is sufficient for all ordinary purposes) keep constant to within 1 per cent. indefinitely.*

Other Sources of Luminosity. Although the number of ways in which a substance can become luminous is very large, those already described are practically exhaustive so far as general use is concerned. Special processes, such as electron bombardment, fluorescence, explosive discharges, etc., are not so much means to be considered when the mechanism for producing luminosity has to be chosen as methods which impose themselves by the conditions of particular problems. They therefore call for no description here. It may be remarked concerning fluorescence, however, that the possibilities of this process have perhaps been insufficiently explored. If a substance shows fluorescence, the spectrum, although usually continuous over a limited range, may nevertheless be characteristic and so afford useful information very simply. For example, slight variations in the composition of certain oils might be readily detected in this way. Fluorescence is often a property not of the main substance which shows it but of a particular impurity present in extremely small amount, and a systematic study of its occurrence with particular substances of interest might well repay the labour expended.

* Other forms of hydrogen discharge tube are described in *The Photochemistry of Gases*, by Noyes and Leighton (Reinhold Publishing Corporation, N.Y.).

CHAPTER

3

THE PRISMATIC SPECTROGRAPH

The Essential Elements. The commonest way of analysing a beam of light into its constituent colours is to pass it through a triangular prism. The instrument in which this is done is called a *spectroscope* if it provides only for visual observation of the spectrum, and a *spectrograph* if it enables the spectrum to be photographed. In view of the importance of understanding the function of every part of the instrument we shall show how it is built up from its simplest form.

If one wishes to see a source of light (say a Bunsen flame in which some common salt is inserted; the visible spectrum of such a source, neglecting the faint radiation of the coal-gas flame itself, consists of two very close yellow colours which with small instruments appear as a single colour and we shall regard it as such) and the space between the source and the eye is occupied by a homogeneous transparent medium such as air, one must look straight towards it since in these circumstances light diverges from the source in straight lines (Fig. 10 (a)). If, however, a glass prism is placed in the path of the light, as shown in section in (b), the flame can no longer be seen unless the eye is moved to a new position and takes a different direction of view. It then sees the flame just as before but apparently in a different place. If, now, a salt of lithium as well as of sodium is placed in the flame, the only change under the conditions of (a) is that the colour of the flame becomes orange instead of yellow, but the conditions of (b) show the yellow flame as before and a red one by the side of it. The paths of the light rays apparently proceeding from these images are shown in Fig. 10 (c).

This is the simplest possible form of spectroscope. It analyses the orange light of the single flame into its component yellow and red colours. Its most obvious defect is that if, instead of two well separated colours, the flame emits a large number of closely adjacent ones, the various images will overlap and the structure of the spectrum will be obscured. To remedy this a narrow slit is placed between the flame and the prism, in a direction parallel to the refracting edge of the prism (i.e. perpendicular to the paper in Fig. 10), so that the rays diverge as from a linear source. The images seen through the prism are then red and yellow lines instead of red and yellow flames. It is usual to have

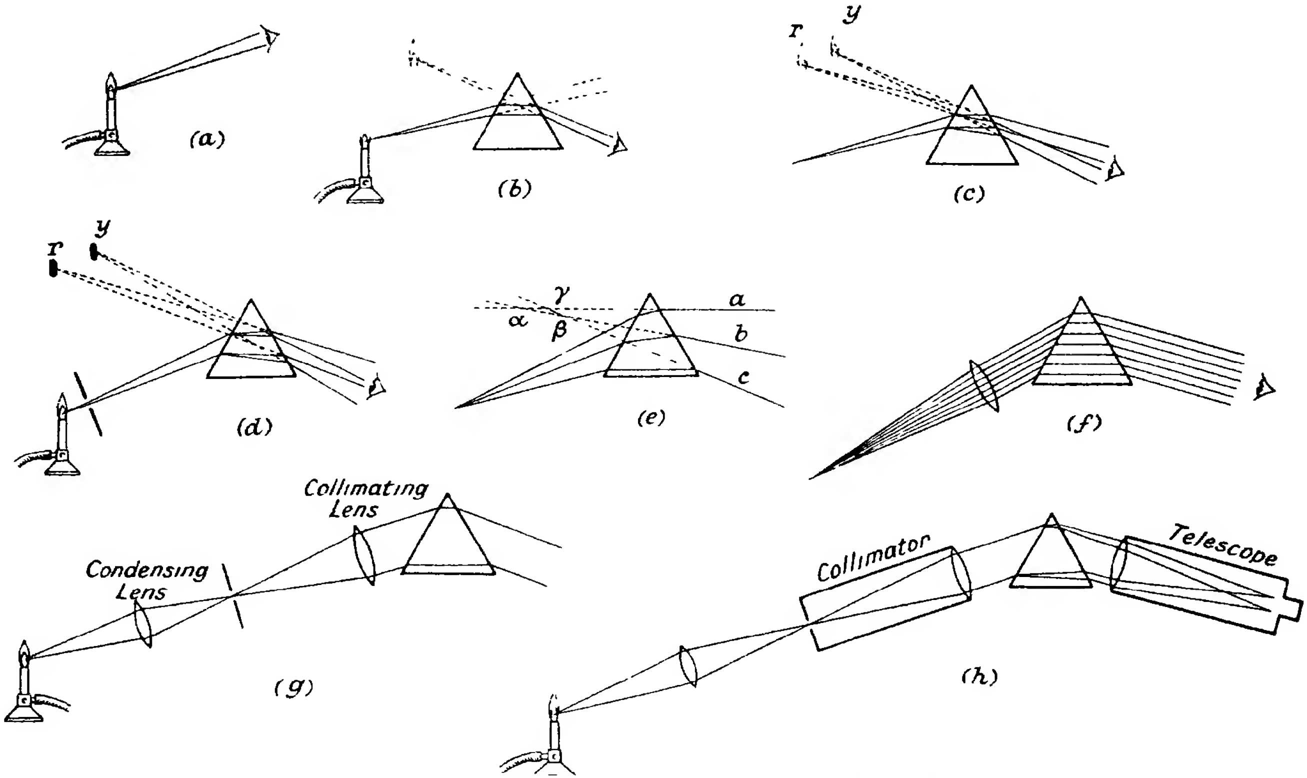

FIG 10 —Successive stages in the development of a simple spectroscope the flame, the slit and the refracting edge of the prism all vertical. In plan, therefore, the arrangement is as shown in Fig. 10 (d), the short lines y and r being sections of the vertical line images of the slit. (In Fig. 10 (b), (c) and (d), in order to make the arrangement clearer, a plan of the prism is associated with an elevation of the flame.)

The slit is one of the most important parts of the instrument, since every spectrum line is an image of it and will therefore partake of its defects. A speck of dust, for example, at any point on it produces the appearance of a horizontal line running along the spectrum. It is important that the slit should be kept clean, and this is best done by widening it to its fullest extent and running a piece of soft wood (e.g. a match-stick) along each edge in turn. While it is being narrowed again the spectrum should be watched continuously to ensure that the jaws are never completely closed as this might damage them. The slit is usually made of platinum–iridium, with the jaws bevelled to sharp edges in order to minimise troublesome reflection of light from them. Before use the slit is narrowed until further approach of the jaws causes a sharp decline in the intensity of the light passing through.

The slit is not sufficient by itself to ensure narrow images, for, owing to aberration in the prism, rays of light diverging from it, although of the same colour, do not all proceed on leaving the prism as if they came from the same line. This is illustrated in an exaggerated form in Fig. 10 (e), where the rays a and b intersect at α, b and c at β, and c and a at γ. Each image of the sharp slit is thus a fuzzy line, and some overlapping of close images still remains. This is removed by inserting an achromatic converging lens (a "collimating lens") between the slit and prism, in such a position that the slit is at its principal focus. All the rays of each colour then fall parallel on the prism. Having the same angle of incidence they will, of course, remain parallel in the prism and on emergence, and will be brought to a focus on the retina by the lens of the eye, as though they proceeded from a sharp image of the slit at infinity (Fig. 10 (f)). Rays of another colour will take different, but also parallel, paths through and beyond the prism, and will appear to diverge from another sharp image of the slit at infinity slightly displaced from the first. The slit and lens are usually fixed at opposite ends of a metal tube known as the *collimator*.

Fig. 10 (f) is drawn as though the rays from the slit include a solid angle large enough practically to embrace the collimating lens and prism. This will not in general be so if the slit is merely placed close to the source of light, unless it is close enough to be damaged thereby or the source is large enough, when removed to a safe distance, to subtend at the slit an angle as large as that subtended by the collimating lens on the other side. This condition is not often fulfilled, and it is therefore customary to form an image on the slit of the source of light by means of an auxiliary lens known as the "condensing lens" (Fig. 10 (g)). This device has the further advantage that each part of the slit (and therefore the images of each part of the slit, i.e. the corresponding parts of the spectrum lines) is illuminated by radiation from a particular part of the source. Accordingly, if the different parts of the source are emitting different spectra, this will be shown by the upper part of the spectrum lines, say, differing from the lower part.

The instrument would now be complete if the eye were as large as the prism, for then it could receive all the issuing light. In fact, however, it is much smaller than the prisms in general use, and therefore most of the light does not enter the pupil and the spectrum seen is much fainter than it need be. This is prevented by collecting the light by a third lens, known as the "telescope" lens in the spectroscope or the "camera" lens in the spectrograph. It brings the light of each colour to a focus, the series of images lying on a surface with which, in the spectrograph, the photographic plate (by slight bending if need be) is made to coincide. The whole system is enclosed in a case to protect it from extraneous light. In the spectroscope an eyepiece is added to magnify the array of images, and this, with the telescope lens, forms the telescope with which visual instruments are always provided. The final form of the instrument is then as shown in Fig. 10 (h).

The whole instrument is thus an optical arrangement for producing an image of the slit in each of the wave-lengths which the incident light contains. If, instead of the system containing collimating lens, prism and camera lens, we had had a single converging lens—an ordinary magnifying glass—we should have obtained one image of the illuminated slit in its original colour, situated on the axis of the lens. The effect of adding a prism and a second lens is, first, to deviate the light, and, secondly, to analyse it so that in general many images are produced instead of one. Nevertheless, each is just as truly an optical image of the slit (or, more strictly, of that part of the slit which is illuminated by the light forming that image) as is the single line formed by the magnifying glass. It will be subject to the usual characteristics and defects of such images—magnification, spherical aberration, diffraction broadening, etc.—and must always be thought of as a typical optical image with the sole distinguishing characteristic that it is monochromatic.

Arbitrary Features of the Instrument. Everything in the instrument as so far described is essential to satisfactory results. Some freedom of construction or arrangement, however, is still left, and this may be used to meet particular needs. We shall proceed almost immediately to consider how this may be done, but it is desirable first to remove a common error. It is still sometimes stated—though not so frequently as formerly—that a "pure" spectrum (i.e. one in which the aberration of the prism is eliminated) can be formed by placing the illuminated slit outside the principal focus of the collimating lens so that the light converges on to the prism. It is true that the aberration in that case is less than when the light diverges, but it still exists and can be completely removed only by making the light parallel before it falls on the prism. This error is perhaps associated with another to which we shall refer again, namely, that for the best definition the prism should be placed in the position of minimum deviation. If the light is collimated the angle of deviation makes no difference to the definition. If it is not, the aberration is less with converging than with diverging incident light, and for this reason converging light, without a telescope lens, is sometimes used for lecture demonstrations where simplicity is more important than perfection of detail. Such an arrangement, however, should never be used in laboratory work; collimation is there essential.

The freedom left us after the essential conditions have been satisfied may be classified under the following heads: (a) material of lenses and prism; (b) shape and size of prism; (c) focal length and aperture of collimating and telescope lenses; (d) angle of incidence of light; (e) width of slit (the length of the slit affects only the length of the spectrum lines which, within reasonable limits, is usually unimportant); (f) focal length and situation of condensing lens; (g) type of photographic plate used. In order to use this freedom to the best advantage we must consider the several ways in which the spectrum may vary and see how they are related to the factors at our choice. The spectrum (good definition having been secured by satisfying the essential conditions) may vary in (i) intensity; (ii) dispersion; (iii) degree of resolution. The first of these characteristics is influenced by every one of the factors (a) to (g); the effect of some of them is obvious, but that of others needs examination. Dispersion and degree of resolution require some analysis before they can be related to instrumental conditions: we proceed to discuss them.

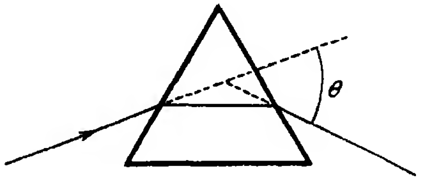

Fig 11.—Passage of light through a prism

The term "dispersion" is used to indicate the degree in which the several wave-lengths are separated from one another in the spectrum. If θ represents the angle of deviation of a ray of wave-length λ from its original direction (the angle θ in Fig. 11), a ray of wave-length $\lambda + d\lambda$ will be deviated by a different angle, $\theta + d\theta$. The greater $d\theta$ is for a given value of $d\lambda$, the greater is the dispersion, and when both are small the ratio $d\theta/d\lambda$ is defined as the *angular dispersion* of the instrument. It is always negative because $d\theta$ has always the opposite sign from $d\lambda$—longer waves are deviated less than shorter ones.

In a spectroscope the angular dispersion represents the quality we are considering in its most useful form, for it tells us the rate at which we must change the orientation of the telescope as we pass along the spectrum. With a spectrograph, however, we are more interested in the linear separation of the lines on the photographic plate. It is clear that if f is the focal length of the camera lens, two beams of parallel rays inclined at $d\theta$ to one another will be focused at places separated by a distance $fd\theta$. Calling this distance ds, we define the *linear dispersion* as $ds/d\lambda$; it is obviously f times the angular dispersion, but it is worth while pointing out that since λ is usually measured in angstroms, f in cm., and θ in seconds of arc, the expression $fd\theta/d\lambda$ is usually not stated as a dimensionless ratio. The commonest practice is to express a linear dispersion as so many angstroms of wave-length per millimetre of the plate.

The degree of resolution of a spectrograph represents its power of showing two neighbouring wavelengths as distinct lines in the spectrum. This bears an obvious relation to the dispersion, but it is not identical therewith. Dispersion is one of the factors which determine the degree of resolution, but it is not the only one. In Fig. 12 (a) two spectrum lines of exaggerated width are represented, which slightly overlap; the edges of one are dotted in order to distinguish it. This would appear, of course, as one broad line. Its components may be resolved in either of two ways. First, we may increase the dispersion, i.e. pull the lines apart; the result of this is shown in Fig. 12 (b). But also, without changing the dispersion (indeed, we may even decrease it), the lines may be separated by narrowing them, giving the appearance shown in Fig. 12 (c). The degree of resolution therefore depends on both the dispersion and the breadth of the lines. The breadth itself is determined by two factors; there is first the optical magnification produced and secondly the effect of diffraction. The first factor clearly produces an effect which varies with the width of the slit, but the second is independent of this, being concerned with the bending of the light round the two jaws of the slit, no matter how close together they are. With a slit indefinitely narrow the image takes the form shown approximately in Fig. 13, where intensity of the light is shown as the ordinate and position on the plate as abscissa. The secondary maxima are usually too faint to be considered, and the image of the slit is therefore represented only by the central hump in the figure, of breadth 2ρ, of which one half is contributed by each jaw of the slit.

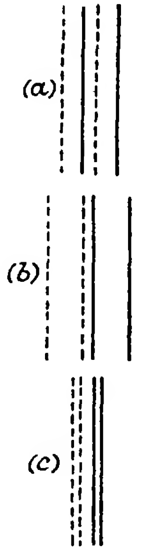

FIG. 12 —Illustrating the two methods of resolving overlapping spectrum lines

It can be shown that, for a given wave-length, ρ depends only on the angular aperture of the collimating lens. The magnification of the image, however, depends on the width of the slit, which is at our disposal, so that these two causes of broadening of the lines are distinguishable by the fact that we can control one by a process which has no effect on the other. On this account the degree of resolution of a spectrograph is represented by two distinct specific measures—the *resolving power* and the *purity*. Each is defined by the ratio $\lambda/d\lambda$, where $d\lambda$ is the wave-length interval between the closest lines that can be resolved at wave-length λ. For the resolving power, however, we add the condition that the slit must be indefinitely narrow, whereas for the purity we make no such condition. With an indefinitely narrow slit, of course, magnification has no effect since any multiple of zero is zero. $d\lambda$ in the expression for resolving power therefore depends only on ρ, and for a given instrument it is a constant, no matter how much we vary the slit width. It is this that gives it its importance, for clearly it can never be actually attained since an indefinitely narrow slit would admit no light at all: nevertheless it tells us the maximum degree of resolution which we can achieve with our instrument. The purity, on the other hand, has a definite significance in relation to a particular *spectrum*, not a particular *spectrograph*; it represents the *actual* degree of resolution achieved in a particular case.

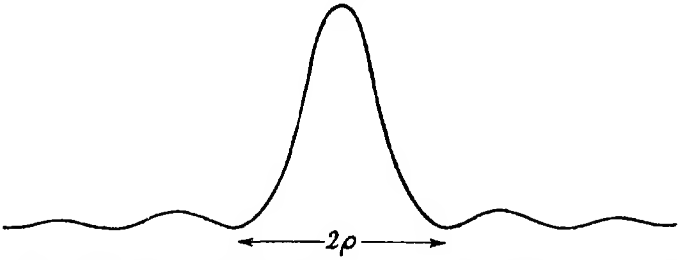

FIG. 18.—Distribution of light intensity in image of indefinitely narrow slit

Factors affecting Dispersion. The linear dispersion, $ds/d\lambda$ or $fd\theta/d\lambda$, may be written $fd\theta/d\mu . d\mu/d\lambda$, where μ is the refractive index of the material of the prism. The advantage of this expression is that the factor $d\mu/d\lambda$ depends only on the *material* of the prism, no matter how it is shaped or presented to the light, whereas $d\theta/d\mu$ depends on geometrical conditions such as the *angle* of the prism. The former factor can therefore be determined by experiment or from a theory of dispersion, whereas the latter can be found by geometrical calculation.

No exact expression has been found for $d\mu/d\lambda$. There are two semi-empirical formulae connecting μ with λ from which sufficiently accurate values can be obtained. The first, given by Cauchy, has the form

$$\mu = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} + \ldots$$

where a, b, c, . . . are constants which must be determined by experiment for each material used. Neglecting terms beyond the second, this gives

$$\frac{d\mu}{d\lambda}=-\frac{2b}{\lambda^3}$$

from which we see that the dispersion in any one prismatic spectrogram varies approximately as the inverse cube of the wave-length. The dispersion at 4000 A. at one end of the visible spectrum is therefore about eight times as great as that at 8000 A. at the other end. The second formula, which does not give so direct a relation between dispersion and wave-length but is more adaptable, as we shall see, to calculation of wave-lengths from position in the spectrum, is due to Hartmann; it is

$$\mu=\mu_0+\frac{C}{(\lambda-\lambda_0)^\alpha}$$

where μ_0, C, λ_0 and α are constants. α is usually near enough to unity to be dropped from the formula, and in that case

$$\frac{d\mu}{d\lambda}=-\frac{C}{(\lambda-\lambda_0)^2}$$

A simple method for determining the other factor, $d\theta/d\mu$, was given by Lord Rayleigh (1842–1919); it is as follows. In Fig. 14 the path of a parallel beam, of wave-length λ, is shown in its passage through the prism and beyond. The lines PQ, RS represent respectively the wave-fronts of the incident and transmitted light, and from the definition of a wave-front it follows that all the rays in the beam pursue equal optical paths in going from PQ to RS. Consider, therefore, the two extreme rays. Equating their optical paths we have

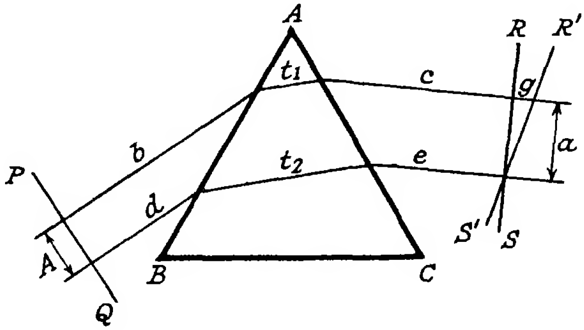

FIG. 14.

$$b+\mu t_1+c=d+\mu t_2+e \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ is the refractive index of the material of the prism for the wave-length λ.

Now consider the light of a neighbouring wave-length, $\lambda+d\lambda$, for which the refractive index is $\mu+d\mu$. The beam will have the same boundaries, b and d, before reaching the prism, but inside and beyond its path will be slightly different. However, we may take account of this by supposing that its path is identical with that of the light of wave-length λ, but that its wave-front on emergence, R′S′, is inclined to RS at an angle $d\theta$, which is the difference in deviation of the two kinds of light. There is a slight error in this, but it is of a higher order of small quantities than $d\lambda$ and $d\theta$ and therefore vanishes in the limit. For the second wave-length we have therefore

$$b+(\mu+d\mu)t_1+c+g=d+(\mu+d\mu)t_2+e \quad . \quad . \quad . \quad . \quad (2)$$

Subtracting (1) from (2) we have therefore

$$d\mu t_1+g=d\mu t_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now if A is the breadth of the incident beam and a that of the emergent beam, $g=a\,d\theta$, so that (3) becomes

$$a\,d\theta=d\mu(t_2-t_1)$$

or

$$\frac{d\theta}{d\mu}=\frac{t_2-t_1}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence the linear dispersion,

$$\frac{ds}{d\lambda}=f\frac{d\theta}{d\lambda}=f\frac{d\theta}{d\mu}\frac{d\mu}{d\lambda}=f\frac{t_2-t_1}{a}\frac{d\mu}{d\lambda} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The dispersion therefore depends on the angular aperture of the camera lens (a/f), the difference in path in the prism of the extreme rays of the beam (t_2-t_1), and the material of the prism. We shall consider presently how to choose these factors so as to produce a desired result.

Factors affecting Resolving Power. We have seen that, even with an indefinitely narrow slit, each image of the slit (i.e each spectrum line) has a width 2ρ. It is proved in books on optics that when an image is formed by light having an angular aperture a/f and wave-length λ, the half-breadth, ρ, is given by $\rho=k.\lambda f/a$, where k is a constant depending on the form of the object. For a narrow rectangle (e.g. a slit) $k=1$, so that ρ in our case is given by $\lambda f/a$, where f and a have the same meanings as in equation (5).

In order, therefore, that two neighbouring spectrum lines shall be completely resolved, the distance between their centres must be at least $2\rho=2\lambda f/a$ (see Fig. 15 (a)). Since the intensity falls off at the edges of the lines, however, it is not necessary for them to be completely separated; a certain amount of overlapping may occur without obscuring the fact that there are two lines and not one. The extent of the permissible overlapping is, of course, rather vague, but experience shows that the approximate limit of distinguishability is reached when the maximum of one line falls on the minimum of the next, so that the distance between the centres is ρ. The appearance in that case is shown in Fig. 15 (b), where the dotted curves indicate the intensity distribution for the two lines taken by themselves, and the continuous curve, obtained by adding the ordinates of the others, shows the resultant intensity distribution. What experience shows is that the weakening in the centre is just sufficient to be detected. (It is assumed here that the lines are equally strong. If they vary considerably in intensity there is, of course, no general rule.)

The resolving power is now immediately calculable. $d\lambda$ is the wave-length interval between two lines separated on the plate by a distance $\lambda f/a$, and putting this value for ds in the dispersion formula (equation (5)) we obtain

$$\frac{\lambda}{d\lambda}\frac{f}{a}=f\frac{t_2-t_1}{a}\frac{d\mu}{d\lambda} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

whence the resolving power,

$$\frac{\lambda}{d\lambda}=(t_2-t_1)\frac{d\mu}{d\lambda} \quad . \; . \; . \; . \quad . \; . \quad (7)$$

Factors affecting Purity. If the slit has a width s, its geometrical image will have a width $s'=Ms$, where M is the magnification produced by the instrument. It is shown in text-books on optics that the angular magnification is equal to the ratio of the breadths of the incident and emergent beams, namely A/a in Fig. 14; and from this it follows that the *linear* magnification is $A/a.f/F$, where F is the focal length of the collimating lens. Hence $s'=s.A/a.f/F$. Now in Fig. 13 each half of the curve may be regarded as arising from light bent round one of the jaws of the slit, a horizontal line of infinitesimal length at the apex, connecting the two halves, corresponding to the light which has passed directly through the slit. The intensity distribution when the slit has a finite width is therefore obtained by separating the two halves of the curve by a distance equal to the breadth of the geometrical image of the slit and joining them by a horizontal line, since the intensity will be uniform and will have the maximum value when the light suffers no diffraction. This is shown in Fig. 16 (a). The limiting condition for resolution is clearly determined, as before, only by the overlapping

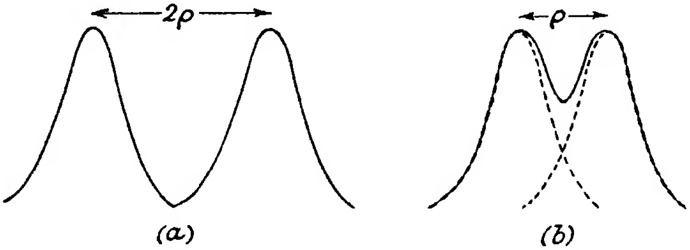

FIG 15 —Distribution of light intensity in adjacent spectrum lines when the slit is indefinitely narrow.

portions of varying intensity, and it is clear from Fig. 16 (b) that when this condition is satisfied the distance between the centres of the lines is $\rho + s.A/a.f/F = \lambda f/a(1 + sA/\lambda F)$. Substituting this value, then, for ds in (5) we have

$$\frac{\lambda}{d\lambda}\left(1+\frac{sA}{\lambda F}\right)=(t_2-t_1)\frac{d\mu}{d\lambda}$$

whence

$$\frac{\lambda}{d\lambda}=\frac{1}{1+\frac{sA}{\lambda F}}(t_2-t_1)\frac{d\mu}{d\lambda}=\frac{1}{1+\frac{sA}{\lambda F}}R \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where R is the resolving power.

Obviously, since $sA/\lambda F$ cannot be negative, the purity is less than the resolving power unless this term vanishes. We shall consider the ways in which this may happen presently.

Choice of Conditions in a Spectrograph. We may now return to those features of the instrument which we saw were at our choice to suit particular requirements, and see how our freedom can best be used. We will assume, as is generally the case, that we wish the intensity, dispersion and degree of resolution to be as high as possible, but it is well to point out in passing that this is not always so. Excess of brightness can usually be compensated for by shortening the exposure time, but it is sometimes desirable to weaken the spectrum itself. Defect of brightness, on the other hand, in a continuous or unresolved band spectrum may make small dispersion necessary, since the intensity at any point in such a spectrum diminishes as the dispersion increases. Even with resolved band spectra it is sometimes necessary to use a very small dispersion to show that we are actually dealing with the bands of molecules and not the lines of atoms. Again, it is sometimes necessary to obtain spectra on the same scale as others (e.g. those of faint stars or nebulae or faint laboratory glows) whose weakness makes the smallest

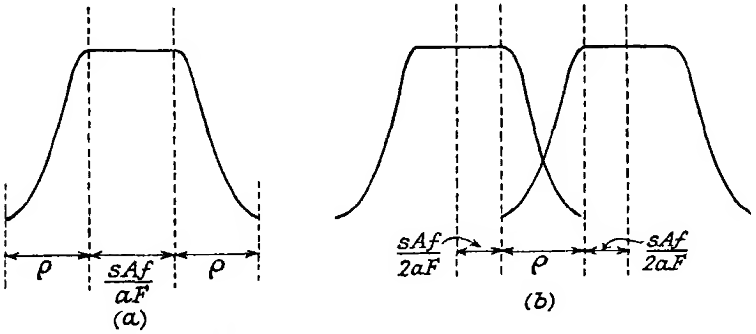

FIG. 16.—Distribution of light intensity in adjacent spectrum lines when the slit has a finite width.

dispersion a *sine qua non*. In general, however, the highest degree of brightness, dispersion, and degree of resolution is the aim.

(*a*) *Material of Lenses and Prism.* It will be seen that the dispersion, resolving power and purity are all directly proportional to $d\mu/d\lambda$. If there were no other consideration it would therefore be desirable to choose the material for which this property is highest. The overruling consideration here, however, is intensity, for the possible materials vary far more in transparency than in refractive index as we move along the spectrum. For the visible region and the portion of the infra-red that concerns us glass is the best material; it is easily worked, has a fairly high value of $d\mu/d\lambda$, can be obtained in considerable variety, and is comparatively cheap. In the ultra-violet, however, it is opaque. Its transparency falls off gradually and varies with the thickness traversed and with the sample chosen, but, generally speaking, glass will not take one far below 3500 A. For shorter waves quartz is universally used. It will transmit visible light also, and if only one spectrograph can be in use for all purposes its optical parts should be of this material. It is less affected than glass by temperature changes. $d\mu/d\lambda$, however, is considerably smaller than for glass, and for this and other reasons now to be mentioned it is inferior to glass where both are transparent.

There are two further disadvantages of quartz. First, unlike glass it cannot be obtained with a variety of refractive indices, so that the lenses are not achromatic. This means that light of various wavelengths cannot be properly collimated before falling on the prism and, further, that the focal surface of the camera lens on which the spectrum falls is very much inclined to the normal to the axis of the lens. The first defect has usually to be accepted, and it is in fact surprising that in spite of this quartz instruments give such good definition as they do. Achromatic combinations of quartz and fluorite are possible, but they are expensive and it is usually not worth while to obtain them. The inclination of the spectrum offers little difficulty since the plate may as well be fixed at one angle as another: it does, however, make focusing a more delicate operation than it would otherwise be.

The other disadvantage of quartz is that it is doubly refracting. A prism cut at random from a quartz crystal would therefore in general show two spectra considerably displaced with respect to one another. For example, the refractive index for the extraordinary ray for yellow light is the same as that for the ordinary ray for blue light. This defect could be removed by passing the light through a Nicol prism which, since the two spectra are polarised in perpendicular planes, would, if suitably oriented, transmit only one of them. Half the light, however, would be wasted by this device, and it is therefore the general practice to cut quartz prisms with the optic axis perpendicular to the refracting edge and parallel to the base when the triangular section of the prism is isosceles: the arrangement is illustrated in

Fig. 17 (a). If, now, the prism is set at minimum deviation, the light passes through it along the optic axis and the two rays coincide. Since there is dispersion in the prism, only one wave-length can fulfil this condition exactly, but the others depart from it only slightly and the effect on the spectrum is negligible.

The doubling of the lines, however, is still not completely removed. We may put the matter briefly by saying that although both rays travel together along the optic axis they do so at different velocities and therefore emerge in slightly different directions. To prevent this Cornu made use of the fact that quartz occurs in two varieties—"right-handed" and "left-handed"—in which the relative velocities of the ordinary and extraordinary rays are opposite. By forming the prism, still with its optic axis as before, with one half of right-handed and the other of left-handed quartz (Fig. 17 (b)), the rays effectively travel at equal velocities, for what one gains in the first half of the journey it loses in the second half. A "Cornu prism," as it is called, set at minimum deviation, is thus a necessity for satisfactory results with light transmitted through a quartz prism.

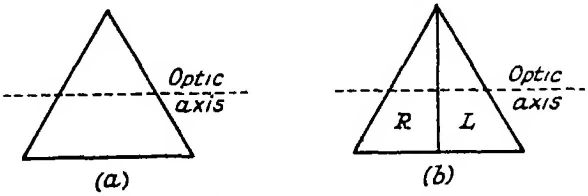

FIG 17 —Illustrating cutting of a quartz prism for spectrographic purposes.

Other materials, including liquids, are occasionally used for prisms, but for the region of the spectrum which concerns us they are so rarely used that it is unnecessary to consider them here. Liquids, of course, need an optically worked transparent container, and require special care in order to prevent irregularities of temperature from spoiling the definition through variations of density. When chosen, the reason, as with Evershed's ethyl cinnamate prisms, is the comparatively high values of $d\mu/d\lambda$ which some of them possess.

(*b*) *Shape and Size of Prism.* The shape of the prism (the triangular form being, of course, assumed) concerns us only with respect to the size of the refracting angle. It is customary to make the sides containing this angle equal so that the section is an isosceles triangle, and it will be assumed here that this is done, though it is not necessary except for the sake of appearance. We may then for brevity speak of a ray passing through the prism at minimum deviation as being "parallel to the base": it will be understood that the actual inclination of the base is of no importance and the phrase merely means "equally inclined to the refracting sides."

The angle of the prism makes no difference to the resolving power or purity if the value of t_2-t_1 is fixed; it does, however, affect the dispersion, the larger the angle the greater being the dispersion. This is easily seen from equation (5), for when f, t_2-t_1 and $d\mu/d\lambda$ are constant, the dispersion is inversely proportional to a, and for given t_2-t_1, a diminishes as the angle increases. Indeed, for a given prism angle the dispersion is independent of the breadth of the beam of light, for it is easily seen that t_2-t_1 and a change in the same proportion as the beam is widened or narrowed. It therefore makes no difference to the dispersion whether we fill the prism with light or use only a very narrow beam. This means that, for a given angle, the size of the prism makes no difference to the dispersion. It does affect the degree of resolution, however, for both resolving power and purity are directly proportional to t_2-t_1, and since the maximum possible value of this is the length of the prism base (when the prism is filled with light t_2 is the length of the base and $t_1=0$), the larger the prism base the greater the resolution attainable. This is true independently of the size of the prism angle.

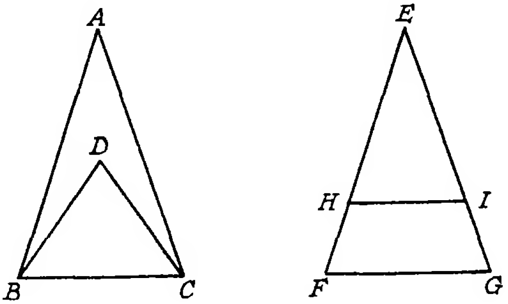

Fig. 18

These results are summarised graphically in Fig. 18. Supposing always that the prisms are filled with light, the prism ABC gives the same resolution as the prism DBC but a smaller dispersion. It gives also a brighter spectrum since it takes more light. On the other hand, the prism EFG gives the same dispersion as EHI, but greater resolution and greater intensity.

It would therefore seem desirable, for the best results, to have a prism with the largest possible angle and base. The base is limited by the amount of material available and by the necessity, in order to make full use of it, of having collimating and camera lenses of corresponding aperture, but there is no *intrinsic* reason why the base should not be indefinitely large. It is otherwise, however, with the angle, for here an inevitable limitation is set by the laws of optics. Consider for simplicity a beam of light passing through the prism at minimum deviation. If i and r are the angles of incidence of light on the prism and refraction into it, then $\sin i=\mu \sin r$; and since, at minimum deviation, $r=\alpha/2$, where α is the prism angle, we have $\sin i=\mu \sin \alpha/2$. Now the maximum value of $\sin i$ is 1; hence the maximum value of α is $2 \sin^{-1} 1/\mu$. Taking $\mu=1{\cdot}65$—a good average value for flint glass—we see that α cannot exceed 74°.

The meaning of this is clear from Fig. 19. The maximum value corresponds to $\sin i=1$, i.e. $i=90°$. The light therefore enters along the side AB (at "grazing incidence"), travels in the prism parallel to the base, and emerges along AC ("grazing emergence"). If, therefore, AC had been inclined to AB at a slightly greater angle, the light would have fallen on it at an angle greater than the critical angle and so would have been totally internally reflected. It is obviously undesirable to work at this limiting condition, if only because the incident beam, being of negligible thickness, would have negligible intensity. We must therefore choose an angle of incidence small enough to give a reasonably broad incident beam and a prism angle large enough to give a good dispersion. The prism angle generally chosen is 60°, as affording a sort of golden mean between spectra which are either too weak or too little dispersed.

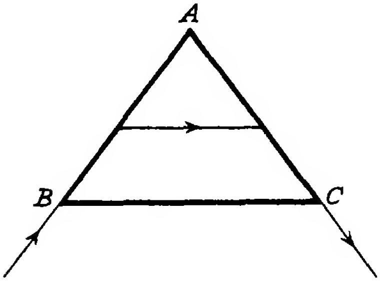

Fig. 19.

The limitation of prism angle may be overcome by increasing the number of prisms used. The dispersion produced by n similar prisms is n times that produced by one, and if the light passes through one of them it can pass through them all. The resolving power also is proportional to the total base-length (i.e. the total difference of path in the dispersing medium of the light at the two edges of the beam). The controlling factor here is the loss of light which inevitably accompanies an increase in the number of prisms. At each one there is loss by reflection at each of the two faces as well as by absorption in the material of the prism itself. The latter is much greater than one would be inclined to think from the apparently complete transparency of the prism. It is instructive to take two photographs in succession, with the same source and exposure time, first with the half of the beam which traverses the prism near the angle and, second, with the half which traverses it near the base; an opaque card placed in front of the appropriate portion of the prism serves to cut out the unwanted light. The observer will probably be surprised at the excessive amount of absorption in the thicker portion of the prism. For this reason it is not in general advisable to use more than one prism—or at most two. However bright the source may be, it is the fainter lines in its spectrum that are often of interest, and unless these are clearly visible, high dispersion and power of resolution are wasted. The only important exception to this is in the photography of the solar spectrum, where the source is extremely bright and the lines are absorption lines on a continuous background.

It is sometimes necessary to modify the form of a spectroscope (less often a spectrograph) to satisfy some particular condition. For example, the deviation of the light is an inconvenience in a small pocket spectroscope, and some form of direct vision instrument is desirable. This can be obtained by combining prisms of different materials in such a way that the deviation is destroyed while the dispersion remains.

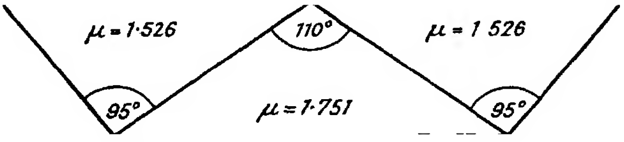

FIG. 20—One form of direct vision prism.

Fig. 20 gives one example of such an arrangement. The paths of red and blue rays through a prism of this kind are shown in Fig. 21, for which I am indebted to Mr. B. K. Johnson. Other combinations are possible, the angles being chosen to suit the refractive indices, and sometimes an additional prism is placed at each end, making five in all. Strictly speaking, only one ray goes through without any deviation; if there is to be dispersion the others must, of course, emerge at different angles. The whole of the visible spectrum, however, can be included within the pupil of the eye without difficulty. With a prism such as this aberration

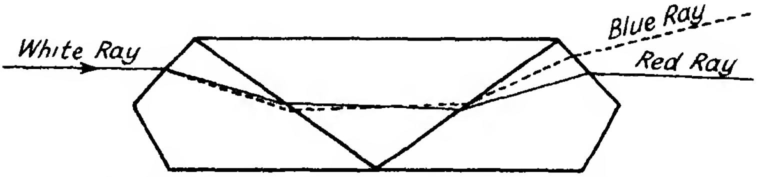

FIG. 21.—Passage of light through a direct vision prism

is automatically eliminated and a collimating lens is unnecessary, though one is usually provided.

For certain routine observations—e.g. those of flame spectra for quick detection of particular elements—the normal procedure of moving the telescope to take in successively light of different wave-lengths is less convenient than one in which the collimator and telescope are fixed and the spectrum is moved across the field of view by rotating the prism. The rotating screw can be attached to a drum bearing a scale of wave-lengths, so that, after preliminary adjustment, the wave-length of the line appearing on the crosswires of the telescope can be read, usually with an error of an angstrom or less, which is sufficiently accurate for such observations. The customary arrangement is to fix the telescope and collimator at right angles to one another. A single prism of the ordinary form will not deviate the light through so large an angle, and what is effectively a mirror is therefore provided to increase the deviation. Actually the prism is given a special form so that one of its sides acts as a mirror; its plan is shown in Fig. 22. The whole prism is in one piece, but it may be regarded as made up of three prisms, as shown by the dotted lines in the figure. The light, represented by a chain line, strikes the face AB at such an angle that a ray near the middle of the spectrum proceeds within the prism parallel to BD. It strikes AD at 45° and is thereupon reflected parallel to DC. From the similarity of the triangles it is obvious that it is deviated on passing through BC by the same amount as at AB, and since QR is perpendicular to RS, ST must be perpendicular to PQ. We have

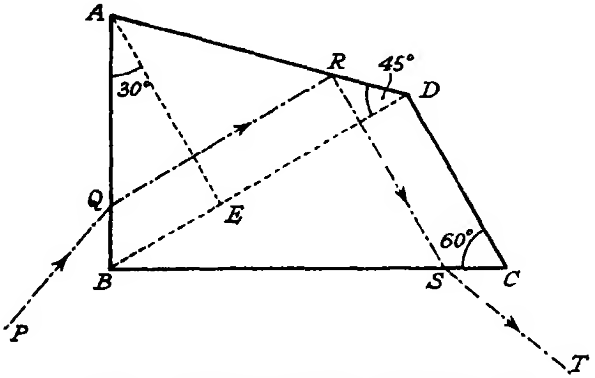

FIG. 22.—One form of constant deviation prism.

therefore simply to make PQ and ST the axes, respectively, of the collimator and telescope, and the spectrum line in the centre of the field is then the one which pursues the path described. Rotation of the prism brings the successive wave-lengths into this position, for it alters the angles of incidence and emergence to suit the variation of refractive index with wave-length.

The dispersion and degree of resolution given by a prism of this kind are those of a 60° prism with a base of length 2BE. It is clear from the figure that the effective parts of the prism are the two triangles, ABE and BDC, the triangle AED serving merely as a mirror. We could, in fact, remove the glass from AED and substitute a plane mirror along AD without changing the course of the light. The total refracting angle is therefore BAE+DBC=60°, and the breadth of the beam, supposing the incident light to fill the side AB, is AE, so that $t_2-t_1=2BE$. The geometry shows that DC is greater than BE, but the prism BDC will clearly not be filled with light, and the difference of path of the extreme rays of the beam will be the same in BDC as in ABE.

(*c*) ***Focal Length and Aperture of Collimating and Telescope Lenses.*** The focal length of the collimating lens does not enter into the expressions for dispersion and resolving power, but the purity is affected by it in such a way that a large focal length makes for greater purity. The focal length of the camera lens, on the other hand, does not enter into the expressions for resolving power and purity, but the linear dispersion is directly proportional to it. This suggests that both lenses should have as great a focal length as possible, though for different reasons.. (Incidentally, it will be noticed that the angular aperture of the collimator, A/F, is the factor of importance in the purity, and not the focal length alone. Assuming, however, that A is determined by the size of the prism available, we are left with F alone to consider.) The practical limit is set by conditions of stability and the available space. Long narrow collimators and cameras very easily get out of adjustment; and it is advisable to have f and F approximately equal; otherwise there will be magnification or minification of the *length* of the slit, which is generally undesirable.

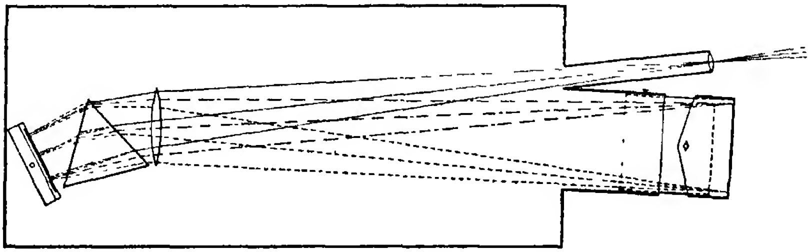

FIG. 23 –Littrow prismatic spectrograph.

A very satisfactory method of preserving stability without unduly limiting f and F is that used by Littrow and generally called by his name. The device is to use the same lens and tube for both collimator and camera; the light, after passing through the prism, being reflected back through it and the lens a second time. The arrangement is shown in Fig. 23. The whole is enclosed in a strong wooden box, which can, if necessary, be double-walled and lagged to keep the temperature constant. An alternative position for the slit is at the side of the box, so that the light enters at right angles to the axis of the lens and is directed along the axis by a small reflecting prism placed just off the line of return of the light to the photographic plate (see Fig. 27 for example). In the Littrow spectrograph, therefore, we have the dispersion and degree of resolution of two prisms, and gain the advantage of large focal length with the minimum of instability.

Instead of a 60° prism with a mirror behind it, a 30° prism (a "half-prism") is sometimes used with the back surface (AB in Fig. 24) itself made reflecting. For the visible region silvering is satisfactory, but silver fails to reflect throughout a large region of the ultra-violet, and here an amalgam of tin and mercury (or, more recently, a layer of aluminium, with better results) is used. The half-prism is almost invariably used in quartz Littrow spectrographs because, owing to the return of the light along its own path, the Cornu combination is unnecessary. Quartz which is right-handed for one direction of the light becomes left-handed for the opposite direction, and a single 30° prism of either kind of quartz is therefore sufficient.

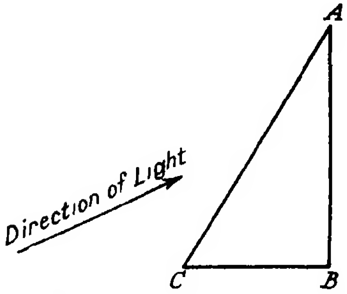

Fig. 24.—A "half-prism."

The Littrow arrangement introduces a difficulty not experienced when the collimator and camera are on opposite sides of the prism—the portion of the light reflected from the lens surfaces, unless it is intercepted, falls on the plate and produces fogging. Light from the front surface clearly diverges after reflection and reaches the plane of the photographic plate as a large circle, with diameter MN (Fig. 25), of rather faint light which, nevertheless, is usually bright enough to cause trouble in any but the shortest exposures. Light passing through the front surface and reflected from

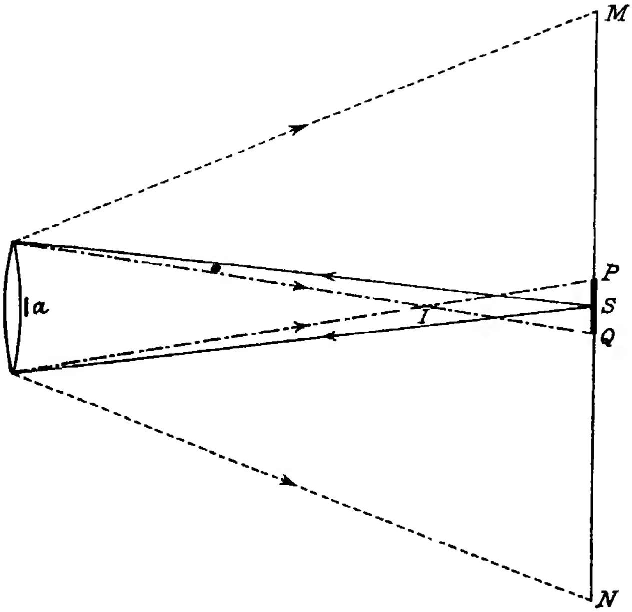

Fig. 25.—Illustrating reflection of light from collimating lens in a Littrow spectrograph.

the back, however, forms an image at some point I (I may be beyond the plate, according to the curvature of the lens surfaces), and thereafter diverges to a small, roughly circular, out-of-focus image, PQ, of the slit, which is intrinsically much brighter than the light in MN.

This difficulty is overcome as follows. The light reflected from the front surface which falls on the plate at the position of the spectrum is simply that reflected from a narrow horizontal strip at the centre of the lens. If, therefore, a piece of dull black card (shown in section at (a) in Fig. 25) is placed before this portion of the surface, the spectrum will be protected from the reflected light. Some loss of light is, of course, caused thereby, but if the card is made no larger than is necessary this is usually not serious. The light forming the image I can sometimes be dealt with by placing a small opaque object, little wider than the image of the slit itself, at I. This also abstracts a negligible amount of light from the incident beam. Such a device is clearly ineffective if I falls beyond the plate. In that case—and often when I is between the lens and plate also—the alternative method is adopted of slightly tilting the lens so that the patch of light PQ falls just above or below the spectrum.

On account of this necessity, and also because of the fact that the slit and plate cannot both be at the actual focus of the lens, one must work slightly off the axis in a Littrow spectrograph. This has no serious effect on the definition provided that the focal length is fairly large so that the angular deviation from axial symmetry is small. On this account Littrow spectrographs of small focal length are not very satisfactory; one and a half metres should be regarded as a minimum, and the greater the focal length the better is the result.

(*d*) *Angle of Incidence of the Light.* A beam of light which covers the whole prism face AB in Fig 14 will be wider, and will lose a smaller proportion of itself by reflection, the smaller the angle of incidence. Hence, so far as intensity alone is concerned, the smallest possible angle of incidence (i.e the smallest angle that will allow the light to emerge from the prism at the opposite face) is the best. On the other hand, equation (8) shows that the purity decreases as A, the breadth of the incident beam, increases, so that on this account a large angle of incidence is desirable. It is easily seen, from the derivation of the equation, that it is the geometrical magnification and not the diffraction broadening that is affected by A; the angular magnification, A/a, is, in fact, zero at grazing incidence and infinite at grazing emergence. As we approach these extremes the change is very marked. It is an instructive experiment to observe, say, the two close yellow lines of sodium through a spectroscope which just resolves them at minimum deviation with a very narrow slit. Making the slit as wide as possible —about 1 or 2 mm.—and gradually increasing the angle of incidence, the spectrum lines will be seen to narrow steadily until, when the light enters practically along the face of incidence, the lines separate and appear, though relatively faint, as clearly resolved as at minimum deviation with the narrowest slit. On the other hand, if the angle of incidence is decreased, even with a very narrow slit, the spectrum lines broaden as grazing emergence is approached and finally become a blur stretching right across the spectrum.

Some compromise is therefore necessary between the claims of brightness and purity. It is for this reason, and this reason alone (apart, in relatively few instances, from the convenience which a recoverable position affords when the instrument is liable by disturbance to be put out of adjustment), that the prism is usually set at minimum deviation for some chosen wave-length. It is a satisfactory compromise, but has no other advantage over any alternative arrangement.

In this connection it should be pointed out that a uniform angle of incidence is possible only for a point source. When a slit of finite length is used the rays from different points of it fall at different angles on the prism, notwithstanding that the slit is in the focal plane of the collimating lens and rays from each point are made parallel. The effect of this is to give a curvature to the spectrum lines. Suppose, for example, that the rays from the centre of the slit fall on the prism at the angle for minimum deviation. Then the rays from other points must suffer greater deviation, and the difference increases at an accelerated rate as we proceed outwards from the centre, giving a line concave towards the side of greater deviation, i.e. the side of shorter wave-length. It can be shown that the curvature increases as the wave-length decreases, and that the line forms a parabola with vertex at the centre. This effect, though perhaps tending to spoil the appearance of a spectrum when a long slit is used, has no serious consequences from the utilitarian point of view. It may be added that with the direct vision prisms illustrated in Fig. 20, there is no curvature of the lines.

(*e*) *Width of Slit.* The slit width does not influence the dispersion, and is by definition zero for the resolving power. Its effect on the purity of the spectrum is shown in equation (8), from which it is clear that the narrower the slit the greater is the purity—as is, of course, directly evident. The intensity curves in Fig. 16 show that, when the slit is wider than a certain minimum, the intensity within the line is not increased by widening it. If, on the other hand, we narrow it, the flat top of the intensity curve preserves a constant height only until a certain point is reached, which occurs before the jaws are actually closed. It is clear that when the slit is indefinitely narrow the amount of light passing through it is indefinitely small, so that as we pass from the conditions of Fig. 16 to those of Fig. 15 there is not only a narrowing but, in the last stages, a decrease in height of the curve as well. It follows that, at a certain slit width, small but finite, the maximum height of the curve will begin to decrease. This is the width to which one should normally adjust the slit. [The best practice, as has already been said, is to narrow the slit slowly while watching the spectrum until further narrowing produces a visible decrease of intensity, and then to stop. The eye, however, is not an infallible detector of the critical point, and if the spectrum cannot be photographed with reasonable exposure when the slit has a certain width it is always advisable to widen it]and try again.

(*f*) *Focal Length and Situation of Condensing Lens.* The condensing lens should always be so arranged that the beam of light entering the slit just fills the collimating lens; i.e. the angles subtended at the slit by the collimating and condensing lenses should be equal. If the condensing lens subtends the smaller angle, the full aperture of the instrument is not being used and there is loss of intensity and resolution. If it subtends the larger angle (usually the lesser of the two evils) stray light enters the spectrograph and falls ultimately on the photographic plate. This suggests that, with a point source of light, a short focus condensing lens is preferable, for, its position being determined by the condition just mentioned, the nearer to it the source is placed the greater will be the proportion of its total radiation that is captured for the spectrograph. A point source, however, though effectively provided by a star, is usually an unrealised ideal in the laboratory; in this connection it means a source whose image for all positions of the condensing lens is narrower than the width of the slit. We have in practice always to do with extended sources, and with these it can be shown that, provided the collimator is filled with light, the type and position of the condensing lens by which this is achieved makes no difference at all to the intensity of the spectrum. What is gained by collecting a larger fraction of light from the source is lost by the fact that the image of the source on the slit is proportionately enlarged and therefore intrinsically weakened in surface brightness. No matter how one tries to increase the intensity by operations outside the spectrograph, there is always a compensating factor, and it is therefore necessary only to ensure that the full aperture of the instrument is being used in order to get the brightest possible spectrum.

For this reason, if the source of light is homogeneous and is large enough, when placed at a safe distance from the slit, to subtend an angle equal to that subtended by the collimating lens, it is a disadvantage to use a condensing lens because of its reflection and absorption of some of the light incident on it. This is a point which is frequently overlooked. Of course, if the source is not homogeneous and a particular part of it is of interest, the condensing lens is necessary to ensure that the spectrum produced is the spectrum of that part only, but so far as intensity is concerned the condensing lens is a source of weakness.

There is another very important consideration. If the condensing ens is achromatic, what has been said above applies indiscriminately to all wave-lengths. For the visible region it is possible to obtain sufficiently achromatic lenses without much difficulty, but for the ultra-violet usually the only practicable material is quartz, achromatic combinations of quartz and fluorite being too rare for general use. The focal length of a quartz lens varies rapidly with wave-length, so that for any one position of the condensing lens most of the light from the source is in focus either in front of or behind the slit, and the condition of just filling the collimating lens cannot be fulfilled. Moreover, a particular part of the spectrum line does not correspond to a particular part of the source except in those wave-lengths for which the source is actually focused on the slit. This is a disadvantage which has to be accepted, but if for any reason a certain part of the spectrum is of more interest than other parts, the condensing lens should be so placed that the light of that part is focused on the slit. This can be done roughly by using filters and, in the ultra-violet, placing immediately in front of the slit a card coated with some material (e.g. naphthalene) that shows fluorescence under the stimulus of the wave-lengths of interest. Alternatively, the focal length of the condensing lens could be determined for different wave-lengths, and the lens placed in the position given by calculation.

(*g*) *Type of Photographic Plate.* Ordinary photographic plates are not sensitive throughout the whole of our range of spectrum. They are completely insensitive to the longer wave-lengths, and need long exposures for the shortest. The whole range, however, can be covered by choosing the most suitable type of plate for each portion. Progress in this matter is fairly rapid, and the best advice is to become familiar with manufacturers' catalogues, which usually give the sensitivity, in the various regions of the spectrum, of the plates listed.

In the region 2500–2000 A. the spectrum obtained on an ordinary plate can be strengthened by covering the film with a very thin layer of some fluorescent substance, such as paraffin. At a place where short-wave radiation falls on the paraffin it stimulates the emission of fluorescent light of greater wave-length and the spectrum line accordingly appears stronger. It is tempting to conclude that the plate is thus rendered more sensitive, but this is misleading unless the word "sensitive" is used in a special sense. An investigation by Hunter and Pearse * shows that if sensitivity is measured by the minimum exposure necessary to give a measurable line, no plate among those examined except the Ilford Q2 is more sensitive in the region 2500–2000 A. than an untreated ordinary plate. The *maximum* intensity attainable, however, by prolonged exposure is much less with the ordinary plate than with most others, and it is this maximum which is raised by oiling. The following table, given by Hunter and Pearse,

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* *Proc. Phys. Soc.*, 50, 256 (1938).

shows for various wave-lengths and plates the relative minimum exposure times necessary to produce a measurable record: the figure for the ordinary plate is taken as unity for all wave-lengths:

Wave-length (A.).	2500	2400	2300	2200	2100	2000
Plate						
1. Imperial ordinary . .	1	1	1	1	1	1
2. Paget ½-tone	7	6	5	5	3	2
3. Hilger Schumann .	9	9	4	3	2	1·5
4. Agfa Schumann	9	3	2	1·5	1·3	1
5. Duclaux-Jeantet	3	2	1·5	1	1	1
6. Q1 .	18	15	12	9	9	6
7. Q2	1	0·7	0·5	0·3	0·2	0·1
8. Ordinary+kerosene	1	1·5	3	3	2	1
9. Ordinary+paraffin	9	14	9	7	4	3
10. Ordinary+white vaseline	2	1·5	2	2·5	1·5	2
11. Ordinary+yellow vaseline	3	2	2	2	2	2
12. Ordinary+apiezon M .	9	24	24	15	6	3
13. Ordinary+sodium salicylate	2	2	2	2	2	2
14. Ordinary+anthracene .	3	4	8	3	3	3
15. Panchromatic+anthracene .	7	5	7	9	27	>27
16. Eastman ultra-violet	3	2	3	4	3	8
17 Agfa ultra-violet .	2	2	8	4	6	6

The conclusion is that the ordinary plate is better than the sensitised plates for recording particular lines, but if comparison of intensities of different lines is of importance the sensitised plates, owing to their higher maximum attainable blackening and consequent range of contrast, are to be preferred.

CHAPTER

4

DIFFRACTION GRATING SPECTROGRAPHS

General Properties. Although in spectroscopy considered as a pure science the grating spectrograph is at least as necessary and frequently used an instrument as the prismatic spectrograph, it is much less applicable to general industrial work. The chief reasons for this are, first, that since it divides the available light into a central image and a number of spectra of different orders, while the prism concentrates it all into a single spectrum, the former is much less suitable for the detection of weak radiations; and secondly (a less important reason), the approximate uniformity of dispersion throughout the grating spectrogram makes it impossible (unless the dispersion is much smaller than that normally used) to photograph the whole spectrum on a single plate. Harrison * has made out an ingenious case for the greater suitability of the grating spectrograph, but nevertheless, if circumstances allow of the employment of only one spectrograph, there seems little doubt that it should be a prismatic instrument unless the problems to be dealt with are of a very special kind and are narrowly restricted in scope. This chapter is included, therefore, not as implying that a grating spectrograph is recommended for general work, but for the help of those who already possess such an instrument.

In calculating the properties of a grating it is generally assumed for simplicity that it consists of an alternation of clear and opaque spaces, of uniform breadths *a* and *b*, respectively, so that the incident light is divided into a series of similar beams, either reflected or transmitted, between successive members of which a constant difference of phase is established. The essential feature of the instrument, however, is simply that it breaks the light up in this way, the particular means by which it does so being comparatively trivial. The customary method of ruling gratings is to draw a diamond point along the surface of a plane or concave block of glass or speculum metal (more recently a film of aluminium has been deposited on a glass surface, sufficiently thick not to be completely penetrated by the diamond), so that a narrow linear groove is formed either by cutting or by pressure. The point is then lifted, withdrawn to the end of the line at which it began,

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* *Spectroscopy in Science and Industry*, p. 81 (Chapman & Hall, 1938).

advanced a very short distance in a direction at right angles to the groove, and made to form a second groove adjacent to the first. The process is repeated, usually many thousands of times, until a series of parallel grooves is made, all similar to one another and extending over a few inches of the block. This constitutes the grating, from which the incident light is reflected into a series of spectra. In the older gratings no care was taken to make the grooves of any particular shape so long as they were all alike. Nowadays, however, the shape is often chosen so as to concentrate most of the light into a particular spectrum, thus tending to neutralise the disadvantage of the grating already mentioned A modern grating may have as many as 20,000 or 30,000 lines to the inch: gratings ruled on Rowland's machine, of which there are many examples still in use, have 14,438 lines to the inch.

The general formula giving the relation between the direction of observation and the wave-length observed in a grating spectrum is worked out in many text-books on optics and only the result need be given here If a and b are the breadths of the clear and opaque spaces (with an ordinary ruled grating, $a+b$ is the width of a groove and can be given a single symbol, but inasmuch as coarse gratings with the conventional clear and opaque spaces are still used for certain special purposes, there is an advantage in retaining both a and b in a general discussion), and i is the angle of incidence of the light, then the wave-length, λ, seen in any direction θ is given by the formula

$$(a+b)(\sin i+\sin\theta)=\pm m\lambda \quad . \quad . \quad . \quad . \quad (9)$$

where m has any integral value from 0 upwards For this formula to be applicable for all values of i and θ and for both reflected and transmitted light, it is necessary to measure both angles according to a fixed convention. The one assumed here is as follows. The angles are measured from the normal to the grating drawn on the side from which the light is incident, and are taken in a counter-clockwise sense from this direction. Thus, in Fig. 26, in which the light is assumed to be travelling in the directions of the arrows, i is the angle NOA and θ the angle NOB as marked.

It is clear from this formula that λ varies with θ. Hence, i having the same value for all wave-lengths, the light seen in any direction θ_1 will have the wave-length given by putting θ_1 for θ in equation (9). As θ is varied, therefore, λ will change continuously, i.e. the light will be spread out into a spectrum. Furthermore, since m may have any integral value there will be a number of such spectra, each corresponding to a particular value of m. When $m=0$ the same value of θ will satisfy the equation for all wave-lengths. Light seen in this direction will therefore be unanalysed. It is said to form the "central image." For $m=1, 2, \ldots$, however, there will be a series of spectra which will overlap one another; for, giving θ the constant value θ_0 for which (9) is satisfied when $\lambda = \lambda_0$ and $m = 1$, it is clear that the equation will still be satisfied when $\lambda = \lambda_0/2$ and $m = 2$; $\lambda = \lambda_0/3$ and $m = 3$; and so on. This means that in each direction θ a series of wave-lengths, λ, $\lambda/2$, $\lambda/3$, . . . will appear (supposing, of course, that they are present in the incident light), and if we wish to study any one of them we must take steps to eliminate the others.

The value of m is said to determine the *order* of the spectrum; thus, when $m = 1$ we have the spectrum of the first order, and so on. There are clearly two spectra of each order, corresponding to the + and − signs in equation (9); one appears on each side of the central image. A grating ruled without regard to the shape of the grooves will in general give spectra which are brighter the lower the order. There are sometimes exceptions to this, but whatever irregularities there may be with the smaller values of m, the spectra invariably get too faint to be observed when m is large; it is very rare for a spectrum of higher order than the fifth to be observable. With a "clear and opaque spaces" grating the intensity of a line in the m'th order is given by the expression $I_m = I_0 \phi^2 \sin^2\phi$, where I_0 is the intensity of the same wave-length in the central image, and $\phi = (a+b)/(am\pi)$. Clearly, as m increases ϕ^2 decreases, giving a general decrease of brightness with advancing order on which a slight irregularity may be imposed in the earlier orders by the fluctuations of $\sin^2\phi$. The formula is, of course, inapplicable with a machine-ruled grating in which a and b have no separate significance, and here, as has been said, the grooves can be so shaped as to concentrate most of the light into one order.

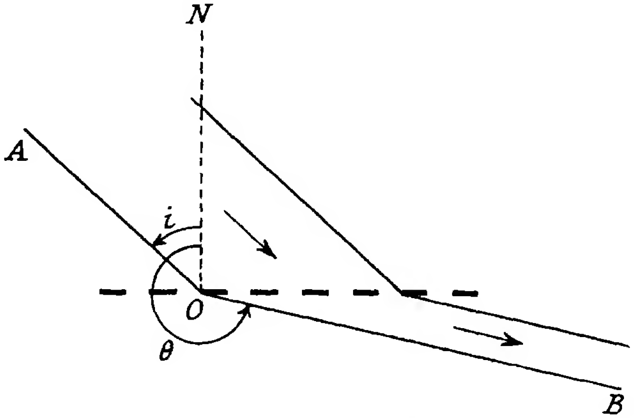

FIG. 26.—Passage of light through a diffraction grating

In most work with gratings it is necessary to adopt special means to eliminate the unwanted orders. In theory this can always be done by passing the overlapping light through a prism after dispersion by the grating, but this is rarely practicable. The separation can sometimes be made fairly easily by suitably choosing the material of the condensing lens and the photographic plate used. For example, suppose we wish to photograph 4100 in the third order. Then, since

$$1 \times 12{,}300 = 2 \times 6150 = 3 \times 4100 = 4 \times 3075 = 5 \times 2460,$$

we shall have to eliminate (neglecting higher orders as being too faint for consideration) the wave-lengths 12,300, 6150, 3075 and 2460. This may be done by using an ordinary photographic plate, which will not record the first two of these wave-lengths, and a glass condensing lens which will not transmit the others. If, however, we had wished to photograph 6150 in the second order, we would have had to use a panchromatic plate. This would still not have recorded 12,300, but it would have left us with the task of eliminating 4100. To do this we would have had to employ a filter—in this case bromine vapour or a solution of potassium ferrocyanide of chosen strength In general it is advisable to have a choice of filters, and for this purpose certain dyes which show strongly selective absorption are very useful. Plate XII shows the iron arc spectrum taken through a solution of nitroso-dimethyl-aniline. Such a substance as this, with two separated absorption bands, is often of great use. Sets of filters provided by photographic plate manufacturers are also very useful, although, as they are generally enclosed between glass cover plates, they do not transmit most of the ultra-violet. For that region the absorbing material must be placed between quartz plates or enclosed in a tube with quartz ends. Baly * gives the following list of absorbents recommended by Ames, the wave-lengths which they *transmit* being placed after the names of the absorbents:

	A.
Saturated solution of salicylic acid in alcohol	3500–8000
Aesculin, 0·25 per cent. aqueous solution with one drop of ammonia to each 30 c.c. (freshly prepared)	4100–8000
Potassium ferrocyanide	4400–8000
Primrose or aniline yellow	5000–8000
Fluorescein or gold chloride	5200–8000
Chrome alum Malachite green Bitter almond green Brilliant green	3200–3700 and 4600–5200
Cobalt chloride	3400–4500
Gentian violet, strong	3600–4600 and 6000–8000
Potassium permanganate	3900–4600 and 5800–8000

The strengths of the solutions, which of course will depend on the length of the absorbing column, must in all cases be determined by

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**Spectroscopy*, vol. I, p. 200 (third edition, 1924).

trial. It might be observed that when working in the first order it is rarely necessary to use a filter, for a glass condensing lens eliminates everything that would overlap the wave-lengths below about 6500 A.

The Plane Grating. In general form the plane grating spectrograph resembles the prismatic instrument with the grating substituted for the prism. There is the same necessity for slit and collimating lens and for bringing the light to a focus after dispersion. The slit should, for the sake of appearance, be parallel to the rulings of the grating, but a slight inclination causes no serious inaccuracy if the light is collimated. The Littrow arrangement is possible and, in fact, is generally used with a plane grating, the grating being of the reflection type and taking the place of the prism and mirror (Fig. 27). The angles i and θ are then obviously equal, and the grating is rotated about a vertical axis until the required spectrum region appears on the plate. The filter, if one is needed, is placed in front of the slit.

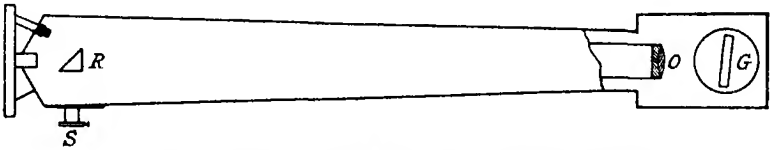

FIG 27.—Littrow mounting for plane diffraction grating.

Dispersion, Resolving Power and Purity of Grating. It is clear from Fig. 26 that the deviation of the light is measured by $\theta - i$, and since i is the same for all wave-lengths, the angular dispersion is represented by $d\theta/d\lambda$ and the linear dispersion by $f.\,d\theta/d\lambda$. Differentiating (9) we have therefore

$$\frac{ds}{d\lambda} = f \cdot \frac{d\theta}{d\lambda} = \frac{fm}{(a+b)\cos\theta} \quad . \quad . \qquad (10)$$

the sign having no importance here. The range of θ is very small since the length of the photographic plate is small compared with the focal length of the camera lens. Hence the dispersion is almost independent of λ on a single plate, whereas in the prismatic spectrograph we found it to be inversely proportional to λ^3. For this reason the grating has very great advantages when a crowded spectrum in the red or infra-red is the object of study. The dispersion is proportional to the fineness of the rulings and also to the order number, which explains why higher orders are often used despite their relative weakness.

The resolving power of the grating is found, as with the prism, by putting $ds = p = \lambda f/\alpha$ (where the breadth of the emergent beam is now called α to save confusion with the grating space), whence

$$\frac{\lambda}{d\lambda} = \frac{\alpha m}{(a+b)\cos\theta} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

The factors on the r.h.s. are not independent of one another. In

Fig. 28, if AB is the grating, of length L, it is clear that $\alpha=L\cos\theta=N(a+b)\cos\theta$, where N is the *total* number of rulings on the grating. Hence the resolving power, R, becomes

$$R=\frac{\lambda}{d\lambda}=Nm \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

The resolving power is therefore directly proportional to the number of beams into which the incident light is divided and to the order number of the spectrum. It can be shown that the effect of increasing N is to narrow the lines, while that of increasing m is to separate them, i.e. to increase the dispersion. The two factors already referred to (p. 35) as determining the degree of resolution are therefore here clearly separated.

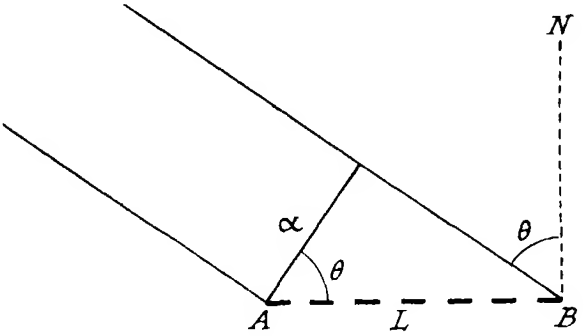

Fig. 28

The purity of the grating spectrum is found by the same process as that already given for the prism, and we merely state the result.

$$\text{Purity}\left(\frac{\lambda}{d\lambda}\right)=\frac{1}{1+(sL\cos i)/(\lambda F)}Nm \quad . \quad . \qquad (13)$$

where s and F are, as before, the width of the slit and the focal length of the collimating lens, respectively. This modification of the resolving power is, in fact, identical with that already found for the prism, for $L\cos i$ is obviously the breadth of the incident beam. As before we have the theoretical possibility of realising the resolving power at grazing incidence ($\cos i=0$).

Our freedom in setting up the grating spectrograph may be discussed under similar headings to those already adopted for the prismatic instrument, but the treatment can be much abbreviated. The factors at our disposal are (a) material of grating; (b) shape and size of grating; (c) focal length and aperture of collimating and telescope lenses; (d) angle of incidence of light; (e) width of slit; (f) focal length and situation of condensing lens; (g) type of photographic plate used. Concerning these, the remarks already made under (c), (d), (e), (f) and (g) apply, with obvious adaptation, to the grating as well as to the prism. The only difference in application is that the greater reflection with increased angle of incidence is not a loss with the reflection grating as it is with the prism. In the extreme ultra-violet, in fact, Siegbahn has adopted grazing incidence as a standard arrangement and has obtained remarkably pure spectra. For ordinary purposes, however, the restriction on the amount of incident light makes this practice undesirable. The angle chosen is determined mainly by mechanical considerations, and, if these allow, normal incidence is often adopted. With the Littrow arrangement, of course, the angle is determined by the region of spectrum to be examined, for here i and θ are automatically equal. It should be added that grating lines, unlike prismatic lines, are not curved when the slit is straight.

There is little to say concerning (a), the material of the grating, for this is the concern of the manufacturers alone. In the region of spectrum which interests us speculum metal is the commonest material, although aluminium has grown in favour in recent years. The size and shape of the grating, (b), give scope for much greater variety. The larger the grating the more light it can accommodate, provided always that the collimating lens is large enough to fill it, and this is almost invariably an advantage The resolving power and purity depend on the total number of lines on the grating, irrespective of how close together they are, and, for a given spacing, they increase with the aperture. The dispersion, however, depends on the number of lines per unit length. Thus a 4-inch grating with 10,000 lines per inch would have the same resolving power as a 2-inch grating with 20,000, but it would give only half the dispersion. A most important feature of the grating is the geometrical form of the surface on which it is ruled. So far we have assumed this to be a plane, but a concave spherical surface is used at least as frequently and has such special features that it needs separate description.

The Concave Grating. The concave grating is ruled on a spherical, not a cylindrical, surface and, owing to the construction of the ruling machine, it is the projection of the rulings on the tangent plane, and not the rulings themselves, that are equidistant. The difference, however, is negligible since the radius of curvature is generally large—from 6 to 21 or 30 feet usually—whereas the aperture does not exceed a few inches.

The particular feature of the concave grating on which its special usefulness depends is that it can be used without a collimator or camera lens. Light diverging from the slit can fall on the grating and be brought to a focus without the intervention of any refracting medium. The slit is made parallel to the rulings and placed with its centre somewhere in the plane which bisects the rulings normally. No matter where it is placed so long as this condition is satisfied, a well-focused spectrum will be found somewhere with the centres of the lines in the same plane. This is often overlooked because there is a particular set of positions of the slit which is almost invariably used. If a circle be drawn in the plane mentioned so that it is tangential to the grating and has a diameter equal to the radius of curvature of the grating, and if the centre of the slit is placed *anywhere* on this circle, the various orders of spectra will be accurately in focus somewhere else on the same circle. The circle is usually known as the *Rowland circle*, after the great experimenter who introduced this type of grating into spectroscopy.

Because of this property, special forms of mounting of the grating have been devised so that the Rowland circle is automatically used.

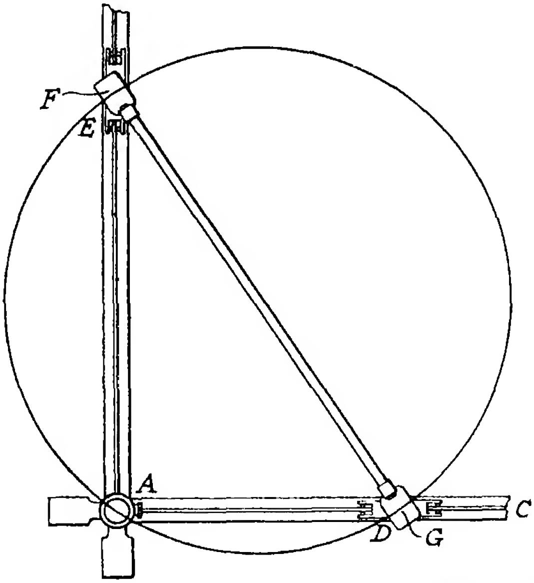

FIG 29.—The Rowland mounting for a concave diffraction grating

Rowland's original mounting is illustrated in Fig. 29. It is still extensively used. AC and AE are two metal arms fixed perpendicularly to one another, while FG is a movable arm to which are attached wheels which can run in grooves in AC and AE, thus forming a right-angled triangle whose hypotenuse is constant but whose other sides are variable. FG is made equal to the radius of curvature of the grating, and the grating itself is fixed normally to it at F and the photographic plate is placed at G. A circle with FG as diameter—the Rowland circle—must pass through A for all positions of FG, so that if the slit is placed at A the plate, provided it is bent into coincidence with the circle, will receive the spectrum in good focus however FG is moved. The region of spectrum examined will vary with the position of FG, for i is the angle AFG while θ is always zero.

A slight variation of this mounting was introduced by Abney, who kept the grating and plate fixed and moved the slit. His arrangement is shown in Fig. 30, where G represents the position of the grating and P that of the plate. The Rowland circle is here fixed in space and is, in fact, the actual material structure along which the slit, S, is moved, by rotating the arm CS, to vary the region of spectrum examined. Here again i is variable and θ is zero; and the chief advantage which this mounting has over the Rowland is that, since it is the lightest part of the apparatus that is moved, stability is more easily maintained.

Both these mountings have two serious defects. Since the radius of curvature is usually large they occupy a great deal of room space which, in order that the plate shall not be fogged, must be kept dark, and in order that good definition shall be maintained during long exposures, must also be kept at constant temperature. This may offer a serious problem. Secondly, the range of spectrum which may be studied is severely limited When $\theta=0$, equation (9) becomes

$$(a+b)\sin i=\pm m\lambda \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and since sin i cannot exceed 1, the maximum value of λ is $(a+b)/m$. With a grating of 20,000 lines per inch ($a+b=0$ 000127 cm.) the first order cannot be examined above 12,700 A., the second above 6350, the third above 4233, and so on. In practice, owing to mechanical necessities, it is, of course, impossible to reach even these limits, since grazing incidence is impracticable with the Rowland mounting. Hence, one of the chief advantages of a grating—the possibility which it offers of large dispersion in the higher wavelengths—is nullified.

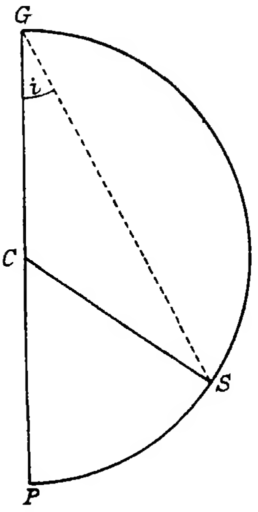

FIG. 30 —The Abney mounting for a concave diffraction grating.

These defects are, to a large extent, removed in the Eagle mounting. in which the light examined is that which returns along the line of incidence, so that $i=\theta$. In the diagram in Fig. 31, in which the circles drawn are successive positions of the Rowland circle, and G and P represent the initial positions of the grating and plate, the light (entering through a slit at the side and reflected to the grating by a prism as in the Littrow spectrograph) travels along the direction PG and back, and when P and G are each in a particular position a particular region of the spectrum appears on the plate, determined by the angle i. To change the region, either P or G must be moved round the circle, but any pair of positions can obviously be copied by moving G to and fro along the line PG and rotating both P and G until the circle of which

P forms a part is tangential to G. For example, G′ and P′ represent new positions in which the spectrum obtained is identical with that corresponding to the positions G″ and P″. Both G′, P′ and G″, P″ lie on a Rowland circle, but the circles are not coincident. The use of G′, P′ instead of G″, P″ enables the whole apparatus to be enclosed in a narrow box whose length need not be much greater than the diameter of the circle, i.e. the radius of curvature of the grating. The Rowland circle does not exist as a physical entity and the space it would occupy is therefore saved. This greatly facilitates the maintenance of constant temperature.

Since with this arrangement $i=\theta$, the formula becomes

$$2(a+b)\sin i=m\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and the maximum attainable value of λ in any order is therefore doubled

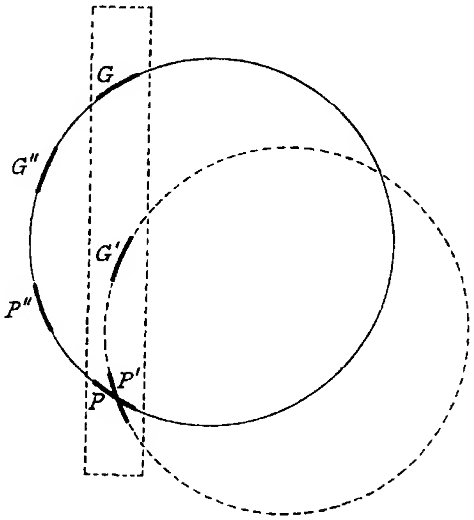

FIG. 31 – The Eagle mounting for a concave diffraction grating.

There still remains a region of interest which cannot be reached in the higher orders, but it is greatly reduced in extent with the Eagle mounting and the limitation is not often serious.

The formulae already given for dispersion, resolving power and purity hold good for the concave as for the plane grating; it can easily be shown that for the term $(sL\cos i)/(\lambda F)$ in the expression for the purity we must substitute $(sL\cos i)/(\lambda\rho)$, where ρ is the radius of curvature of the grating.

Defects of Grating Spectra. (*i*) *Astigmatism.* The absence of a collimator in either a prism or a grating spectrograph results in aberration, by which the spectrum line is not a clearly defined image of the slit. This does not, however, rule out the concave grating mountings just considered as effective instruments because, if the slit is made accurately parallel to the rulings, the effect of aberration (*astigmatism*, as it is called in this case) is simply to lengthen the image without broadening it. We therefore have sharp long lines produced, and it is a simple matter to reduce the length by a suitable screen placed in front of the plate. On the whole, however, astigmatism has a distinct disadvantage in a spectrograph because it greatly reduces the intensity of the lines; the light is wasted by being drawn out, and so the line is weakened. The astigmatism is considerably less with the Eagle than with the Rowland and Abney mountings. Because of this property it is particularly important in using a concave grating spectrograph to ensure that the slit is accurately parallel to the rulings, for the image of the slit will be parallel to the slit but the aberration will be parallel to the rulings. Consequently, any lack of parallelism between slit and rulings will result in the line being broadened unsymmetrically. This is indicated sufficiently well for our purpose by the unsymmetrical tapering of the ends of the lines. The slit should be oriented so that, so far as the eye can judge, the ends are perfectly symmetrical. Astigmatism has the slight merit of making small defects of the slit, or specks of dust on it, unimportant, for the irregularities in the spectrum lines which would otherwise result are smoothed out.

(*ii*) *Ghosts.* In the higher orders of grating spectra, whether the grating is plane or concave and whether a collimator is used or not, there almost invariably appear, in the neighbourhood of strong lines, false lines known as "ghosts." There are various types of ghosts but the chief ones arise from periodic irregularities in ruling the grating which are almost unavoidable.

Ghosts arising in this way are symmetrically situated on either side of the real line, and this often serves to identify them. In Plate XVIIIC there is only one actual line (the strong one), the remainder being ghosts whose light has the same wave-length as that in the strong line, deviated to different positions on the plate. There is no remedy for ghosts: one can only learn to recognise and ignore them. Experience will tell how strong a line has to be in a given order for its ghosts to be visible.

(*iii*) *Effects of Casual Irregularities in Ruling.* As well as the periodic irregularities in gratings which arise from peculiarities of the ruling machine, there are usually casual irregularities caused by inhomogeneity of the metal, slight changes of temperature during ruling, etc. On account of these it is necessary always to fill the whole ruled surface of the grating with light, in order that the position of a line of given wave-length shall always be the same. If this is not done, lines of the same wave-length may appear on successive spectra in different positions and so be wrongly identified. For, to take a particular example, suppose one half of the grating, through casual irregularity of ruling, has a larger value of $(a+b)$ than the other half. The position of the line, determined by θ, will then be different for each half. If the whole grating is illuminated, however, the position of the line will be that corresponding to the average value of $(a+b)$ for the whole grating. The line will be slightly broader than it would have been with a perfect grating, but that is unimportant compared with the errors arising from shift of position. The same thing is true, of course, for prismatic spectrographs if the material of the prism is not homogeneous with respect to $d\mu/d\lambda$. In both instruments, as we have seen, it is necessary to use the full aperture in order to get the full resolving power also, so we have here simply an additional reason for a practice desirable on independent grounds.

CHAPTER

5

DETERMINATION OF WAVE-LENGTHS

IN ORDER TO IDENTIFY a spectrum line and to assign it to the atom from which it originates, its wave-length must first be ascertained. Because of the way in which the angstrom is defined (p. 5), the measurement of a wave-length in angstroms involves the comparison of its wave-length with that of the red line of cadmium. To do this directly we need an interferometer, and the measurement is one which, though susceptible of great accuracy, needs also extreme care; it is a quite impracticable operation for routine work. On this account a large number of wave-lengths have been measured under standard conditions at very frequent intervals throughout the spectrum, and these are used as standards (*tertiary* standards they are usually called to distinguish them from the *primary* standard—the red cadmium line, and the *secondary* standards—a group of lines at intervals of about 50 A. on the average, which have been carefully compared by interferometer with the *primary* standard and have served in their turn to facilitate the measurement of the more numerous tertiaries). They are mainly lines of iron, as these are very numerous and are easily produced from an arc in air under conditions which do not allow of appreciable fluctuations of wave-length.

For most industrial applications it is unnecessary to take great care to produce a standard arc. Any arc run in air at 100–200 V. between terminals of iron gives lines whose wave-lengths are sufficiently near the standard tabulated values for ordinary purposes. It might be noted, however, that lines from the region of the poles are subject to what is known as "pole effect" (probably an effect of the strong electric fields there), by which they are displaced by a slight amount which varies irregularly from line to line. To get consistent results it is necessary to have a long arc and to work with light from the centre of it; this can always be magnified by the condensing lens to fill as much of the slit as it is desired to use. In the standard arc recommended by Pfund and adopted by the International Astronomical Union, the arc should be 12–15 mm. long and only the central 1–1½ mm. should be used. Except for fundamental work one need not be perturbed if this specification is not rigorously followed.

The iron arc spectrum, with various dispersions, is shown in Plates I to XI; this range is sufficient for most work. Shortly below 2330 the iron arc suddenly becomes much weaker but prolonged exposure enables it to be used for some distance in this region. The iron arc spectrum in the shorter wave-lengths down to about 2100 is therefore reproduced in Plates X and XI by permission from an enlargement by Messrs. Hilger & Watts, Ltd. This firm publishes the whole iron arc spectrum, similarly marked with over 1000 wave-lengths, in eight sections; the spectrum is enlarged from photographs taken on a Hilger Large Quartz Spectrograph. On the few occasions on which it is necessary to identify a line beyond the iron range, it is usually simpler to take a comparison spectrum of the suspected substance than to measure the line by independent standards. A list of the iron arc wave-lengths, published by Burns in 1913, is given in Table II in the Appendix, and there will probably be no difficulty in identifying the lines from the scales given. Slightly more accurate values, in deriving which Burns has taken a prominent part, have since been published for the most trustworthy of these lines, but the original list is unrivalled for completeness and its accuracy is quite sufficient for analytical purposes. The list includes a number of lines of Mn, Ni and other elements which are frequent impurities in commercial iron; they are identified by the chemical symbols in the "Intensity" column Since their abundance relative to iron varies with the sample used, it would be misleading to give intensity numbers for them. The worker may expect them with any intensity, or not at all.

In the region 2300–2800 the spectra given by the centre and the two poles of the iron arc differ considerably, so that a single map is insufficient to enable one always to identify the lines. In Plate IX the spectra from the three regions are shown together, and the worker can choose whichever happens to correspond to his own plate. The dispersion in this Plate is large, and this should be allowed for if one is working with an instrument of small dispersion. It may happen that the plate under examination corresponds to one of the spectra in Plate IX in one part of the region and to another in another part. The reason for this is that, with a quartz condensing lens, the arc can be focused on the slit in only one wave-length at a time. The images of the arc in the other wave-lengths will therefore be spread over a larger area in the plane of the slit, and the light falling on the small portion which the diaphragm (p. 68) lets through to the spectrograph will be composed of light from all parts of the arc in varying proportions. Since the focal length of a quartz lens varies rapidly with wave-length this effect is very marked, and it may thus happen that in one region the light entering the instrument is mainly from the positive pole and in another mainly from the negative pole. In practice, however, one should have no difficulty in finding his whereabouts in this region from

Plate IX. I have never come across a plate in which one or other of the spectra shown there is not sufficient to identify the region with ease.

In order to measure a wave-length, then, it is necessary to photograph it adjacent to the iron arc spectrum, so that the position of the line relatively to the iron lines can be determined. This is done by placing in front of the slit a diaphragm of the form shown in Fig. 82, in which are two holes whose vertical diameters, if placed in the same line, would slightly overlap. The diaphragm is placed first so that the slit lies along the vertical diameter of one hole, the source of the spectrum to be measured is focused on its exposed portion, and the spectrum is photographed. Without otherwise disturbing the apparatus in the slightest degree, the diaphragm is then moved until the slit lies along the vertical diameter of the other hole, the iron arc is focused on its exposed portion, and the spectrum is photographed. The plate is then developed, when, since each spectrum consists of a series of images of the part of the slit illuminated, the two spectra will be seen slightly overlapping, as in Plate VII. The overlapping portion then contains both iron and unknown lines easily distinguishable from one another.

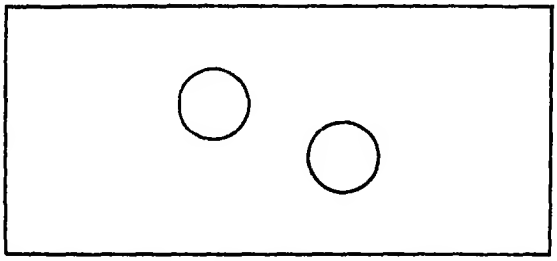

FIG 32 —Diaphragm for obtaining comparison spectra.

The experienced spectroscopist can now easily estimate the wave-lengths of the unknown lines, with sufficient accuracy for identification, by simply observing with an eye-piece their positions with regard to the known iron lines. He has then simply to look up the tables of spectrum lines to make the identification. It may happen, however, that there is some doubt about which of two or more close lines is the one in question. In that case more exact measurement must be made. The procedure is to measure accurately the position of the line relatively to the neighbouring iron lines and, from the relation between wave-length and position in the spectrum, to determine the wave-length of the former.

Measurement of Prismatic Spectrogram. If the distance of a line, measured in the direction of dispersion, from some arbitrary zero is called s, then in a prismatic spectrum the relation between λ and s is given approximately by the formula

$$\lambda=\lambda_0+\frac{C}{s+s_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where λ_0, C and s_0 are constants. This relation has the same form as the Hartmann formula connecting μ and λ (p. 37): *it is known as the Cornu-Hartmann formula, since it was given independently by Cornu and Hartmann.* If, therefore, we can determine the constants, we can calculate the wave-lengths of the unknown lines by simply measuring the values of s for them. The plate is accordingly placed on a travelling micrometer arranged so that movement of the microscope makes the point of intersection of the crosswires travel along the overlapping portion of the spectra. A setting is made on each line in turn, whether iron or unknown, and the reading of the scale of the instrument then gives us s. Choosing three iron lines whose wave-lengths are known, one at each end of the range to be measured and a third about half-way between, we have then three pairs of values of λ and s (λ_1, s_1; λ_2, s_2; λ_3, s_3), and inserting these in equation (16) we have three equations from which to determine the constants s_0, C and λ_0. The solution is

$$\left.\begin{aligned} s_1+s_0&=\frac{(\lambda_2-\lambda_3)(s_2-s_1)(s_3-s_1)}{(\lambda_1-\lambda_2)(s_3-s_2)-(\lambda_2-\lambda_3)(s_2-s_1)}\\ C&=\frac{(\lambda_1-\lambda_2)(s_1+s_0)(s_2+s_0)}{(s_2-s_1)}\\ \lambda_0&=\lambda_1-\frac{C}{s_1+s_0} \end{aligned}\right\} \quad . \quad (17)$$

A form for solving the equations logarithmically is given in the Appendix (Table III): specimen figures have been included in which the unit for s is taken as 0·001 mm. to avoid decimal points. In using the form it is helpful to notice that logarithms are on the left-hand side and antilogarithms on the right. The method of use will be clear when one attempts to work out an actual case.

It is advisable to repeat the readings of the lines with the plate reversed—i.e. turned about a vertical axis so that the film side is still upwards. The reason is not only to increase the accuracy by a double set of readings, but also to obviate a psychological effect, which is peculiar to each observer, by which one tends systematically to set the wires a little to the left or right of the centre. If the setting is made to the left, for example, it will be on the opposite side of the centre when the line is reversed, and the mean of the two sets of readings should then be accurate. If all lines were identical in form this tendency would introduce no error, but since some are broader than others, it must be guarded against. The two sets of readings are then reduced by subtraction to an arbitrary zero, and the mean taken. It is usually convenient, as in Table III, to make $s_1=0$ always.

The constants having been determined, the values of s for the unknown lines enable the corresponding wave-lengths to be found from the formula. A form for doing this, again with specimen readings inserted, is given in Table IV in the Appendix. This, like Table III, is taken from an actual analysis, not specially prepared for illustration, but it is not the same example as that chosen for Table III. In the first column the lines whose wave-lengths are given occurred in the comparison spectrum and are all iron lines except the first, which is an Al line that chanced to appear there. This, and the two iron lines, 3820·430, 3719·988, were chosen as standards, λ_1, λ_2, λ_3, and the other iron lines were measured for a reason which will be explained in the next paragraph. The lines of the unknown spectrum are represented in the first column by numbers indicating their intensities according to rough eye estimates. The "average reading" in column 2 is the average of the s values obtained from two or more settings. In practice column 4 is obtained direct from column 2 by a single addition, but the two steps have been shown separately in Table IV to prevent any possibility of misunderstanding. The construction of the remainder of the Table up to column 8 will be obvious.

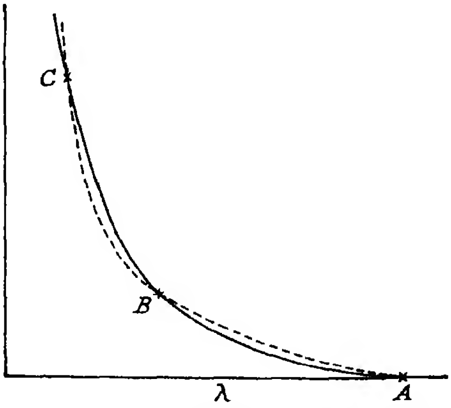

Fig 33.—Real and calculated dispersion curves for a prismatic spectrogram.

If the formula accurately represented the relation between λ and s the work would now be finished, but actually it is slightly incorrect. In Fig. 33 A, B and C represent the three standard lines, λ_1, λ_2, λ_3, used for determining the constants, and the dotted line is the curve of equation (16)—clearly a rectangular hyperbola with the asymptotes parallel to the axes. The true relation between λ and s, however, is represented by some neighbouring curve such as the continuous curve in the Figure. The value of λ (λ_{calc}) calculated from the formula is, therefore, above the true, or "observed," value (λ_{obs}) between A and B and below it between B and C, and if the differences, $\lambda_{obs} - \lambda_{calc}$, are determined and plotted against λ_{calc} we shall get a curve such as that in Fig. 34, in which the slight deviations of the points from a smooth curve are due to errors of setting, irregularities of the plate, etc.* We cannot get $\lambda_{obs} - \lambda_{calc}$ from the unknown lines because we do not know λ_{obs} for them, but we can do so for the iron lines by calculating their wave-lengths by the formula and comparing the results with the true values. That is the reason for calculating the wave-lengths of the iron lines in Table IV. The italicised values of $\lambda_{obs.} - \lambda_{calc.}$ in column 9 of that table are data from which a curve similar to

---

* $\lambda_{obs.} - \lambda_{calc}$ may be positive between A and B and negative between B and C, as in the example chosen for Table IV.

Fig. 84 is drawn, and then, from the values of $\lambda_{calc.}$ for the unknown lines in column 8, the corrections for the unknown lines can be read from the curve and the final values of the wave-lengths of the unknown lines determined. These are shown in column 10.

The process of measurement may thus be summarised as follows:

(1) Obtain scale readings for all lines, iron and unknown, between the chosen limits, with opposite orientations of the plate, reduce to common zero, and take mean.
(2) Choose three iron lines and calculate constants in Cornu-Hartmann formula (Table III).
(3) Calculate wave-lengths of unknown and remaining iron lines from the formula (Table IV).
(4) Draw Fig. 84 for iron lines, using Tables II and IV.
(5) Apply corrections from Fig. 84 to calculated values for unknown lines.

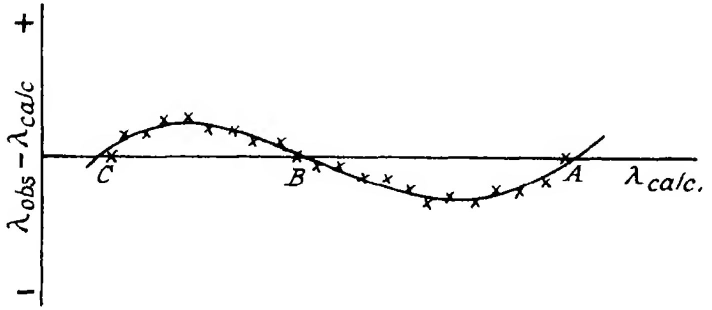

FIG. 84.—Curve of corrections to wave-lengths calculated by the Cornu-Hartmann formula prismatic spectrogram

The results, if the work has been carefully done and the spectrogram is a good one, should be accurate to about 0·01 A.

Measurement of Grating Spectrogram. It has already been pointed out that the dispersion in a grating spectrum is almost normal, i.e. equal distances on the plate correspond approximately to equal intervals of wave-length. This enables a linear formula to be used in place of the Cornu-Hartmann formula, viz.

$$\lambda = a + bs \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where a and b are constants. Only two lines—one at each end of the range under inspection—are therefore necessary for determining the constants, and the correction curve corresponding to Fig. 84 is wholly on one side of the axis of wave-lengths. The whole calculation is, therefore, much simpler than that for the prism, and as its course will be obvious it is unnecessary to give an example in detail.

Alternative Processes. The need for exact measurement of lines can never be quite eliminated, but it decreases as the experience of the worker grows. One very useful device in analysis is to identify a few of the strongest lines by eye and to confirm the identification by taking another spectrogram with the unknown spectrum adjacent to the spectrum of the suspected substances. Exact coincidence is necessary for confirmation, and the eye, aided by an eye-piece, can judge this very accurately. The slightest visible deviation from coincidence is sufficient to rule out the identification, and even if the observer merely suspects a deviation, it almost always exists. All lines which occur in both spectra can then be attributed to the substances in question, provided that the specimens used for obtaining the spectrum are perfectly pure, which they never are. A table of the spectrum lines of the substances should therefore be at hand and consulted during the process. One can usually detect impurity lines by the fact that their intensities relatively to those of the main substances are rarely the same in the two spectra. For example, if Ca is suspected and a spectrogram of the unknown substance is obtained adjacent to the spectrum of Ca, it is probable that Sr will show as an impurity in the latter. If it is also present in the unknown substance the Sr as well as the Ca lines will appear as coincidences, but their relative intensities will probably be different from those of the Ca lines.

For approximate determination of wave-lengths more expeditious processes may be used. Instrument makers sometimes provide an arrangement by which a scale of wave-lengths can be photographed on the plate by the side of the spectrum. This is useful for providing a preliminary identification of lines, and in certain special problems of limited range, in which, for example, one is concerned with a particular element present in fair strength so that several of its lines appear, it can lead to tolerably certain results, for the occurrence of several lines with the correct relative intensities and sufficiently accurate wave-lengths is very strong evidence of identification. In such problems the saving of time which the scale affords more than compensates for the loss of superfluous exactitude of measurement When the lines of interest are weak, however, or when several substances are present whose lines are close together, this method is attended by considerable risk.

In visual work, again of limited range, the wave-length scale attached to the rotating screw of a constant deviation prism, described on pp. 45–6, is useful. Approximately equal accuracy can be achieved with an ordinary visual instrument, having no such scale, by setting the prism in some standard position, such as that of minimum deviation, noting the scale readings of the telescope for certain standard lines, and plotting them against the known wave-lengths of those lines. A curve is thus obtained, from which the wave-length of an unknown line can be determined from its scale reading. Suitable standard lines for the calibration are given in the following table:

6707 8	Li	5460 7	Hg	4607 3	Sr
6562 8	H	5350 5	Tl	4554 0	BaII
6136 6	Fe	5183 6	Mg	4358 3	Hg
5895 9	Na	5172 7		4226 7	Ca
5890 0		5167 3			
5790 7	Hg	4861 3	H	4047 2	K
5769 6		4810 5	Zn	4044 1	
5535 6	Ba	4722 2			
		4680 1			

CHAPTER

6

QUALITATIVE SPECTRUM ANALYSIS

(*I*) *GENERAL PROCEDURE*

In the foregoing chapters the whole technique of spectrographic analysis, considered as a routine process, has been covered. We have now to see how to apply it to particular problems of analysis, selecting from possible alternatives those most suited to particular cases. We begin with qualitative analysis. Although, strictly speaking, this is concerned only with the presence or absence of substances, the methods to be described are applicable also to certain problems which are literally quantitative in character. For example, if, of two specimens almost identical in general composition, one is suspected of containing more than the other of a particular element, it is safe to say that if the lines of that element are consistently stronger in the spectrum of the first than in that of the second, the suspicion is confirmed There is no need to undertake the much more elaborate procedure necessary to discover *how much* more the first specimen contains.

Problems of qualitative analysis are of two broad kinds. We may be asked to discover every element that the specimen contains, or we may require only to know whether it contains one or more particular elements In this chapter we shall assume that our problem is of the first kind. Its solution, of course, necessarily includes the solution of the second also, but if only certain elements are of interest the work can be greatly reduced. Details concerning individual elements are reserved for the next chapter.

In the first place, it should be said that, unless one is prepared to undertake an investigation involving an inordinate amount of difficulty, only about 70 of the 92 elements in the periodic table can be confidently regarded as admitting of spectrographic detection. The number is a little indefinite since a few elements remain to be discovered with certainty and some of the radioactive elements may be considered as on the borderline. It has already been pointed out that some elements do not reveal themselves in the ordinary processes of producing luminosity. They need to be enclosed in vacuum tubes, where care must be taken to prevent them from becoming occluded in the electrodes or the walls of the tube, and examination of the far infra-red or ultra-violet may be necessary even then in order to reveal them. Such elements are therefore not generally regarded as "spectroscopic" elements, and we shall leave them out of consideration. The phrase in the previous paragraph—"every element that the specimen contains" —must therefore be understood as referring to every element other than the non-spectroscopic ones, of which those so describable with certainty are given in the following table:

Non-spectroscopic Elements

Argon (A)
Bromine (Br)
Chlorine (Cl)
Hydrogen (H)
Helium (He)
Iodine (I)
Krypton (Kr)
Nitrogen (N)
Neon (Ne)
Oxygen (O)
Radon (Rn)
Sulphur (S)
Xenon (Xe)

Choice of Exciting Agency. Suppose, then, we are presented with a specimen for analysis. The first thing to do is to prepare it for the process of vaporisation and incandescence. If it is a liquid, we may either examine it as such or evaporate it to dryness at a low temperature and examine the residue as a powder In the latter process, water or other liquids which may escape contain only non-spectroscopic elements, unless the liquid is a solution in an organic liquid containing carbon (which is usually of no interest), and the only significant difference in elementary composition between the powder and the original liquid is then due to whatever the liquid may have dissolved out of the containing vessel. This is a very common source of contamination. In an examination of human milk, for example,* it was found that Si appeared strongly, although it was absent from cow's milk. The explanation was that the women were milked into glass test-tubes and the cows into metal pails. Whenever a specimen is heated in a vessel, therefore, it is necessary to prove, in order to verify the presence of an element whose lines appear in the spectrum, that the spectrum of the vessel does not show the lines. This may entail dividing the specimen into portions to be heated in different vessels which have no elements in common In the investigation of milk just cited, vessels of glass, rubber, Cu, Zn and Pt were used for collecting the milk, and the specimens were evaporated in crucibles of porcelain, glass, Cu, Zn and Pt.

All organic materials, even if already in powder form, should be freed from carbon compounds by charring at as low a temperature as possible. This greatly increases the chance of detecting small traces of mineral constituents. There is again a risk of substances being introduced from the containing vessel, and the same precautions are necessary. If an arc spectrum is to be obtained the charring could be

* *Biochemical Journal,* XXXII, No. 6, p. 1078 (1938).

performed on the arc itself instead of by a separate preliminary operation; the only impurities that could then be introduced are those in the electrodes, which would appear in any case. It is doubtful, however, if this is preferable to separate charring. It is necessarily conducted at a very high temperature, with the result that the more volatile constituents are liable to be driven off before charring is complete, so that to get a complete analysis we must expose for a considerable time, both throughout the charring and later; this tends to produce fogging of the plate by scattered light and halation in the neighbourhood of the strongest lines, with consequent obscuration of weak lines.

The preliminary processes just described leave the substance in the form of a powder. With all such specimens the arc is the most satisfactory instrument for excitation The alternative forms are liquids to be used as such and solids in bulk, ranging from small fragments up to objects of definite form (e.g. a configuration found in an early Egyptian tomb, which was once submitted to me) which it is important to mutilate as little as possible

Liquids are not very adaptable to arcing, though, it is true, carbons steeped in them for a few days yield their spectrum lines readily. The weaker constituents, however, being distributed within the carbon, are apt to be missed. Flame spectra may be obtained by spraying the liquid into the flame, but this is more suitable for quantitative work, with elements already known to be present and detectable in this way, than for general detection. The same is true of absorption spectra. The spark is, on the whole, the best general source of the spectrum of a liquid (see p. 24), but unless there are strong reasons to the contrary it is more satisfactory to reduce the liquid to a powder and examine it in the arc than to adopt any of the methods applicable to the liquid state.

The advantage of the spark with solids of manageable size is that a good spectrum can be obtained with the minimum damage to the specimen, and there are no additional poles to introduce impurities. The disadvantage is that the spectrum characterises only the points between which the spark passes and so may not give the general composition. In the arc the whole specimen, or as much of it as one chooses, can be subjected to analysis and the whole contents discovered.

By far the commonest case in practice, then, is that of a powder examined in the arc. It is this case that will be tacitly assumed in the remainder of this chapter, although, of course, most of what is said is applicable to other conditions also.

Examination of Spectrogram. The spectrogram, with an iron comparison, having been obtained, a general analysis demands its systematic examination for the *raies ultimes* of all the spectrographic elements. The first step should invariably be the verification that no accidental shift of the plate has occurred between photographing the spectrum of the specimen and the iron comparison spectrum. This is best done by selecting one or two lines whose identity is beyond question and ensuring, by measurement if necessary, that they occur in the right positions. There will always be such lines, the most satisfactory being sensitive lines of iron, if they occur in the specimen, since coincidence can be judged very accurately by eye. If there has been a shift the plate should be discarded. It is not a sufficient correction to measure the amount of shift and allow for it, since it will vary along the spectrum if the plate has rotated. With ordinary care a shift will be infrequent but it is never safe to ignore its possibility.

The next step is to identify the elements With a little experience, the worker will find that the most expeditious way of doing this is to go through the spectrum from one end to the other with an eye-piece, having before him a list of the *raies ultimes* in order of wave-length Each element can then be marked in turn as "present" or "absent," assuming that one can decide the matter sufficiently well by a cursory examination. "Absence" may often be decided in this way, "presence" not so often, but more frequently as the observer gains experience. It becomes automatic, on observing a line which appears to belong to a certain element, to look at once for the other *raies ultimes* of that element and so to confirm its presence or absence. Unless, however, one knows immediately where to look for the other *raies ultimes*, and their intensities relatively to the first line, it is perhaps best to mark the line "probably present" and look later for the confirmatory evidence. A decision on one line only should be avoided as far as possible, but may have to be made either because the substance is present in too small quantity to show more than one line or because its other possibly existing *raies ultimes* are too close to lines of other elements, known to be present, to be distinguished. In such cases the wave-length of the line should be measured and should agree, within the limits of unavoidable experimental error, with the tabulated wave-length, and one should be satisfied that there is good reason, such as faintness or blending, for the non-appearance of the other lines.

The list of *raies ultimes* used for this inspection ("the inspection list" it may be called) will depend on the character of the spectrograms —their dispersion and so on. Table V in the Appendix gives the *raies ultimes* and their intensities according to Harrison and Hilger, and Table VI, as an example, an inspection list I have frequently used. In this list the region 3700–3500 (approximately) is excluded altogether, because the spectrograms have been obtained by exposing simultaneously to two instruments (the source was placed between them and focused by separate lenses on the two slits), covering the regions 6800–3700 and 3500–2500. The loss of this region is made less serious by the fact that it contains a portion of the strong CN band beginning at 3883 which would often obscure many lines occurring there. Apart from that, however, the list is not recommended for general use. It was prepared for particular types of specimens, and the lines are not always the most suitable, particularly when one is not familiar with the possible sources of confusion. The reader should construct his own list, and gradually modify it in the light of his own experience. Occasionally the spectrograms have to be supplemented by others, taken on different instruments, for lines above 6800 or below 2500. This, however, is comparatively rare. The list does not include the rare earths (except La) or the strongly radioactive elements, since these are of such infrequent occurrence that they are best ignored in general work and looked for separately if their presence is suspected or is a matter of importance.

It will be noticed that some elements in the main lists have several *raies ultimes.* The most sensitive are usually those with the largest intensity numbers, but for reasons explained in the next chapter this is far from being a rule to be followed blindly. At this stage it may be said that one should choose for the preliminary inspection list the strongest lines, which alone may remain when the substance is in very small quantity, and modify the list as the result of experience with the particular instruments and plates used. If the dispersion is small, for example, some of the most sensitive lines may be so close to others belonging to commonly occurring elements, with which they may be confused, that other *raies ultimes* are advisable. It is then necessary, if the utmost completeness of analysis is required, to look afterwards for the strongest *raies ultimes* of those elements which have been marked "absent," in case they are observable, before concluding finally that the elements are absent. This formality, however, is not generally so important as it appears. There is no absolute sensitivity in a spectrographic test, and the strength and number of lines that will appear depend upon the amount of specimen available, the length of exposure, the sensitivity of the plate, and a host of other factors, which make the word "absent" mean simply "not detected." The second most sensitive line with a long exposure may, therefore, be a better criterion than the first with a shorter exposure. In any case, identification by a single line in a crowded neighbourhood needs very exact measurement for confidence, and what one loses in sensitivity by looking for a less critical *raie ultime* is often gained in certainty.

The next step is to eliminate lines arising from impurities. These are of two classes—those belonging to impurities introduced in the course of preparing the specimen for examination, and those coming from the material of the electrodes. In a qualitative examination the only reason for purposely introducing extraneous material into the specimen is to increase its bulk. This is sometimes necessary if the amount available is extremely small and it is desired to take more than one spectrogram; a larger bulk then facilitates division. In such cases the additional material should always be the powdered material of the electrodes, which should be thoroughly mixed with the specimen. The only other impurities of the first class, if due care is taken, are those which come from containing vessels in the manner we have described. It is possible that any constituents of a containing vessel might be selectively abstracted by the specimen Hence for the greatest certainty it is necessary to take several spectrograms so that, for every element represented in both the spectrum of the specimen and that of the vessel in which it has been treated, another spectrogram of the specimen will exist, corresponding to a vessel whose substance does not contain that element. This involves fewer spectrograms than might at first be supposed, if a judicious choice of vessels is made: a vessel of pure quartz is as free from spectroscopic elements (other than Si) as any readily obtainable. If the choice of vessels is limited, however, there will probably remain over one or two elements—notably Fe and perhaps Cu—which exist in small traces in the material of every one available These elements—unless present in such quantity that the strength of their lines when the specimen is used leaves no doubt of their presence in it—must be regarded as doubtful in the specimen. No general rule can be laid down, but experience often helps one to decide in particular cases. It must be remembered that a substance does not necessarily extract a particular constituent of the containing vessel, and if a specimen shows, say, Fe lines of the same strength when treated in an iron vessel and in a vessel of another substance containing only a trace of iron, the probability is that the Fe is actually in the specimen. Such criteria as these are all that are available to indicate the balance of probability in doubtful cases

Impurities of the second class are distinguished by the same principle but there are important differences in application One chooses, as far as possible, electrodes such that every spectroscopic element is absent from at least one pair but this is even more difficult here than with containing vessels because the electrodes must fulfil the additional condition that they are conductors of electricity. This, of course, eliminates quartz. Again, the determination of what impurities are present in the electrodes is not so straightforward as the corresponding problem with containing vessels. A spectrogram of the electrodes alone does not necessarily show all the elements which the electrodes contain unless the exposure is greatly prolonged, and even then the strengthening of the impurity lines, when even a trace of some other material is placed on them, is often so striking that the observer, unused to the phenomenon, records with confidence as elements in his specimen what are actually elements in the electrodes which the specimen has served to exhibit. This is illustrated in Plate XIX, which shows at the bottom the spectrum of graphite electrodes alone, next the same electrodes with a trace of a Na salt on them, and finally Cu poles with a similar trace of the same salt. The point of interest here is the appearance of lines of V and Ti in the middle spectrum. If the third had not been taken one might have concluded without hesitation that V and Ti were in the Na salt, but their absence from the third spectrogram would then be puzzling. The true explanation is that these elements are present as impurities in the graphite electrodes but not in the Cu, and the salt is necessary to bring out their lines. The mechanism by which this occurs has not been satisfactorily explained

From the practical point of view, however, the important thing is to know what impurity elements are thus liable to appear, and to be on one's guard against drawing false conclusions. The effect has long been known in spectroscopic laboratories, but seems first to have been published by Webb.* It appears to be mainly, if not entirely, restricted to carbon electrodes, which give an arc of much smaller conductivity than the metallic vapours, but it is unsafe to assume that other electrodes are above suspicion. One should therefore examine a sample of every kind of electrode in general use by getting its spectrum alone and then with a pinch of salt. Additional lines, which are not common to all the electrodes, must then be attributed to electrode impurities. Needless to say, no trace element should be considered as definitely present in a spectrum unless its lines appear with electrodes from which the element is known to be absent.

Webb gives a list of several elements whose lines are intensified in this way, and others which appear not to show the effect. The phenomenon, however, is so dependent on the kind of electrodes used, and possibly on the way in which the impurities are distributed in them, that one person's results are an unsafe guide for another. With the graphite electrodes which I have been accustomed to use, for example, I find little trouble with any elements except V and Ti; while Webb, using a different brand of graphite, found enhancement not only of the lines of these elements, but also of those of Fe, Cu, Ca and Li. My electrodes contained these elements, but they did not behave abnormally. It is, however, necessary for each investigator to be guided by his own experience.

Impurities are not always evenly distributed through the electrodes, and this makes special precautions necessary when one is comparing spectra of two slightly dissimilar specimens. For such work it is advisable to ensure identity of poles by the following device. Graphite can be supplied in rods of about 1 foot in length, while 3 inches is ample for each electrode. The rods should, therefore, be broken into four approximately equal lengths and used for the two specimens in the way which will be obvious from Fig. 35. The actual poles are then as nearly as possible identical.

When the identity of a spectrum line is suspected but not established,

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* *Nature*, 139, 248 (1937) In a later paper (*Sci. Proc. Roy. Dub. Soc.*, 21, 487 (1937)) Webb reports further investigations of the matter.

the most direct way of settling the question is to compare the spectrum of the specimen directly with that of the suspected element. The exactness with which the eye can judge coincidences has already been referred to, and on this account a great saving of labour can often be achieved by photographing the spectrum of a mixture of suspected elements next to that of the specimen, using the diaphragm described on p. 68. Since the possibility of making exact measurements should never be excluded, the Fe spectrum should also be photographed on the other side of the spectrum of the specimen. In a complete analysis of an unknown mixture all elements may be suspected, and on this account mixtures containing all the spectroscopic elements (or as many of them as are normally of interest) in such relative strengths as to show only a few lines of each, are sometimes used for comparison purposes Messrs. Hilger, for instance, supply a "R.U. Powder" containing 50 elements in small amounts, and their list of *raies ultimes* included in Table V is, in fact, a record of the spectrum lines which this mixture shows with reasonable exposures. If we suppose that each element is introduced in the form of a compound containing, on the average, an equal number of atoms of a non-spectroscopic element (e.g. KCl), a mixture of 50 elements in equal amounts would contain about 1 per cent. of each. This quantity would give many more lines than the *raies ultimes*, and the spectrum would be inconveniently crowded with lines. The mixture is, therefore, embedded in a larger quantity of a "base" material, which in Messrs. Hilger's powder is a mixture of zinc, magnesium and calcium oxides. The "base" material should, of course,

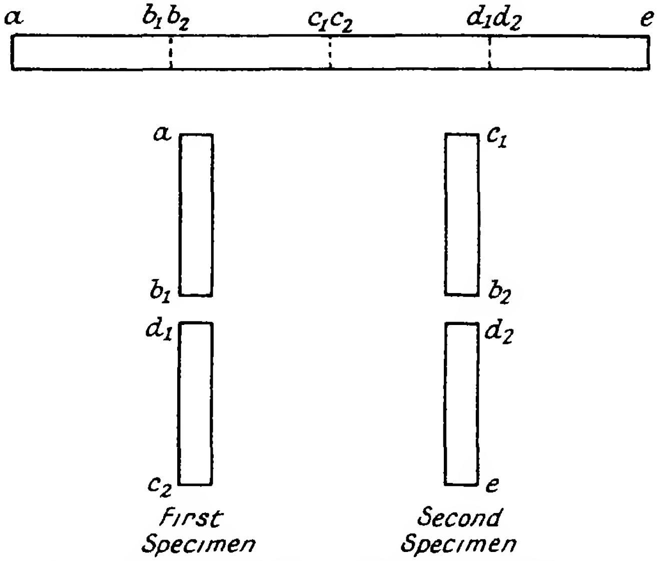

FIG. 35.—Illustrating breaking of graphite rods for comparison spectra

be one which gives as simple a spectrum as possible. At the Imperial College we have used a mixture, prepared by Mr. E. W. Foster, containing all the spectroscopic elements except most of the rare earths, the radioactive elements and indium, the last-named at the time of preparation being unobtainable. Plates I–V, VII–VIII, show the spectra of this mixture. Further reference to these Plates will be made in the next chapter.

Theoretically, it would seem that a mixture of this kind would be sufficient for all analyses, and that measurement would therefore never be necessary. This is not so, however. It is impossible, even with good dispersion, to avoid blends of lines when such comprehensive powders are used, and these make a coincidence with one unresolved component look like a lack of coincidence with a single line. Moreover (probably owing to the difficulty of making a completely homogeneous mixture of so many constituents, some of which are insoluble), spectra of the mixture taken at different times are not always identical, so that the "centre of gravity" of blended lines is not always in the same place. A slight variation in relative intensity is sufficient to cause such apparent "displacement." This obvious method, therefore, should be regarded as a very useful but not an infallible or self-sufficient process.

A somewhat analogous purpose is served by maps of the iron spectrum with the relative positions of the strong lines of the elements marked on them. Such maps in the region 3500–2500 have been prepared very carefully by Bardet. These also are sometimes useful, but the danger here is that blended lines in the spectrum of the *specimen* may escape recognition because of their apparent displacement. Moreover, since the judgement called for here is not that of coincidence but that of relative positions with respect to Fe lines, the uncertainty is much greater than with the *raies ultimes* mixture, and the chief service performed by the maps is to indicate probabilities which need later confirmation

General Precautions. In carrying out the various procedures described above certain pitfalls may be encountered, of which the commoner ones of a general nature will now be mentioned. Those restricted to the determination of particular elements are deferred until the next chapter.

The first has already been referred to, namely, the possible occurrence of "blends"—unresolved groups, usually of two, possibly of more, lines of different elements which appear as one. If measured as one, the wave-length, of course, will either not appear in the Tables or will appear as that of a line which is not present at all. It is only the latter alternative that may lead to a false identification; the former, if the observer exercises due care, leads only to perplexity. The best safeguard against misinterpreting a blend is its intensity—blended lines are usually abnormally strong, taking into account the intensities of the other lines of the element concerned. If a blend is suspected the Tables will indicate what lines may contribute to it, and the presence of the elements which give those lines should then be investigated. Obviously blends will be commoner with small resolving power—i.e. in general with small dispersion. For this reason, as well as for increased accuracy in measurement, large dispersion is always to be recommended for this work.

In most arc spectrograms some lines are "reversed"—i.e. appear as broad bright lines of which the narrow centre is absorbed by the flame surrounding the arc (on the negative, of course, this means a broad dark line with a clear centre). An example is shown in Plate XIII, where the line of Tl at 2379·69, which has the normal appearance in the spark spectrum, is reversed in the arc spectrum. In Table V the intensity number of a line which is reversed in the arc is usually followed by the letter R. In such cases it is the absorbed centre that has the wave-length of the line. Reversed lines are those involving the innermost orbits of the electron in the atom, for the energy of the comparatively cool flame must be sufficient to raise the electron to the higher of the two orbits concerned. The *raies ultimes* also correspond to transfers between the lower orbits, and for this reason they are usually reversed when the element is present in considerable quantity. If only a trace is present, however, the lines are not reversed, since the amount that gets out into the flame is insufficient visibly to absorb the light issuing from the centre of the arc. The only danger of misinterpretation arising from reversal is that occasionally a reversed line is indistinguishable in appearance from two close lines, the bordering unabsorbed light on each side covering such a short range of wave-length that it appears as a single narrow line. Two false wave-lengths are then measured, and the intervening space, which corresponds to the true one, is regarded as empty. There is no precaution against this, except the kind of instinct that comes with experience, stimulated perhaps by difficulty in identifying the two false lines measured.

In considering a possible identification one should always bear in mind the general strength in the specimen of the element concerned. For example, if there is doubt whether a particular line belongs to element α or element β, and α is known from other lines to be present, we might at once be able to reject the line in question as an α line because of its abnormal strength. It is usually safe, when the element is only weakly represented, to ignore all but its *raies ultimes*, but tables of the complete spectra of the stronger constituents should be before one, since even their weaker lines may appear. This is an obvious precaution, but its neglect often causes needless uncertainty.

The only complete lists of spectra of the various elements are those in Kayser's *Handbuch der Spektroscopie*. Volumes 5 and 6, though many years old, contain most of the necessary data, but it must be noted that many of the wave-lengths are given on the older "Rowland" scale, and are larger than the present "International" wave-lengths by an amount varying slightly irregularly from 0·25 A. at 7000 to 0·06 A. at 2000. Later volumes give more exact measurements, all on the International scale, for some elements, but these can usually be found from the other volumes mentioned below when a line is suspected. In practice one needs complete lists only in order to identify weak lines of elements present in overwhelming strength. For most of the work the indispensable books are *Tabelle der Hauptlinien der Linienspektra aller Elemente nach Wellenlange geordnet*, by Kayser/Ritschl (1939 edition), and the *Massachusetts Institute of Technology Wave-length Tables*, by G. R. Harrison (1939, John Wiley & Sons, Inc., New York; London Agents. Chapman & Hall, Ltd.). The former of these contains some 27,000 lines and the latter more than 100,000. Both are therefore useful—the former for preliminary work and the latter, when needed, for weaker lines.

A word of warning is necessary concerning the intensity numbers. These are simply rough eye estimates and necessarily refer to the impression on a particular kind of photographic plate under particular conditions in the source of luminosity, none of which are specified. They must therefore necessarily fall short of exactness for all applications, but apart from this they are inexcusably defective, and the most urgently needed improvement in such tables is a trustworthy revision of the intensity numbers. The following example—a "multiplet" (a group of lines in the same spectrum region which are so related that their relative intensities are much less variable with physical conditions than are those of lines chosen at random—see p. 89) of V—gives some indication of the scope which exists for improvement.

	Kayser	*Harrison*	*Moore*
4379 238	10R	200R	150rw
84 722	120R	125R	125r
89 974	100	80R	100
95 228	10	60R	80
4400 575	60	60	60
06 641	80	40	80
07 637	70	15h	70
08 204	70R	80	70
08 511	50R	30h	90
16 474	20	15w	20
21 573	20	30h	20
26 005	15	25h	20
29 796	15	30	15

(The figures in the last column are taken from Miss C. E. Moore's *A Multiplet Table of Astrophysical Interest* (Princeton University Observatory, 1945).)

Needless to say, a comparison of recorded intensities of lines of different elements means nothing at all.

Another pitfall which lies in wait for the unwary is the occasional indistinguishability in appearance of lines and heads of bands of compounds present in very small quantity. This is illustrated in Plates III, V and VII, where the band-heads of LaO, CN and OH at 4418·2, 3883·4 and 3063·6, respectfully, might all be taken as lines by the inexperienced. There are so many possibilities of this kind, since the number of compounds is extremely large, that a list here is impracticable. If there is any reason to suspect that what appears as a line is actually a band-head, reference should be made to Pearse and Gaydon's book, *The Identification of Molecular Spectra* (Chapman & Hall). If a line shows signs of being unsymmetrically shaded on one side there is ground for suspicion, but not necessarily for conviction, since many true lines have this characteristic.

CHAPTER

7

QUALITATIVE SPECTRUM ANALYSIS

(II) INDIVIDUAL ELEMENTS

IN THIS CHAPTER we shall consider the spectroscopic elements in turn, taking them in alphabetical order of chemical symbol and discussing briefly the peculiar problems to which each gives rise. When a substance is present in considerable quantity there is usually no difficulty in identifying it, since (for all but a few elements, most of whose lines are out of the ordinary region of examination) many lines of its spectrum will appear. Traces of elements are represented only by the *raies ultimes*, and although the lines listed as *raies ultimes* usually persist over a many-fold reduction in quantity of substance after the bulk of the lines have disappeared, there is no absolute division between *raies ultimes* and other lines. Moreover, the *raies ultimes* themselves do not all disappear at once as the amount of substance is further reduced · there is an order of disappearance, which again is not absolute but depends on conditions. For this reason, although it is often possible to give a general indication of the order of sensitivity of the *raies ultimes*, one should not be surprised to find his experience on one occasion apparently contradicted by that on another.

There are two general factors which determine the relative strengths of the *raies ultimes*—first, the orbital transitions in the atom which accompany the emission of the lines, and secondly, the particular experimental conditions under which the spectrum is produced and photographed. They each admit of some analysis and we will consider them in detail

When the active electron in an atom has been raised from its normal, innermost orbit to an outer one, it tends to return inwards, radiating a particular spectrum line for each such transition. If the orbit to which it is removed is a distant one there will be several lower orbits at which it may halt, and it is found that there is a definite probability, known as the "*a priori* probability," of its returning to each of them. Thus, if an electron is removed from orbit I to orbit V, say (numbering the orbits in order of increasing diameter), it may return to orbit IV, III, II or I, and the probabilities may be, say, $\frac{2}{6}$, 0, $\frac{1}{6}$, $\frac{3}{6}$, respectively. (There is also a definite probability of its *going to* orbit V in the first place, but for simplicity of explanation we will ignore this complication.) This means that of the large number of atoms in the arc which at any instant have their electrons in orbit V, one-third will emit the line corresponding to the transition V–IV, none (or a negligible number) the line corresponding to the transition V–III, and so on. The relative intensities of the four lines in question will therefore be 2, 0, 1, 3, respectively. These *a priori* probabilities are an intrinsic property of the atom and do not depend on the number of atoms available. They therefore continue to hold good as the substance is gradually reduced in quantity, and if that were the whole story the most sensitive *raie ultime* (ignoring again, for simplicity, such transitions as IV–III, etc.) would be the last, the next most sensitive the first, and so on—the second, of course, not being a line at all.

To indicate completely the probabilities for all transitions is impossible in the present state of knowledge. We shall, therefore, content ourselves with a simplification which is generally applicable and trustworthy, though its application may not always be completely free from ambiguity. We shall call the normal orbit, corresponding to what is generally called the *ground state* of the atom, orbit 1. The numbers 2, 3, etc., will then indicate higher orbits in the correct order, but any orbits not concerned in the emission of *raies ultimes* will be ignored, so that, for example, orbit 3 is not necessarily the third smallest orbit possible to the electron but the third of those which take part in the radiation of the *raies ultimes*. The transition corresponding to a particular line can then be represented by such a symbol as 2–1, indicating that the electron has fallen from orbit 2 to orbit 1 in emitting the line. We can now state as a general rule that the most sensitive *raies ultimes* are those in which the final orbit number and the difference between the orbit numbers are smallest. The most sensitive line would then be 2–1, but the next would be somewhat ambiguous, for 3–1 would have the smaller final orbit number and 3–2 the smaller difference of orbit numbers. In such cases experience must indicate which line is to be preferred, and, in fact, the second factor mentioned above—the experimental conditions—often gives the casting vote in practice whatever the theoretical order might be. These orbit numbers, amplified in a manner to be explained later, are given in the notes on individual elements later in this chapter They may be compared with the sensitivities given by Harrison and Hilger, but it must be borne in mind that these workers are concerned with the final impression on the plate, which is variable, whereas we are now considering only the first of the factors which determines that impression—the intrinsic properties of the atoms—which is constant.

We must now turn to the second general factor—experimental conditions. The effect of these on the recorded relative intensities of lines arises from three distinct possibilities of variation—in the source of luminosity, in the formation of its image on the slit and in the characteristics of the photographic plate. The source of luminosity itself may affect the relative intensities in two ways. First, the transition probabilities discussed in the preceding paragraphs are applicable only if there is sufficient energy in the source to remove the electron to the more distant orbits, so that we may be sure that, at any instant, the numbers of atoms with their electrons in all the orbits with which we are concerned are actually in the proportions of their *a priori* probabilities. If this is not so, however—if for example, there is energy enough to send the proper proportion to orbit IV, but not enough to send more than an occasional electron to orbit V—then a transition, which might in more favourable circumstances give a strong line, might have no chance of occurring at all. This is a very common occurrence with flame spectra but is of little importance in the arc or spark since the energy there is sufficient in every actual case to give full scope to the *raies ultimes*.

The second way in which conditions in the source of luminosity may affect the relative intensities of *raies ultimes* is of importance when some *raies ultimes* belong to the neutral and some to the ionised atom. The relative intensities will then be affected by the relative numbers of neutral and ionised atoms present, and these will be determined, not only by the energy available to ionise the atoms, but also by the number of free electrons present to make them neutral again. This latter number in its turn will be influenced by the general composition of the substance. If, for example, to an arc of vanadium, which shows lines of both neutral and ionised atoms, we add a substance such as one of the alkalis, which have low "ionisation potentials" (i.e. need little energy to ionise them), a large number of alkali atoms will be ionised and the electrons thus liberated will be available to recombine with ionised vanadium atoms to make them neutral again. The relative intensities of lines of neutral and ionised vanadium atoms will, therefore, be different according to the character of the other substances present in the arc. This is illustrated in Plate XV where three spectra of similar graphite poles are shown, each with an iron comparison spectrum. The poles, which contained vanadium as an impurity, were supplied with different amounts of a substance having a low ionisation potential. In the uppermost spectrum the V I line is slightly stronger than the V II lines, in the middle spectrum it is much weaker—scarcely visible, in fact—and in the lowest spectrum it is much stronger.

The next effect of experimental conditions on relative intensities arises from the characteristics of the condensing lens. With a quartz lens (and to a lesser extent also with a glass lens, since no glass is truly achromatic), as we have remarked before in other connections, the image of the source of light is in focus in the plane of the slit in only one wave-length. If, then, the image in that wave-length is, for example, just large enough to fill the exposed portion of the slit, the images in the other wave-lengths will cover a larger area and only a portion of their light will enter the spectrograph: the corresponding lines will, therefore, be weakened in varying degree. Thus, the relative intensities on the plate of two *raies ultimes* a considerable distance apart in the spectrum, may be altered very considerably by a slight displacement of the condensing lens.

The third effect of experimental conditions arises from the properties of photographic plates. This needs no elaboration, but the reader should refer to p. 52 to be reminded of an effect not well enough known, by which the relative intensities of two lines may be reversed merely by a slight lengthening of exposure time.

The conclusion to be drawn from all these considerations is, therefore, that no standard order of intensity of the *raies ultimes* of any element which would be trustworthy as a practical guide can be given in a general form; one must find by experience, with his own instruments and experimental arrangements, which lines serve him best, and even then he must be prepared for exceptional cases. It will be noticed, however, from the discussion we have given, that if there are *raies ultimes* of a particular element which are close to one another in wave-length and for which the initial and final orbits also are close together, all the disturbing factors become small and a fairly trustworthy order of intensities becomes possible. It happens that for most elements there are such lines, forming what are called *multiplets,* and we proceed to give some account of them. A full account, with the accepted notation, would involve too great a digression, with disproportionately small advantage, and we shall therefore take the liberty of employing an *ad hoc* simplified description which, it is hoped, will be a safe and sufficient guide to the worker who is concerned only with practical applications of the theory. The discussion will also help us later to form some idea of the relative sensitivity of spectrum analysis for the different elements.

The orbits, or "levels," which we have numbered 1, 2, etc., are generally not single but composed of a number of components which varies from element to element. These components themselves are of different classes and to each class belongs a definite complexity. We shall indicate this by saying that *level* 1, for example, is composed of ***sub-levels,*** 1A, 1B, 1C, etc., and each of these is divisible into ***components,*** such as $1A_1$, $1A_2$, . . .* In the detailed notes on the several elements to be given shortly we shall record the sub-levels involved in the lines given, except for certain simplifications when they may be made. For example, in the spectra of some elements the sub-levels either

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* The spectroscopist will note that a "level" represents all the terms arising from a given n_l electron configuration; A, B, . . . distinguish S, P, D . . . terms from one another, and the suffixes 1, 2, . . . stand for (but are not numerically identical with) the *j*-values of the terms. For example, in Ti the configuration of the ground-state, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$, corresponds to terms $^3F_{2,3,4}$, $^1D_2$, $^3P_{0,1,2}$, $^1G_4$, $^1S_0$. These would be represented in our present notation by $1A_{1,2,3}$, 1B, $1C_{1,2,3}$, 1D, 1E.

consist of only one component or contain only one of interest for our purpose: we shall, in such cases, drop the letter A, B, . . . and write simply 2, say. It will not usually be necessary to give the suffixes distinguishing the components of the sub-levels, but their existence will be indicated by the complexity of the group marked, say, by 2A–1A, which may contain as many as twelve lines, or even more. It may be taken as a general rule (not, however, without exception) that lines whose final level is 1 are more sensitive than others, and lines whose final level is 1A are more sensitive than those whose final level is 1B or 1C, etc., provided, of course, we ignore the effect of experimental conditions. If, then, the *raies ultimes* include lines involving 1B but not 1A, the reason will always be that the latter are out of the range of spectrum with which we are concerned.

This division into a hierarchy of sub-levels is not a mere convenience of classification, but corresponds to actual physical distinctions. No transition normally occurs between sub-levels of any one level: thus, we do not meet with such a group as 2B–2A, whatever values the suffixes may have. On the other hand, a transition from level 2 to level 1 means, in general, a transition from any of the sub-levels of 2 to any of those of 1: i.e. from 2A, 2B, 2C, . . . to 1A, 1B, 1C, . . . For any one such transition, however—say, 2B to 1C—only certain of the components occur. For example, if 2B has three components, $2B_{1,2,3}$, and 1C has four, $1C_{1,2,3,4}$, we may have transitions from $2B_1$ to $1C_1$ and $1C_2$, from $2B_2$ to $1C_1$, $1C_2$ and $1C_3$, and from $2B_3$ to $1C_2$, $1C_3$ and $1C_4$, but no transitions from $2B_1$ to $1C_3$ or $1C_4$, from $2B_2$ to $1C_4$, or from $2B_3$ to $1C_1$. We should thus have a group of eight lines instead of the twelve which would appear if all the transitions occurred.

A group of this kind, consisting of the lines generated by transitions from the components of one sub-level to those of another, is called a *multiplet*. The energy differences between the components of a sub-level are much smaller than those between the sub-levels of a given level, and these in turn are much smaller than the differences between the levels. It follows that a multiplet consists of a fairly compact group of lines in the spectrum, formed by transitions from a close group of upper to a close group of lower sub-levels. The separations of the lines increase in general with the atomic number of the element—thus in Na (atomic number 11) the interval between a particular pair of components is 17 units of wave-number (showing itself as a separation of 6 A. between members of the well-known pair of yellow lines), while in Cs (atomic number 55) the corresponding interval is 554 units of wave-number. Even in the heaviest elements, however, the distances between the lines of a multiplet are generally less than the average distance between one multiplet and another. In a given multiplet the *a priori* probabilities of the various component transitions are in definite, fairly simple, proportions, so that we may assign trustworthy intensity numbers to the lines. In a multiplet, therefore, we can satisfy the conditions which we saw were necessary to ensure trustworthy relative intensities on the plate. The trustworthiness, it is true, decreases as the atomic number of the element increases, and with the heaviest elements the varying sensitivity of the plate with wavelength may cause serious disturbances,* but in general one should always look for the whole multiplet of which any *raie ultime* is a member.

Recorded lists of *raies ultimes* do not give the multiplet relationships of the lines. Sometimes a whole multiplet is included among them and sometimes only the strongest line or lines. It is clearly important, however, to ensure that, if part of a multiplet is absent, it is the part that would be expected to be absent because of its relative weakness (or, in a rarer case, such as that mentioned in the footnote, because of plate characteristics), and one should never be satisfied that an element is present unless it passes this test. For this reason, in the notes which follow on individual elements, the whole multiplet (whenever it is known) is given, with relative intensities of the lines, for every *raie ultime* recorded. It must be clearly understood, however, that the intensity numbers indicate the *order* of intensities but are not a *measure* of them: thus, if two lines have intensity numbers 3 and 1, respectively, the first is certainly stronger than the second, but not necessarily three times as strong. All intensity tables that I know of have this limitation. It gives no trouble in practice because one never undertakes the very laborious task of measuring intensities absolutely except for definite theoretical reasons; and the blackening of the plate, which is what one very inaccurately estimates, by no means varies linearly with the intensity of the light falling on it.

It remains to consider the relative sensitivity of the spectrographic test for different elements. This varies over a wide range; it is very difficult, however, to give anything like precise figures. In Messrs. Hilger's list of sensitive lines quoted in Table V, an attempt is made (not reproduced here) to give a partial order of sensitivity, but it is by no means universally applicable. One may realise the principles involved, and the complexity of their application, by the consideration that what

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* A striking example of this is shown on Plate XIII. Here the lines 5350, 3776 of Tl (atomic number 81) form a "doublet" (a multiplet of two lines) of which the former should be the stronger according to the transition probabilities. It is obviously weaker on the plate because it occurs in the green, while the other line occurs in the near ultra-violet, to which the ordinary plate used is much more sensitive. The same plate shows a good example of the phenomenon mentioned on p 88 of the violation of the relative intensities of lines when the energy available in the source is insufficient to bring all the relevant orbits into play. Tl has a multiplet consisting of three lines, 3529, 3519 and 2768, of which, in a full spectrum, the first should be weakest, the second strongest, and the third intermediate In the Tl flame, however, the third does not appear while the first does, the reason being that there is insufficient energy in the flame to raise the electron to the orbit from which it must fall to yield 2768. The line appears strongly in the arc and spark spectra, but its predominance over 3529 in Plate XIII is obscured by the blending of that line with the much stronger 3519.

determines the fraction in a given line of the energy radiated per average atom of a given element is the *a priori* probability of the transition generating that line when all the possible transitions are taken into account. Theoretically there are an infinite number of possible transitions, but in practice those involving very high energy levels may be ignored. Even so, however, it is extremely difficult to know where to draw the line, and impossible to draw it on a common plan for all elements, and the very great diversity of possibilities, even among the low levels, for the different elements may be illustrated by two examples. Na has one component in its ground level, $1A_1$, and two in the next higher level, $2A_{1,2}$. Eu has 98 components in its ground level, 1, and 1827 in its next higher level, 2. If, then, we suppose the available energy is sufficient to bring only these two levels into play, the energy absorbed by Na will all be radiated in two lines, while that absorbed by Eu will be radiated in $98 \times 1827 = 179{,}046$ lines —reduced, it is true, by a considerable number for which the transition probably is zero, but still an extremely high number. The result is that, for the same total energy radiated, a line of Na will be enormously stronger than any of the lines of Eu. When higher levels are taken into account the discrepancy becomes greater. Eu is not the worst case, though Na is equal to the best, but the range of sensitivity suggested will indicate the difficulties of assigning comparative values to the several elements.

***Raies Ultimes* Plates.** A useful guide to the identification of lines is provided by plates giving the spectra of mixtures of large numbers of elements in known proportions. Such plates may be called for convenience "*raies ultimes* plates," although they may contain many more lines than the *raies ultimes*. Hilger's powder, already referred to (p. 81), provides an example. At the Imperial College, as already stated, we have made a more comprehensive mixture, containing all the spectroscopic elements except In and most of the rare earths and strongly radioactive elements. The last-named were omitted so as not unduly to overcrowd the spectra with lines, but La and Yb, whose spectra are much simpler than those of most of the rare earths, were included, as well as Th as a single example of the radioactive elements. The spectrum of this mixture has been obtained by simultaneous exposures on two instruments, approximately covering the regions 6800–3700 and 3560–2530 A., respectively. The plates are reproduced in Plates I–V and VII, VIII, while Tables VII and VIII give lists of the lines appearing.

A judicious use of these tables and plates may serve a number of useful purposes, but it is necessary to bear in mind the conditions under which they were obtained. A mixture was prepared of salts of the various spectroscopic elements represented, in amounts giving equal numbers of atoms of each such element. The whole was then mixed with about ten times its weight of NaCl. Each element except Na, therefore, formed only a small proportion of the whole, but nevertheless was present in sufficient strength to show more than the *raies ultimes* of most of the elements. Had the mixture been completely homogeneous the results might have given valuable information on the relative sensitivity of different elements to the spectroscopic test, but with so many substances complete homogeneity was almost impossible. The most satisfactory method of mixture, if a universal solvent could have been found, would have been to dissolve them all and evaporate to dryness. Actually mechanical mixing was relied on, and although this was carried on for some time, the inevitably hygroscopic character of some of the constituents added to the difficulty and prevented perfect uniformity from being obtained. This is most obviously shown by the fact that in the result Cs and Hg did not appear at all in the small sample taken for the plates, while Zn was abnormally faint. In any case, even if mixing had been complete, the value of the result would inevitably have suffered from impurities which must have been present in some of the salts used, as well as in the graphite electrodes—especially V, which makes that element the best represented of any except sodium.

Although both the photographs (one yielding Plates I-V, and the other Plates VII, VIII) were taken from the same burning of the arc, one with a glass instrument having separate telescope and collimator and the other with a quartz Littrow instrument, no conclusions can be drawn from the relative strengths of lines from the same element appearing on different plates, not only because the photographic plates used were of different types, but also because there was much more scattered light in the glass instrument, making invisible faint lines which with the other instrument would have been clearly seen. To this must be added the fact that most of the Na lines, giving very extensive halation, occur in the visible region, so that a considerable section of that region was either effectively not represented or else represented very imperfectly. This must always be borne in mind in considering the significance of the non-appearance of lines falling fairly close to Na lines.

One use of such plates as these is that if one is in doubt whether a certain line is due to some element which has a tabulated line approximately at its position, the relative strengths of the various lines of that element appearing in the spectrum in question may be compared with those in Plates I to VIII, whereupon, conditions as to plate sensitivity, etc., being borne in mind, a decision might be arrived at. In this connection, however, it must be remembered that, owing to the preponderance of Na in the general mixture, the degree of excitation for these spectra is low, as is indicated by the V I and V II lines around 2924 (compare Plate XV). Hence one should not necessarily expect the relative intensities of neutral and enhanced lines to be a general guide to what might occur under other conditions. Again, the absorption by the glass in the longer wave-length region increases rapidly as the ultra-violet is approached, and the intensities of the lines from, say, 3900 to 3700 get progressively weakened on this account. Nevertheless, when one considers lines of the same multiplet which do not cover a great range of wave-length, the relative intensities should be almost independent of physical conditions and trustworthy conclusions can usually be drawn.

The lines have been tabulated with this end in view. In Tables VII and VIII the elements responsible for the lines have been arranged so that those of the same multiplet appear in the same column; e.g. the symbol La has been placed in the fourth column in Table VII for the lanthanum lines 6578·513 and 6455 988, which belong to one multiplet, and in the fifth column for the lanthanum lines 6543·151, 6394·234 and 6249·929, which belong to another (Unless the contrary is indicated —e g. LaII—it is to be understood that each chemical symbol refers to the neutral atom) Although reasons of space make unavoidable the use of each column for multiplets of several elements, different multiplets of the same element always appear in different columns, with three exceptions, namely V in Table VII and V and Fe in Table VIII. Here there are so many multiplets that it has been necessary to give two multiplets of V in each of columns 6, 7, 8, 10, 14, 16, 17, 18, 19, 20 in Table VII, two multiplets of V in each of columns 4, 5, 6, 7, 9, 10, 12, 14, 19 in Table VIII, and two multiplets of Fe in each of columns 2 and 3 in Table VIII. The multiplets concerned, however, are fairly compact and the separation between those appearing in the same column has been made as large as possible so that no confusion should arise on this account. With these exceptions one can be assured that, however far apart lines of an element may be whose identification symbols appear in the same column, those lines belong to the same multiplet. Many of the multiplets, of course, are not completely represented on the Plates, the weaker lines not appearing. The Table, therefore, cannot be used as a general multiplet table though it may serve some of the purposes of one.

Any line, of whatever element, which stands by itself—either because it is a singlet, or has not yet been classified, or is the only representative of its multiplet on the plate—is identified by its chemical symbol, in italics, in the first column. Sometimes the same line is attributed to two multiplets, either of the same or different elements: such coincidences have always been noted in the "Remarks" column, and two symbols are given for the line. Again, blends are not very infrequent and these also have been noted in the "Remarks" column. A blend is a line which appears single on the plate but is in reality two or more different lines unresolved. The wave-lengths of both lines have been given in the Tables, although the blend itself would of course be a single line with a measured wave-length which is a weighted mean of the individual ones. Care has been taken not to assert a blend without sufficient evidence, including that of the appearance of the line, its wave-length, and the probability of the various lines being present when the general strength of representation of the corresponding elements has been taken into consideration. Whenever, in measuring a plate, the worker obtains a wave-length which does not appear in the Tables, the possibility of a blend should be considered, and Tables VII and VIII are often very useful in suggesting what blends might occur.

There remain a few lines whose identification is doubtful. These have been marked with a " ? " in the "Remarks" column. Sometimes the most probable identification has been given as well, but if no element stands out as the most likely one, the identification has been left open. The lines are almost all very faint, and the existence of some such lines is not surprising. It must be remembered that in a mixture containing so many elements there is a maximum chance of including a trace of one of the few "missing" elements of the Periodic Table, and as the spectra of these become known it might be worth while to look for them in Tables VII and VIII It is more likely, however, that the lines have already been identified, but for some reason have escaped general lists such as Harrison's, and have not been classified into multiplets.

It should be added that in both tables, and in general throughout the book, with the exception of Tables II and IV, Harrison's wave-lengths have been adopted when they exist for the sake of consistency.

INDIVIDUAL ELEMENTS

We now proceed to consider the individual elements. The notes which follow, in which the elements are arranged with their chemical symbols in alphabetical order, give such information as may be found useful according to the experience of the writer, but it cannot be too often repeated that each worker, with his own familiar problems and equipment, will inevitably acquire and should learn to profit from experience which it is impossible to record in general terms.

Silver (Ag)

The multiplets containing the *raies ultimes* are

$$\left.\begin{array}{l}3382{\cdot}891\ (9)\\ 3280{\cdot}683\ (10)\end{array}\right\}2\text{–}1 \qquad\qquad \left.\begin{array}{l}5471{\cdot}551\ (5)\\ 5465{\cdot}487\ (8)\\ 5209{\cdot}067\ (7)\end{array}\right\}3\text{–}2$$

2437 791 (2) 3A–2 AgII
2246·412 (1) 3B–2 AgII

One of the easiest elements to identify. It is rarely necessary to look further than the very sensitive pair at 3383, 3281, which are usually well isolated. If Rh is present, care should be taken that its rather sensitive line at 3280·55 is not mistaken for Ag, and if Cu is present in strength and the dispersion is small, its line at 3279·82 might be a source of error. If graphite poles containing Ti are used, the TiII line at 3383·761 will probably appear. Its almost exact coincidence with Fe, 3383·70, will help to identify it. Generally speaking, however, if two lines are present of the correct relative intensities and, so far as the eye can judge, at the correct positions for Ag, it is rarely necessary to resort to measurement.

Aluminium (Al)

The multiplets containing the *raies ultimes* are:

3961·527	(10)	2–1
3944·032	(9)	
3092·842	(3)	3–1
3092·713	(8)	
3082·155	(7)	
2669·166	(2)	2A–1 AlII
2816·179	(2)	3–2B AlII
6243·36	(2)	5–4 AlII
6231·76	(1)	
6226·19	(0)	

Another very easy element. I have never had need to resort to the lines of the ionised atom, AlII; they would, of course, be more prominent in the spark than in the arc, but even there are rarely needed. It should be noted that 6243 is a blend of three and 6232 of two close lines which will not be resolved on most instruments. This, of course, increases their sensitivity compared with that of the individual lines. One quickly learns to recognise at sight the pair at 3961, 3944 by their situation with respect to the CaII lines 3968, 3933, which almost always appear fairly strong in whatever is examined. The group around 3090 is only slightly less sensitive: the faintest line will be blended with the strongest when small or moderate dispersion is used.

There are no lines which even a moderately careful observer can confuse with the 2–1 pair. A sensitive Mg triplet at 3096·899, 3092·991, 3091·077 (in descending order of intensity) frequently appears and should not be confused with the neighbouring Al group. The VII line, 3093·108, usually appears with graphite poles, and possibly the neutral V line, 3082·109.

Arsenic (As)

The multiplets containing the *raies ultimes* are:

2349·84	(7)	2B–1B
2288·12	(8)	
2271·36	(3)	
2492·91	(4)	2A–1B
2456·53	(5)	
2437·23	(2)	
2381·18	(3)	
2368·05	(0)	
2898·71	(2)	2B–1C
2860·45	(5)	
2780·20	(6)	
2744·99	(4)	
2370·77	(3)	2C–1C
2369·67	(2)	
2344·03	(0)	

The most sensitive group, 2A–1A, is out of range in the 1900 region. Both Hilger and Harrison give 2B–1B as the most sensitive group and it usually is so, the group 2A–1B, which according to the general rule would be expected to be stronger, being, to use technical language, an intercombination between doublets and quartets, while 2B–1B is a pure doublet combination. In this region, however, plate sensitivity plays a prominent part in the relative line intensities, and this accounts for the fact that Hilger gives 2350 as more sensitive than 2288, whereas theoretically the latter should persist longer. The worker must be prepared for either order of intensity according to the kind of plate used and the exposure given. The value of 2288, however, is greatly decreased by the fact that the sensitive *raie ultime* of Cd at 2288·018 is so close as to be unresolvable by moderate instruments. As should therefore never be marked present on account of 2288 alone unless Cd is certainly known to be absent Fortunately, in this region of high dispersion there is a good chance of settling a doubt by taking comparison spectra of the mixture and As and Cd compounds on the two sides. In the 2B–1C group, the strongest line, 2780, has close neighbours in Bi, 2780 521; Mg, 2779 834; and Sn, 2779·817, but there should be no difficulty in distinguishing them even without measurement. 2860 must not be confused with V, 2859 971, which is sure to appear with graphite electrodes containing V. The group 2C–1C is unlikely to be called upon: if it is, 2369 must not be confused with Cu, 2369·89.

Gold (Au)

The sufficient *raies ultimes* are the components of the doublet

$$\left.\begin{array}{l}2675{\cdot}95\ \ (9)\\ 2427\ 95\ (10)\end{array}\right\}2\text{–}1$$

There is nothing that can be mistaken for 2675 unless rare substances are present in large quantity, and if it is accompanied by 2427 the evidence is conclusive The latter line alone might be confused with Sr, 2428·095, or with Pt, 2428 203, if these elements are well represented.

Boron (B)

The arc spectrum of B contains only two lines in our region, of which the stronger is ample for identification. The wave-lengths are.

$$\left.\begin{array}{l}2497{\cdot}733\ (10)\\ 2496{\cdot}778\ \ \ (9)\end{array}\right\}2\text{–}1$$

There are no lines which can be mistaken for these, except in the very rare case in which B is so weak that only the former line would be expected to show and also Ge or Os is present in strength. In such a case it would usually be safer not to record B as established, even although measurement confirmed that the single line had the right wave-length, for B is a common impurity in electrodes—it is almost always present in carbon electrodes—and in the glass of vacuum tubes, and it would be hazardous to assume that such a faint appearance certainly indicated the presence of B in the subject under test. Cu poles are advisable in looking for B, as these can be obtained practically free from it.

Barium (Ba)

This is a fairly easy element to identify, and, though not exactly a rare constituent of mineral and biological specimens, it is less commonly found than the other abundant alkaline earths. The multiplets containing the *raies ultimes* are:

$$\begin{array}{ll} 5535{\cdot}551\ (10) & 2B\text{–}1 \end{array}$$

$$\left.\begin{array}{l} 4934{\cdot}086\ \ (9) \\ 4554{\cdot}042\ (10) \end{array}\right\} 2\text{–}1 \quad \text{Ba II}$$

The most sensitive lines are usually the pair of the ionised atom, because Ba is very easily ionised in the arc, the low levels of the ionised atom have no sub-levels, and the line of the neutral atom occurs in a region of weak plate sensitivity. 5535, however, is unmistakable if it does occur, though measurement may be necessary to distinguish it from the Sr line, 5534·807, which is one of a prominent group of seven lines in this region; and if Ba is present in even moderate quantity, 5535 will be accompanied by a multiplet (a "triplet") of Ba containing six lines, of which the strongest are at 5777·665, 5519·115 and 5424·616. 4554 is near Ru, 4554·509, but 4934 cannot be mistaken. Harrison erroneously gives the arc and spark intensities of the enhanced pair in opposite orders; his intensity scales for arc and spark are also obviously incompatible.

Beryllium (Be)

Be is another alkaline earth whose spectrum has a similar structure to that of Ba, but the corresponding lines are of much shorter wave-length. They are:

$$\begin{array}{ll} 2348{\cdot}60\ (10) & 2B\text{–}1 \end{array}$$

$$\left.\begin{array}{l} 3131{\cdot}072\ (7) \\ 3130{\cdot}416\ (8) \end{array}\right\} 2\text{–}1 \quad \text{Be II}$$

$$\left.\begin{array}{l} 3321{\cdot}343\ (7) \\ 3321{\cdot}086\ (6) \\ 3321{\cdot}013\ (6) \end{array}\right\} 3\text{–}2A$$

Here, in spite of plate characteristics, 2348 is more sensitive than the pair of the ionised atom because Be has a considerably higher ionisation potential than Ba: the line is also well isolated. If the instrument is not set for this region, however, it may be more convenient to look for the pair at 3131. In that case care must be taken not to confuse it with the lines of V II and Ti II at 3180·267 and 3180·800, respectively. These lines appear in the arc spectrum of graphite containing V and Ti, with, of course, somewhat variable intensity according to the particular poles used, but generally with the former stronger; and a rather careless glance, especially when the dispersion is small, may easily result in their being mistaken for Be. Many a marine animal has been credited with wearing a precious beryl in its head through this mistake. Plate XVIIIB shows one example of this pair and the Be pair, with a Fe comparison, the dispersion being the largest likely to be used. If there is any doubt in the matter, the group 3–2A, usually only slightly less sensitive, and when the degree of excitation is low even more so, should be looked for. It is a close triplet and is likely to appear as a rather hazy single line, possibly with some suggestion of complexity.

A word should be added concerning the lines near 2650 and 2494 given in Hilger's list. At each of these positions there is a close group of six lines, extending from 2650·781 to 2650·470 and 2494·733 to 2494·559, respectively, according to Harrison's Tables, with which Paschen closely agrees. It is difficult to reconcile Hilger's wave-lengths with these, but the lines are unlikely to be called upon for identification of Be.

Bismuth (Bi)

The spectrum of Bi is theoretically difficult to analyse (in technical language it exhibits strong *j-j* coupling) and the multiplets cannot be expressed in ordinary terms. The chief *raies ultimes* are very sensitive, however, and the element is among the easier ones to detect with certainty if care is exercised. Its chief *raies ultimes* are:

3067·716	(10)	2–1A
2897·975	(8)	3–1B
4722·552	(7)	2–1B

3067 is normally the best line, being the most sensitive, well situated with respect to Fe for easy identification and free from neighbouring strong lines of other elements. If Bi is weak, however, there is great danger of its being thought present when what is actually seen is a line of the OH band which is often produced in an arc in moist air. I have known this to happen with somewhat serious consequences. The coincidence is almost exact and the band line is the strongest in the neighbourhood, so that the mistake is very easy to make. Plate XVII shows the Bi line and the OH band in an arc not containing Bi. This coincidence makes 2897 sometimes the chief criterion for Bi. It is not so sensitive as 3067, but its position with respect to Fe lines makes it easy to identify at sight and there is no possibility of a mistake except in the unlikely event of Pt being present in strength. 4722 is too close to strong lines of Zn and Sr to be of much value in a region where the dispersion is usually fairly small.

Carbon (C)

C has only one normally practicable line in the arc, namely 2478·573, which, however, is unmistakable. Cu electrodes, ascertained to be free from C, should be used. The line is 2–1C. Transitions to lower sub-levels of the ground state have wave-lengths too small for practical use.

Calcium (Ca)

Ca is unmistakably indicated by the three lines·

4226·728 (10) 2B–1

$$\left.\begin{array}{l}3968\cdot468\ \ (9)\\3933\cdot666\ (10)\end{array}\right\}2\text{–}1\quad \text{Ca}_{\text{II}}$$

The "constellation" formed by these lines cannot fail to be recognised after a very little experience, which cannot be avoided, since Ca almost invariably occurs in whatever spectrum one examines. The positions of the lines with respect to the CN bands with heads at 4216, 3883, assist in their ready recognition. Although the second group belongs to the ionised atom, it occurs in great strength in the arc, and I cannot say which of the three lines is most sensitive, since I have never known Ca too weak to show them all. The lines are the analogues of the corresponding groups in Be, but since they occur in a region of much greater plate sensitivity, a third group is never needed. It may be added, however, that Hilger's inclusion of 4456 620 and omission of the more sensitive 4454·781 suggests an error.

Columbium (Cb). See Niobium (Nb)

Cadmium (Cd)

The multiplets containing the *raies ultimes* are·

2288 018 (8) 2B–1

3261·057 (7) 2A–1

$$\left.\begin{array}{l}5085\cdot824\ (6)\\4799\cdot918\ (5)\\4678\cdot156\ (4)\end{array}\right\}3\text{–}2\text{A}$$

$$\left.\begin{array}{l}3614\cdot450\ (1)\\3612\cdot875\ (2)\\3610\cdot510\ (6)\\3467\cdot656\ (2)\\3466\cdot201\ (5)\\3403\cdot653\ (4)\end{array}\right\}4\text{–}2\text{A}$$

The line 2288 is in a region of weak plate sensitivity and is almost unresolvable from As 2288·12. 3261 is therefore the most generally useful line. The red line at 6438, which is used to define the standard of the wave-length scale, is in general less sensitive than 3261, and does not appear in Hilger's list. 5085 is close to a rather sensitive line of Sc at 5085·547, but this is one of a group of ten lines, several of which should appear if this does. The plate sensitivity, however, is weak in this region. In the 4–2A group, 3610 is close to the strong Ni line, 3610·462, and 3466 to the *raie ultime* of Co at 3465·800. Cd is a metal which it is usually profitable to test for by a comparison spectrum of the substance itself, as several of its lines are easily mistaken for others.

Cobalt (Co)

The multiplets containing the *raies ultimes* are:

3533·358	(5)	2A–1A
3529·033	(6)	
3513·480	(8)	
3465·800	(10)	
3456·926	(2)	
3415·580	(1)	

3529·813	(9)	2B–1B
3509·843	(7)	
3495·687	(7)	
3453·505	(12)	
3449·441	(8)	
3449·170	(8)	
3443·641	(9)	
3385·224	(3)	
3367·109	(5)	

3483·410	(3)	2C–1B
3474·022	(8)	
3462·803	(6)	
3433·040	(6)	
3417·160	(4)	
3409·177	(6)	
3405·120	(10)	
3388·173	(3)	
3354·377	(2)	
3334·137	(3)	

It is doubtful whether 3465 or 3453 is the more sensitive line. The former would be expected to be so theoretically, but the latter is blended with another line of Co, the light of which, though it would not appear alone in the weakest concentrations, might intensify its sensitive companion to a degree difficult to estimate. 3465 has strong lines of Fe (3465·863) and Cd (3466·201) as neighbours, but 3453 is better isolated and should be looked for first. It often appears as a weak line in the Fe spectrum which has no nearer neighbour than 3453·023, and this offers a ready means of identification. 3405 also is a blend of two Co lines and there should be no difficulty in distinguishing it from the strong Pd line at 3404·580. It is, however, very close to a band-head of CN which is a common feature in the carbon arc, and this detracts seriously from its value in many spectrograms. Several of the other lines of the three multiplets are close to lines of Fe and Ni, and care must be taken not to confuse them. In any but the very weakest concentrations, however, Co should offer no difficulty on account of its many sensitive lines in the same region of the spectrum. It might be noted that Harrison gives among the *raies ultimes* 3529 in the 2A–1A multiplet, but not the stronger line 3513. The last-named should always appear if 3529 does, and it is well isolated.

Chromium (Cr)

The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{l}4289{\cdot}721\ \ (8)\\4274{\cdot}803\ \ (9)\\4254{\cdot}346\ (10)\end{array}\right\}\text{2A–1A}\qquad\qquad\left.\begin{array}{l}3605{\cdot}333\ (6)\\3593{\cdot}488\ (6)\\3578{\cdot}687\ (7)\end{array}\right\}\text{3–1A}$$

$$\left.\begin{array}{l}5208{\cdot}436\ (7)\\5206{\cdot}039\ (6)\\5204{\cdot}518\ (5)\end{array}\right\}\text{2B–1B}$$

The first group is usually sufficient. Cr is often present in the Fe comparison spectrum, which makes the identification immediately decisive. The lines are isolated, except 4289 which is close to a strong Ca line at 4289·364. The narrow green triplet, 2B–1B, suffers from weak plate sensitivity. The group 3–1A, if Cr is weak and the CN bands strong, is liable to be lost in the tail of the strong 3883 band; otherwise the last two lines are unmistakable (there is a strong Ru line at 3593·022, but the substance is rare), but 3605 is very close to a strong Co line at 3605·356.

Caesium (Cs)

Like the other alkalis, this element is very sensitive to the spectrographic test. The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{l}8943{\cdot}50\ \ (8)\\8521{\cdot}10\ (10)\end{array}\right\}\text{2–1}\qquad\qquad\left.\begin{array}{l}4593{\cdot}177\ (6)\\4555{\cdot}355\ (7)\end{array}\right\}\text{3–1}$$

In spite of the need for special infra-red and relatively insensitive plates, the 2–1 pair is the most sensitive criterion: the lines, when they appear, are unmistakable. It is, however, always advisable to look first for the blue pair since they do not demand special plates. There are no lines which, when ordinary care is exercised, could be mistaken for them unless Ti, 4555·49, is strong enough. The isolated Fe lines at 4592·655 and 4556·125 are useful pointers.

Copper (Cu)

Cu has two outstandingly strong and sensitive lines at:

$$\left.\begin{array}{l}3273{\cdot}962\ \ (9)\\3247{\cdot}540\ (10)\end{array}\right\}\text{2–1}$$

These lines, when present, are unmistakable. If they are not both clearly seen, Cu is so extremely weak as to be marked absent with safety.

Fluorine (F)

F, though in certain circumstances a "spectroscopic element," is by far the least certain of such. Its detection is possible because a compound with Ca (CaF) gives a system of bands in the arc of which the most prominent have heads at 5921·0 (degraded to red) and 6064·4 (degraded to violet), the former being the more sensitive. A little Ca salt added to the arc, in the unlikely event of its not being already present, may suffice to bring out the bands. The only possible source of error might arise from the ScO band-head at 6064·8, but this is degraded to the red and should be accompanied by a stronger band with head at 6036·2.

Iron (Fe)

Since Fe is almost universally used as a comparison spectrum it is usually unnecessary to look for particular lines. If Fe is present in any strength the number of coincidences obvious on inspection will be decisive. On the other hand, extremely small amounts of Fe can rarely be detected with certainty owing to the presence of this element in almost every pair of electrodes. I have never yet found electrodes quite spectroscopically free from Fe. In metallurgical work, however, where no auxiliary electrodes are used, the presence or absence of Fe lines is a definite criterion for the presence or absence of Fe. The most sensitive line is given by Hilger as 2483·270. Harrison, however, does not list this line among the *raies ultimes* at all; his most sensitive line is 3719·935. This certainly has the advantage of occurring in a part of the spectrum where the plate is more sensitive, though if the 3883 CN band is strong it might be obscured, but I have found little to choose between the two. Neither line has any neighbours likely to be mistaken for it, particularly when a Fe comparison spectrum is taken. In the very rare cases in which a single-line identification is necessary, the presence of either is sufficient. Since the only occasions demanding minute examination are those in which only one or two lines are left, there is less need for the whole multiplets than with other elements. They are given, however, for completeness The intensities are not of much significance, since the lines are frequently reversed, and the second group falls in a region where the lines may be much confused by pole effect (see Plate IX).

3748·264	(7)	2–1	2491·155	(7)	3–1
3745·903	(7)		2490·644	(8)	
3745·564	(8)		2489·751	(6)	
3737·133	(9)		2488·148	(9)	
3733·319	(5)		2484·187	(6)	
3722·564	(6)		2483·270	(10)	
3719·935	(10)		2479·776	(5)	
3707·824	(3)		2472·909	(4)	
3705·567	(6)		2472·880	(4)	
3683·058	(4)		2462·644	(5)	
3679·915	(5)		2462·180	(2)	
3649·304	(3)		2447·708	(3)	

It should be added that the line at 3457·086, recorded in Table V as given by Hilger, is actually given as 3456·87. There is no Fe line at this position, and I have given the nearest likely wave-length, but it is probable that the line should not have been included at all.

Gallium (Ga)

Ga, though a rare element, is very widely distributed and is not at all unlikely to be found in dust taken at random from the street. I have found it also in mud from the bottom of the Indian Ocean, a thousand miles from land. It is a sensitive element spectroscopically, the spectrum being similar in structure to that of Al. The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{l}4172\cdot056\ (10)\\4032\cdot982\ \ \ (9)\end{array}\right\}2\text{–}1 \qquad \left.\begin{array}{l}2944\cdot175\ (3)\\2943\cdot637\ (8)\\2874\ 244\ (7)\end{array}\right\}3\text{–}1$$

With a small supply of material and with graphite poles, 4172 is liable to be lost in the strong CN band with head at 4216, while 4032 is very close to the strong and sensitive Mn line at 4033·073. For this reason the most sensitive pair is less useful than it appears and it is usually necessary to depend on the other group, which, however, is a sensitive criterion The strongest line is close to a group of V lines which often appear with graphite poles, the nearest members being 2944·571 (VII) and 2943·196 (VI). There is also a strong line of W at 2944 395, but it is rarely troublesome. The Fe line at 2874·172 is a good pointer to the neighbouring Ga line.

Germanium (Ge)

Ge, like Ga, has a wide distribution, partly because of its occurrence in some coal dusts. It is therefore to be expected more frequently than its terrestrial abundance would suggest. The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{l}2754\ 592\ \ \ (8)\\2709\cdot626\ \ \ (7)\\2691\cdot344\ \ \ (6)\\2651\cdot575\ \ \ (7)\\2651\ 178\ (10)\\2592\ 537\ \ \ (6)\end{array}\right\}2\text{A–1A} \qquad \begin{array}{lll}3039\ 064 & (10) & 2\text{B–1B}\\ & & \\4226\cdot570 & (9) & 2\text{B–1C}\end{array}$$

It is difficult to say which is the most sensitive line of Ge. The line at 3039 involves a higher level than the 2A–1A group, but, being a "singlet," it has not to share its intensity with other components. 3039 is easier to locate relatively to Fe, but in the very rare event of In being present, it is liable to be confused with the *raie ultime* of that element at 3039·356. Its position with respect to the rather weak Fe line at 3039·316 assists in the distinction. The isolated Fe line at 2651·706 helps in the location of the neighbouring Ge pair; otherwise the group is not situated in a very easily recognisable part of the Fe spectrum. The line at 4226 is close to the *raie ultime* of Ca at 4226·728, which is rarely absent from any spectrum. There is no other line in this neighbourhood that is likely to be mistaken for Ge.

Hafnium (Hf)

For this rare and recently discovered element the *raies ultimes* are less well established than for most, and the spectrum has not been sufficiently analysed for the multiplet classification to be given with confidence. Harrison's list is adequate, but it should be noted that it includes lines of both HfI and HfII. The line at 2773·357 of HfII has been stated to be the most persistent in arc spectra This does not concur with my experience; I have known spectra in which the *raies ultimes* of Hf have been present in strength without a trace of 2773 or 4093. In this connection it must be remembered that arc spectra vary considerably according to the general composition of the arc. When substances of low ionisation potential, like the alkalis, are present, neutral lines are strengthened at the expense of those of the ionised atom. With a rare element like Hf it might sometimes be advisable to mix the specimen with a considerable amount of a Na salt, so as to increase the sensitivity by strengthening the lines of HfI. In general, it is a good rule never to introduce other elements because of the unknown impurities they may bring with them, but there is little danger when Hf is the element of interest. The two most sensitive lines in these circumstances are probably 3072 877 and 2898·259. Only ordinary vigilance is needed to distinguish the former from Zn (3072 062) and Co (3072 344) and the latter from Bi (2897·975) and As (2898·71).

Mercury (Hg)

The most sensitive Hg line is 2536·519 (2–1), which is the only representative of the "intercombination" multiplet in which it occurs. It is sensitive enough to show Hg in a pure graphite arc in a laboratory in which a Hg diffusion pump is working, and it is invariably present as a very fine absorption line in a continuous spectrum taken in such a laboratory. The next most useful group is:

$$\left.\begin{array}{lr} 5460{\cdot}740 & (10) \\ 4358{\cdot}35 & (9) \\ 4046\ 561 & (8) \end{array}\right\} 3\text{–}2$$

Here the middle line, although actually weaker than the well-known green line at 5460, is more sensitive owing to plate properties. 2536 has no prominent close neighbours, but as the Fe spectrum is so difficult to recognise in this region, care should be taken that it is not confused with P, 2535·65, the strongest of the group of four lines by which P is best identified. The other lines are unmistakable if they occur.

Indium (In)

In is one of the rarest of elements. Its *raies ultimes* correspond with those of the other members of its family—Al, Ga and Tl. The multiplets in which they occur are:

$$\left.\begin{array}{l}4511{\cdot}823\ (10)\\ 4101{\cdot}773\ \ (9)\end{array}\right\}2\text{–}1 \qquad \left.\begin{array}{l}3258{\cdot}564\ (3)\\ 3256{\cdot}090\ (8)\\ 3039{\cdot}356\ (7)\end{array}\right\}3\text{–}1$$

If the available material is very scanty, both lines of the first group may be hidden in CN bands if graphite poles are used. In that case it is probably better to rely on the second group, which is slightly less sensitive, than to resort to other poles.

Iridium (Ir)

The most sensitive line, according to Hilger, is 3133·321, but this is not included in Harrison's list of *raies ultimes*. The line, however, is usually better avoided since it is almost exactly coincident with a line of V II at 3133·328, which often appears with graphite poles. The lines recommended are:

3513·645 (5)
3220·780 (5)

The spectrum has been insufficiently analysed for the multiplets to be given. 3513 is rather close to the Co line at 3513·480, but the strong Fe line at 3513·820 should make distinction possible at sight when the dispersion has been noted. This line, however, is in general less suitable than 3220.

Potassium (K)

Like all the alkalis, an easy element to detect in small quantity. The multiplets forming the *raies ultimes* are.

$$\left.\begin{array}{l}7698{\cdot}979\ \ (9)\\ 7664{\cdot}907\ (10)\end{array}\right\}2\text{–}1 \qquad \left.\begin{array}{l}4047{\cdot}201\ (6)\\ 4044{\cdot}140\ (7)\end{array}\right\}3\text{–}1$$

In spite of much weaker plate sensitivity, the former group provides by far the most critical test for K. Its lines may appear strong when the violet pair does not appear at all. The latter pair is, nevertheless, good enough for all but the smallest concentrations of K, and should always be looked for first. The occurrence of the strong Fe line, 4045·815, almost half-way between the lines, makes them easy to locate and unmistakable after having once been seen. Harrison's Table of *raies ultimes* (see Table V) indicates that the red lines do not appear in the spark. This is evidently an error, since his main tables give them spark intensities of 200 and 400, respectively.

Lanthanum (La)

Although, in one sense, a rare earth, La has a very much simpler spectrum than most of the other members of this family and for our purpose is more appropriately considered as an ordinary element. Hilger's and Harrison's lists of *raies ultimes* show unusual disagreement. It is probable that, apart from plate sensitivity, the most sensitive lines are in the far red or near infra-red, but with ordinary panchromatic plates the group 2B–1A is probably the best criterion. The close pair at 5930 in this group will be unresolved with most instruments. and the sensitivity is thus increased The strong Fe line at 5930·186 is a very convenient pointer in a rather difficult region, as are the Fe lines 5501·469 and 5455·433 to the neighbouring La lines in the 2C–1A group. The multiplets are:

$$\left.\begin{array}{ll}6325{\cdot}923 & (5)\\ 5930{\cdot}667 & (9)\\ 5930{\cdot}628 & (10)\end{array}\right\}\text{2B–1A}\qquad \left.\begin{array}{ll}5839{\cdot}791 & (2)\\ 5501{\cdot}340 & (8)\\ 5455{\cdot}146 & (8)\\ 5158{\cdot}693 & (5)\end{array}\right\}\text{2C–1A}\qquad \left.\begin{array}{ll}6917{\cdot}22 & (2)\\ 6903{\cdot}08 & (0)\\ 6692{\cdot}87 & (3)\\ 6661{\cdot}399 & (5)\\ 6616{\cdot}577 & (5)\\ 6543{\cdot}151 & (9)\\ 6410{\cdot}995 & (8)\\ 6394{\cdot}234 & (10)\\ 6249{\cdot}929 & (9)\end{array}\right\}\text{2A–1B}$$

Lithium (Li)

The sensitive lines of Li are close doublets, which are unresolved with instruments ordinarily used for analytical work, and the recorded wave-lengths are thereby rendered somewhat indefinite. The most sensitive lines are 6707·844 (10), 6103·642 (9), 4603·00 (8) The red line at 6708 is easily the most critical and is a sufficient criterion by itself, but it is not easy to locate. A comparison spectrum of a Li salt is useful. 6103 is spoilt by the neighbourhood of the frequently occurring Ca line, 6102·721.

Magnesium (Mg)

Mg, like Ca and the other alkaline earths, can be detected in the arc by either the neutral or the ionised atom. The multiplets are·

$$2852{\cdot}129\ (10)\quad \text{2B–1}\qquad \left.\begin{array}{ll}2802{\cdot}695 & (9)\\ 2795{\cdot}53 & (10)\end{array}\right\}\text{2–1}\quad \text{Mg II}$$

All the lines are close together and form an easily recognised group. 2852 is close to the commonly occurring Na pair, 2852·828, 2853·031. 2802 has a near neighbour in Pb 2802·008, while 2795 is close to Mn 2794·817. The Mn line is the strongest of a group of three of almost equal strength, the others being at 2798·271 and 2801·064. If Mn is present the whole group should appear. Very little experience, however, is needed to make the Mg line immediately recognisable, with or without the presence of other elements. If Mg is present in even moderate strength, the appearance of a symmetrical group of five equidistant lines, extending from about 2777 to 2783, will strike the eye immediately, and one need look no further. In the visible region the well-known green triplet (the *b* group in the solar spectrum) at 5183·618, 5172·699, 5167·343 is another unmistakable criterion.

Manganese (Mn)

Mn is sufficiently indicated by the following multiplet:

$$\left.\begin{array}{ll} 4034\cdot490 & (8) \\ 4033\cdot073 & (9) \\ 4030\cdot755 & (10) \end{array}\right\} \text{2B–1}$$

Commercial Fe invariably contains Mn, and the presence of this group in the Fe comparison spectrum makes identification unmistakable. It is, therefore, unnecessary to consider lines which might otherwise be mistaken for these. The group near 2800, referred to under Mg, is also a sensitive and easily recognised criterion. It is not given among the *raies ultimes* by Harrison, and Hilger curiously records only the central line of intermediate strength. This line, of course, cannot indicate Mn unless 2794·817 also is visible or obscured by Mg.

Molybdenum (Mo)

The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{ll} 3902\cdot963 & (8) \\ 3864\cdot110 & (9) \\ 3798\cdot252 & (10) \end{array}\right\} \text{2A–1} \qquad \left.\begin{array}{ll} 3193\cdot973 & (5) \\ 3170\cdot347 & (6) \\ 3132\cdot594 & (7) \end{array}\right\} \text{3A–1}$$

The most sensitive group is often of little value because 3902 is almost coincident with a strong Fe line at 3902·948 (a Cr line at 3902·915 is less troublesome because Cr is not so often present in sufficient strength to make it a possibility), while the other two lines may be obscured by the strong CN band in this region. The group 3A–1 is, however, little less sensitive and it is rather surprising that Harrison gives lines of the ionised atom precedence over it in his list of *raies ultimes*. The relative strengths of lines of the neutral and ionised atoms vary, of course, with the general composition of the mixture, but my experience has been that as a rule the 3A–1 group is the best criterion. If Cu is conspicuous its line at 3194·095 may be present, but the strongest line of the Mo group at 3132·594, which can scarcely be confused with anything else, is easily identified by the neighbourhood in the comparison spectrum of the weak Fe line at 3132·514, which will not be present in the spectrum under examination unless Fe is overwhelmingly strong there. This line by itself is almost sufficient to establish Mo. It should be noted that some specimens of graphite may contain Mo, and Webb has reported that it is one of the impurities that does not appear in the spectrum of the graphite until some salt is added (see pp. 79–80). I have not experienced this, but if one is particularly interested in Mo it would be well, for safety, to take a preliminary spectrum of the poles with a little common salt placed on them.

Sodium (Na)

The multiplets containing the *raies ultimes* are:

5895·923	(9)	2–1	3302·988	(5)	3–1
5889·953	(10)		3302·323	(6)	

The yellow pair, perhaps the best known of all spectrum lines, provides a complete and unmistakable identification. They are rarely absent from any spectrum owing to the ubiquity of Na, and some enhancement of strength is necessary before Na can be declared present in the specimen under test. The ultra-violet pair, though considerably less sensitive, is nevertheless a good criterion. Two lines of a very sensitive Zn multiplet are very close to it, at 3302·941, 3302·588, but these will not appear unless the Zn line 3345·020 at least is also present and stronger. After the Na lines have been seen a few times, however, there is little chance of their being mistaken.

Niobium (Nb)

The *raies ultimes* are all contained in a single large multiplet (in technical terms, a "sextet DF combination"), containing fourteen lines. They are.

4217·945	(3)	2–1
4214·733	(1)	
4205·311	(2)	
4195·094	(0)	
4168·126	(5)	
4164·660	(6)	
4163·657	(5)	
4152·576	(7)	
4139·707	(7)	
4137·095	(4)	
4123·810	(7)	
4100·923	(8)	
4079·729	(9)	
4058·938	(10)	

Unfortunately these lines (except the first, which is insensitive) are all liable to be obscured by the CN band if there is a scarcity of material. In that case Cu poles should be used. The chief lines are not liable to be confused with others if reasonable care is taken.

Nickel (Ni)

The multiplets containing the *raies ultimes* are·

3722·484	(2)	2A–1	3515·054	(9)	2B–1
3610·462	(5)		3458·474	(8)	
3597·705	(4)		3433·558	(6)	
3524·541	(10)		3414·765	(10)	
3510·338	(7)		3361·556	(4)	
3492·956	(9)		3286·946	(1)	

There is little to choose between the groups, but 3414 is probably the most sensitive line. It often appears as an impurity in the Fe spectrum, as does also 3524, and this makes identification easy and certain. This element offers little difficulty.

Osmium (Os)

The spectrum of this element has been insufficiently analysed for complete multiplets to be given. Harrison's and Hilger's lists are consistent and the chief lines are repeated here for convenience:

4420·468	(6)
3267·945	(8)
3262·290	(6)
3058·66	(8)
2909·061	(10)
2488·548	(7)

2909 is the most sensitive line, but Os is a difficult element in a complex source, like a mineral specimen, because its chief *raies ultimes* are very close to strong lines of other elements. Cr (2909·052), as well as V (2908·817) with small dispersion, detracts from the value of the best line, while V (3267·702) and Sn (3262·328) may rule out two others. Identification may, therefore, in unfavourable cases depend on a balance of evidence or on large dispersion and accurate measurement. Fortunately the element is only of rare occurrence.

Phosphorus (P)

The *raies ultimes* form a single multiplet, the sensitivity of the lines being in the order of their intensity. They are:

2554·93	(6)
2553·28	(8)
2535·65	(10)
2534·01	(5)

The strongest line might be mistaken at a casual glance for Hg 2536·519, since the Fe spectrum in this region is very difficult to recognise, but the dispersion of most instruments is high at these wave-lengths and a rough measurement will settle the matter. Except for the weakest concentrations of P, the symmetrical character of the group makes it unmistakable.

Lead (Pb)

The sufficient *raies ultimes* are contained in a single multiplet, namely:

$$\left.\begin{array}{ll} 4057{\cdot}820 & (10) \\ 3683{\cdot}471 & (7) \\ 3639{\cdot}580 & (8) \\ 2833{\cdot}069 & (7) \end{array}\right\} 2\text{–}1$$

4057 is undoubtedly the most sensitive line and with the smallest quantities of Pb may appear alone. It has, however, some disadvantages, being situated in the tail of the CN band with head at 4215 and having some neighbouring lines that might be mistaken for it. For this reason I have always looked first for 2833, which is very sensitive, easily located and unmistakable. It is rarely necessary to look further if Pb is present.

Palladium (Pd)

The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{l} 3332{\cdot}291\ (2)\\ 3799{\cdot}190\ (2)\\ 3634{\cdot}695\ (7)\\ 3571{\cdot}155\ (3)\\ 3516{\cdot}948\ (5)\end{array}\right\}\text{2A–1}\qquad\qquad \left.\begin{array}{ll} 3609{\cdot}548 & (6)\\ 3481{\cdot}152 & (4)\\ 3460{\cdot}774 & (3)\\ 3404{\cdot}580 & (10)\\ 3218{\cdot}974 & (1)\end{array}\right\}\text{2B–1}$$

The most sensitive line is probably 3404, in spite of its belonging to what would normally be the less sensitive group. There is so little difference, however, in the energy necessary to excite the groups (as is shown by their proximity in the spectrum, the lower level being the same for both), that they may be considered almost as a single group for this purpose. The position of Fe, 3404·359, helps to distinguish the Pd line at sight from the sensitive Co line at 3405·120 and the Cd line at 3403·653, and the Fe spectrum is also the best safeguard against confusing Pd, 3634·7, with the Ti line at 3635·463 (which is bound to appear with graphite poles containing Ti) and Pd, 3609·5, with Ni, 3610·462, and Cd, 3610·510. It should be noted that 3481·152 is practically coincident with the sensitive ZrII line at 3481·146, and should therefore be used with care.

Platinum (Pt)

This element, like Ir and Os, has a complex spectrum of which no complete analysis has been made. The two most sensitive lines are.

3064·712 (10)
2659·454 (10)

Of these the former is probably the more sensitive, but it has a close neighbour in the strong Ni line at 3064·623. 2659, however, in a region where the dispersion is fairly large, is not likely to be mistaken.

Rubidium (Rb)

The multiplets constituting the *raies ultimes* are:

$$\left.\begin{array}{ll} 7947{\cdot}60 & (9)\\ 7800{\cdot}227 & (10)\end{array}\right\}\text{2–1}\qquad\qquad \left.\begin{array}{ll} 4215{\cdot}556 & (5)\\ 4201{\cdot}851 & (6)\end{array}\right\}\text{3–1}$$

As with Cs, the infra-red pair is the more sensitive and Rb should never be marked absent until it has been looked for. It is of special importance with Rb because of the inconvenient situation of the violet pair. 4215 is right at the head of a strong CN band and 4201 also is likely to be lost in the same band unless the line is strong or the CN bands have been almost entirely eliminated. In addition, 4215 is almost coincident with the frequently occurring *raie ultime* of Sr, 4215·524. Rb is rarely strong enough for any other lines to appear, so that an infra-red investigation is almost always a necessity when looking for it. The pair in that region, however, is unmistakable if present.

Rhenium (Re)

The multiplets containing the *raies ultimes* are:

3464 722	(9)	2A–1	5275·53	(8)	2B–1
3460·47	(10)		4889·17	(10)	
3451 808	(8)				

3460 is the most sensitive line, though not always the strongest. Measurement may be necessary to distinguish it from Pd, 3460 774, and Mn, 3460 328, if those substances are present, since there are no very close Fe lines to facilitate identification at sight. 4889 is well isolated, as is 5275 except in the unlikely event of Cr being strong enough to show a close triplet in the midst of which it is situated.

Rhodium (Rh)

The multiplets containing the *raies ultimes* are:

4084 285	(1)	2A–1	3700 909	(5)	2B–1
3913·513	(2)		3507 316	(6)	
3806 758	(3)		3502 524	(7)	
3713 429	(2)		3474 780	(6)	
3692 357	(10)		3434 898	(10)	
3657·987	(9)		3380·636	(2)	
3612 470	(7)		3372·254	(5)	
3596·194	(8)		3254 97	(1)	
			3214·325	(4)	

The weakest lines of these multiplets will, however, not appear unless Rh is present in fair strength. 3435 is the most sensitive line: a not very strong line of Mo at 3434·79 should not be overlooked when testing for it, but the danger of confusion is not great. 3692 is close to a strong V line at 3692·225, which will probably appear with graphite poles, and 3658 is near a line of Ti at 3658·100, which also may appear in the same circumstances. Usually, however, 3435 affords sufficient identification.

Ruthenium (Ru)

The multiplets containing the chief *raies ultimes* are:

3901·242	(4)	2A–1	3596·179	(8)	2B–1
3856·459	(3)		3593·022	(8)	
3819·033	(4)		3589·215	(4)	
3798·052	(3)		3539·369	(3)	
3760·031	(4)		3514·488	(2)	
3742·280	(7)		3498·942	(10)	
3730·433	(4)		3483·292	(3)	
3728·030	(8)		3463·144	(2)	
3726·926	(8)		3436·737	(9)	
3705·357	(2)		3406·591	(1)	
3657·173	(2)		3344·532	(2)	
3609·107	(2)		3301·587	(5)	

As with Rh, the weaker lines are usually not to be expected. The 2B–1 group is slightly the more sensitive and 3499 is the most persistent line. It is well isolated and easily located, the most probable, but very rarely occurring, source of confusion being Rh, 3498·730, which appears when Rh is present in moderate strength. 3437 is easily distinguishable from Ni, 3437·280 and Ir, 3437·015, though measurement may be necessary. The pair at 3727, 3728, should be readily recognisable if the CN band does not obscure it, though with graphite poles one should be careful of the V lines 3728·341, 3727·345.

Antimony (Sb)

The multiplets containing the *raies ultimes* are.

2311·469	(8)	2A–1A	2598·062	(8)	2B–1B
2175·890	(9)		2528·535	(8)	
2068·38	(10)		2445·515	(4)	

2877·915	(7)	2A–1B	3504·469	(1)	2B–1C
2769·939	(6)		3267·502	(5)	
2670·643	(4)		3232·499	(4)	
2598·062	(8)		3029·807	(2)	
2510·529	(2)				

The structure of the spectrum is identical with that of As and corresponding levels are given the same symbols. In Sb, however, the most sensitive group, 2A–1A, which with As was out of range, is accessible but it is in a region of low and variable plate sensitivity, with the result that the theoretically weakest line of the multiplet often appears as the strongest. This is probably the last line to disappear with small amounts, although Hilger, doubtless because of the peculiarities of plate mentioned on p. 52, gives three lines as having greater intensity. It will be noticed that 2598 appears in two groups, 2A–1B, and 2B–1B. This gives it abnormal strength. The coincidence is, in fact, almost exact, the interval between the two lines which occur there being only 0·01A, which is unresolvable on any instrument normally used for this work.

Near 2068 are moderately sensitive lines of Sn (2068·5), Ge (2068·65) and Pd (2068·80)—all elements whose presence is easy to test by other lines: the Ge line, for instance, will not be present unless 2094·23, in the same multiplet, is present in greater strength. 2175 is close to Pb (2175·579) and 2311 is between a pair of Ni lines at 2312·34 and 2310·965, of which the latter is the stronger. In the 2A–1B group, 2769 is almost coincident with a sensitive Cr line at 2769·915, while 2670 is close to a Zn line at 2670·530 which, however, though strong, is the weakest line of a triplet whose stronger lines at 2712·488 and 2684·161 must certainly be present if the line at 2670 is due to Zn. The line of Au at 2510·49 might be mistaken for an Sb line if Au is present in moderate strength, but I have never been in danger of the error. In the 2B–1B group, however, 2528 is very commonly masked by the strong Si line, 2528·516, one of a group of six lines, very likely to be present with carbon poles, which one very soon learns to recognise as a group. This often makes the line useless as a criterion for Sb. In the 2B–1C group, a line of V II at 3267·702 will probably appear if the graphite electrodes contain V. A broad, generally reversed Li line at 3232·61 might be mentioned, though it is hardly likely to be mistaken for Sb, nor is the Cr line at 3030·245, since it is on the opposite side of the prominent Fe line 3030·149, from the Sb line.

Scandium (Sc)

The multiplets containing the *raies ultimes* are:

3933·381	(2)	2A–1A
3911·810	(9)	
3907·476	(7)	
4047·792	(3)	2B–1A
4023·688	(9)	
4020·399	(7)	
3996·607	(4)	

5741·36	(1)	3–1B
5739·30	(2)	
5724·073	(3)	
5717·246	(3)	
5711·754	(8)	
5708·600	(3)	
5700·230	(8)	
5686·826	(9)	
5671·805	(10)	

The most sensitive lines are the two strongest pairs from the first two of these multiplets. They are not far apart in the spectrum and form an easily recognised set of 4. The third group, 3–1B, is given because, if present, it is sometimes an even readier means of identification, the four strongest lines (the others are not likely to appear) standing out apparently as a regular series converging towards the red. The strongest line of this group is given by Miss Moore * as the *raie ultime*, but it is certainly not so persistent under ordinary conditions as the violet lines. I have obtained plates on which the latter are really strong, without any trace of the 3–1B group.

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* *A Multiplet Table of Astrophysical Interest* (Princeton University Observatory, 1945).

Selenium (Se)

This is not usually considered a spectroscopic element, and one would not normally adopt a spectrographic method for its detection. Very few lines appear in the arc, but several occur in the spark, though their strength with small amounts is probably vanishingly small. Apart from plate sensitivity the lines in the extreme ultra-violet in Harrison's list (which, together with the strongest of all, at 1960 26 in air, form a triplet) should form the best criterion, but the region is difficult and the blue lines are probably better for practical purposes. The absence of spectrographic evidence of Se, however, should never be taken as a sure indication of its absence.

Silicon (Si)

Si is one of the commonest elements and is detected without the slightest difficulty. Cu poles are necessary if the Si content of the specimen is small, since graphite poles invariably contain Si as an impurity. The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{ll} 2528{\cdot}516 & (9) \\ 2524{\cdot}118 & (8) \\ 2519\ 207 & (7) \\ 2516{\cdot}123 & (10) \\ 2514\ 331 & (6) \\ 2506\ 899 & (9) \end{array}\right\}\text{2A–1A} \qquad 2881{\cdot}578\ (10)\quad \text{2B–1B}$$

2881 is the most sensitive line: it appears with even the smallest trace of Si. Usually, however, the 2A–1A group also appears and is immediately recognisable.

Tin (Sn)

The multiplets containing the *raies ultimes* are:

$$\left.\begin{array}{ll} 3175{\cdot}019 & (9) \\ 3034{\cdot}121 & (9) \\ 3009{\cdot}147 & (8) \\ 2863\ 327 & (10) \\ 2839\ 989 & (9) \\ 2706{\cdot}510 & (9) \end{array}\right\}\text{2A–1A} \qquad \begin{array}{ll} 3262{\cdot}328\ (8) & \text{2B–1B} \\ 4524\ 741\ (8) & \text{2B–1C} \end{array}$$

Sn has several lines of almost equal strength and sensitivity; it is consequently an easy element to identify. 2840 is generally sufficient: it is easy to locate and is unlikely to be mistaken.

Strontium (Sr)

Like the other alkaline earths, Sr can be identified almost equally well in the arc by the neutral or ionised atoms. The multiplets containing the *raies ultimes* are:

$$4607{\cdot}331\ (10)\quad \text{2B–1} \qquad \left.\begin{array}{ll} 4215{\cdot}524 & (9) \\ 4077{\cdot}714 & (10) \end{array}\right\}\text{2–1 Sr II}$$

4215 is often of little use since it occurs at the head of a strong CN band and is almost coincident with the *raie ultime* of Rb, 4215·556. Whether 4607 or 4077 is the more sensitive line depends on the conditions in the arc. The latter has the advantage in regard to plate sensitivity, but if the degree of ionisation is not large, 4607 may nevertheless be more persistent. It is free from sources of confusion (except in the unlikely event of Nb being strong enough to show 4606·766, in which case measurement may be necessary, though the proximity of the Fe line, 4607 654, usually settles the matter). If the CN band is strong and Sr weak, 4077 as well as 4215 may be lost in it, and the possible though unlikely presence of Y, 4077 366, should not be forgotten. In the normal case, however, both 4607 and 4077 will be strong enough to show unmistakably.

Tantalum (Ta)

The arc spectrum of Ta has not been analysed sufficiently for multiplets to be given Harrison and Hilger show unusual disagreement in their lists, Harrison giving as the most sensitive line 3311·162, while Hilger gives 2714 674, which is not given as a *raie ultime* by Harrison at all. My experience is that Hilger is correct; I have observed 2714 well above the minimum visible intensity when 3311 has been quite undetectable. (See, for example, Plates VII and VIII, where several lines of Ta appear, but not 3311.) It may be noted that Kiess and Stowell * include 2714 among a group of lines shown in absorption in the under-water spark which, they say, are associated with the ground state of the atom. Measurement may be necessary to distinguish it from Os, 2714 642, if that element should be prominent, with a Fe comparison spectrum there are no other lines with which it may be confused at sight.

Tellurium (Te)

This element, like Se, has few lines in the arc and is not well represented in the spark when in small quantity. The pair at 2383, 2385, given by Harrison, might be looked for, but their absence should not be taken as evidence that small amounts of Te are not present.

Titanium (Ti)

Ti is usually present in graphite, and Cu or other poles must therefore be used for its detection. It shows many lines of the ionised atom (Ti II) in the arc, and their strength relative to that of the lines of the neutral atom (Ti I) is very sensitive to the excitation conditions. This may partly, though not entirely, account for the fact that the line 4981·733, given by Harrison as the most sensitive line of Ti I, does not

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* *Bur. Stand. Journ Res.*, Washington, 12, 459 (1934).

appear in Hilger's rather long list, which includes lines of both Ti I and Ti II. Apart from plate sensitivity, the most sensitive lines of Ti I are in the infra-red; and in the more accessible regions of the spectrum there are several multiplets whose chief lines are almost equally sensitive. There is little point, therefore, in listing them. For the ionised atom, however, the most sensitive multiplet is undoubtedly 2–1, which is given below:

3409·809 (2)
3407·205 (1)
3394·575 (5)
3387·837 (6)
3383·761 (9) } 2A–1A Ti II
3380·280 (4)
3372·800 (8)
3361·213 (9)
3349·406 (10)

Harrison has, apparently through a confusion of neighbouring strong lines, given 3349·035 instead of 3349·406 as the most sensitive line. Both are persistent, but the former belongs to another multiplet of which both the initial and final levels are higher than those for the multiplet given above. The only line with which, Nb being absent and reasonable care being taken, the more sensitive of these lines can be confused is the other, so the practical difference is slight. Usually, however, it is the neutral atom that constitutes the best criterion, and unless Na is overwhelmingly strong, 4981 is recommended as the first choice, but occasions are very rare on which one is reduced to a decision by a single line.

Thallium (Tl)

Tl has the same sensitive groups as Al, Ga and In. They are:

5350·46 (10) } 2–1
3775·72 (9)

3529·43 (3)
3519·24 (8) } 3–1
2767·87 (7)

5350, the visible green line from which Tl gets its name, is a sufficient check, and the others would scarcely be necessary if it were not for the weak sensitivity of most plates in this region. It is situated, however, in an empty part of the Fe spectrum, and with the small dispersion common in this region measurement is sometimes necessary to distinguish it from the strong Ca line at 5349·474 which frequently occurs. 3775, on the other hand, is very liable to be lost in the backwash of the strong CN band with head at 3883. 3519 is close to sensitive lines of Zr (3519·605), Ni (3519·766) and Co (3520·081), and there is no Fe line conveniently situated to distinguish the line at sight. 3529 also has two close neighbours of Co (3529·813, 3529·033).

Vanadium (V)

Like Ti, V is usually present in graphite poles, and shows many lines of both neutral and ionised atoms, the relative strengths of which vary considerably with the excitation conditions. There is here, however, no ambiguity about the most persistent line, namely, 4379. It stands at the end of a characteristic group which one soon learns to recognise at sight by its set of five or six almost equidistant lines overlapping the well-known Fe triplet near 4400. The full multiplet is given below for completeness, but the first four lines, weaker than the rest and standing somewhat apart, are quite superfluous for identification. There is no line which can easily be confused with 4379, but the group as a whole is, except with the most minute amounts, the immediate and unmistakable criterion. In the ultra-violet the little "triplet" around 3184 is an easily recognised and very useful criterion and, though less sensitive than the blue group, is often a more convenient means of identification. It is included on this account. It is part of a larger multiplet containing nine lines in all, but the others are unnecessary. It may be noted that the middle line is a blend of two, whose wave-lengths are practically identical, and it is abnormally strong on that account:

4429·796 (1)
4426·005 (2)
4421·573 (2)
4416·474 (2)
4408·511 (7)
4408·204 (5)
4407·637 (5) 2–1B
4406·641 (6)
4400·575 (4)
4395·228 (6)
4389·974 (8)
4384·722 (9)
4379·238 (10)

3185·396 (8)
3183·982 (8) 3–1A
3183·406 (7)

If the excitation in the arc is strong—as, for instance, with slightly impure graphite poles without any added salt—V II may be more prominent than V I, and the line at 3093·108 becomes important. It is, however, very close to strong lines of Al and Mg, and on this account the chief lines of the large multiplet to which it belongs are given below. Some of these also are liable to be mistaken, and evidence often rests on the group rather than on individual lines. It is, however, only very rarely that one has to depend on the ionised atom.

3125·284 (6)
3118·383 (7)
3110·706 (8) 2–1 V II
3102·299 (9)
3093·108 (10)

Tungsten (W)

The multiplets containing the *raies ultimes* are:

4294·614	(9)	2–1	4757·549	(3)	2–1
4074·364	(6)		4302·108	(6)	
4008·753	(10)		3867·975	(4)	

Harrison gives 4302 as the most persistent line, but this is not recorded at all by Hilger, who chooses 4008. On theoretical grounds one would expect 4008 to be correct; the spectrum is complex and it is not possible to make the usual classification of the upper states into sub-levels; I have, therefore, recorded both multiplets as 2–1 without giving an order of priority. W is a difficult element in small traces because both lines are very liable to be obscured—4008 by Ti (4008·928) and 4302 by Ca (4302·527). In addition, if CN is strong and W weak, 4008 is apt to be missed in the tail of the 4215 band. It is, therefore, often advisable to look for W with Cu poles and to depend on 4008, for there is much less chance of Ti than Ca being present in the substance under examination. 4294, if present, is sufficient evidence of W, but it is less sensitive than the other lines.

Yttrium (Y)

Harrison and Hilger are greatly at variance with respect to this element, since the most sensitive line given by each is not given at all by the other, while Miss Moore * gives yet a third line, 5466·472, as the *raie ultime*. The element is chemically analogous to Sc and there is a somewhat similar discordance in the data for that element. Plate characteristics may account for the ignoring of 5466 by Harrison and Hilger The multiplets are given below for all three lines·

5740·22	(1)	3–1B			
5726·88	(0)		4760·971	(5)	2A–1A
5675·263	(2)		4674·848	(9)	
5644·680	(3)		4643·695	(10)	
5630·123	(7)				
5606·828	(3)		4167·507	(5)	2B–1A
5581·868	(8)		4102·376	(10)	
5527·540	(9)		4077·366	(9)	
5466·472	(10)				

Only the four strongest lines of the 3–1B group need be expected unless Y is very abundant, which it scarcely ever is. The strongest lines of each group should be looked for first, and the greater sensitivity of the plate in the region of the 2B–1A group should be borne in mind. 5466 and 4643 are readily located by their proximity to the Fe lines, 5466·407 and 4643·475. 4102 has to compete with the CN band and with the neighbouring line of V, 4102·159, making it often less useful than the others when graphite poles are used; and its companion, 4077, is

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* *Loc. cit.*

inconveniently close to the strong and frequently occurring SrII line, 4077·714. There is a close parallel between the lines of Sc and those of Y, and, with a given instrument and under the same conditions, the relative strengths of the groups are likely to be the same.

Ytterbium (Yb)

This element, although included among the rare earths, has a relatively simple spectrum. The multiplets containing the *raies ultimes* are:

$$3987\ 994\ (10)\quad 2\text{–}1 \qquad\qquad \left.\begin{array}{l} 3694\ 203\ (8)\\ 3289{\cdot}37\ \ (8)\end{array}\right\}2\text{–}1\quad \mathrm{Yb\,II}$$

3987 is generally the most satisfactory line. It is in a convenient part of the spectrum, where the plate sensitivity is high and there are no close lines likely to occur with which it could be confused. 3694 is rather close to Ti, 3694·447, and 3289 to Rh, 3289·138, which, however, is rarely seen Unless these lines of YbII are extremely faint, one should not appear without the other, as the theoretical order of intensity appears to be counterbalanced by variations of plate sensitivity.

Zinc (Zn)

The multiplets containing the *raies ultimes* are:

$$2138\ 56\ (8)\quad 2B\text{–}1 \qquad \left.\begin{array}{ll} 4810\ 534 & (10)\\ 4722{\cdot}159 & (9)\\ 4680{\cdot}138 & (8)\end{array}\right\}3\text{–}2A \qquad \left.\begin{array}{ll} 3345{\cdot}934 & (3)\\ 3345{\cdot}572 & (6)\\ 3345\ 020 & (10)\\ 3302{\cdot}941 & (6)\\ 3302\ 588 & (9)\\ 3282\ 333 & (8)\end{array}\right\}4\text{–}2A$$

When Zn is present in strength the blue triplet stands out visibly and may be recognised without a photograph In traces, however, the choice between it and 2138 is largely a matter of plate sensitivity. 2138, for all but the smallest concentrations, usually appears as a reversed line. Many instruments need special adjustment to reach this region and in these circumstances the blue triplet becomes the first choice. Its identification needs some care. 4810 occurs in a rather wide gap in the Fe spectrum, and since the dispersion is comparatively small in this region it may easily be confused at sight with the strong Sr line, 4811·881, particularly since the next line of the triplet is close to the related Sr line, 4722 278. It is for this reason that the ultraviolet group, 4–2A, has been given also. The three lines at 3345 may be imperfectly resolved and appear as a broad line, which should then be immediately identifiable. The two lines at 3302, however, fall very close to the strong frequently occurring Na pair in that region and are of little use for quick identification. 3282 presents no difficulty but may be too weak to appear.

Zirconium (Zr)

This element is chemically similar to Ti and the spectrum structures also are similar. Numerous lines of both ZrI and ZrII appear in the arc, their relative strengths depending on the conditions. Hilger's list of *raies ultimes* contains only ZrII lines, and Harrison, who gives lines of both spectra, omits the group which Kiess and Kiess * cite as containing the true *raies ultimes*. This group is included as 2A–1A below. Kiess and Kiess point out that although, when Zr is present in fair strength, the lines of this group are definitely weaker than those of the groups 2B–1B and 2C–1A, they become relatively stronger when Zr is reduced to a trace, and ultimately remain alone. Nevertheless, Miss Moore † gives 4687·803 as the *raie ultime*. In the normal case, however, if Zr is indicated at all it shows many lines. No universal rule can be given for determining the most persistent line in all circumstances. The group to be looked for first may, therefore, be that which occurs in the region most convenient to examine. It will be noticed that the four multiplets given below consist of two overlapping pairs, this simplifies the search. In particular the strongest lines of the first two groups, near 4688, form a close pair whose presence is sufficient evidence for Zr. The line at 3481·146 (ZrII), given as a *raie ultime* by Hilger, is unresolvable from Pd, 3481·152, and is therefore useless if Pd is present.

4851·363	(0)	2A–1A
4782·599	(2)	
4698·14	(1)	
4688·448	(8)	
4633·985	(8)	
4575·515	(7)	

4905·083	(0)	2B–1B
4893·121	(0)	
4887·72	(0)	
4851·363	(2)	
4824·288	(2)	
4815·629	(7)	
4805·870	(3)	
4788·669	(1)	
4772·312	(8)	
4739·478	(9)	
4710·075	(9)	
4687·803	(10)	

3680·374	(1)	2C–1A
3634·151	(4)	
3601·193	(10)	
3591·725	(2)	
3547·682	(8)	
3519·605	(9)	

3672·665	(0)	2–1 ZrII
3613·100	(3)	
3572·473	(7)	
3551·951	(5)	
3505·669	(3)	
3496·210	(9)	
3438·230	(10)	
3391·975	(10)	

Radio-active Elements and Rare Earths. The spectra of these elements, even in small concentrations, contain so many lines that the ordinary technique of identifying them by means of *raies ultimes* is not recommended. If one of them is suspected, the best procedure is to take a comparison spectrum of a simple substance, such as a Na or Mg salt, containing a trace of the element in question, and to look for coincidences. A sequence of four adjacent spectra in the order, Na

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* *Bur. Stand Journ Res*, Washington, 6, 667 (1931).

† *Loc. cit.*

salt; Na salt+trace of suspected substance; substance under examination; Fe arc, should be taken, thus enabling the lines of the suspected substance to be at once recognised and their occurrence in the specimen tested. If several rare earths are present—as, from the difficulty of separating them, may easily be the case—Harrison's lists of *raies ultimes* may be used, but it is always advisable to confirm the results by a comparison spectrum because the lines are so numerous that the danger of wrong identification is exceptionally great. Moreover, Harrison's lists include lines of the ionised atoms, which may not be the best criteria when the degree of excitation is low. Plates VII and VIII afford an example of this. As Table VIII shows, 34 Th lines appear, identified by the method just described, but Harrison's *raies ultimes* are not included among them.

General Conclusion. The general conclusion to be drawn from the last two chapters is that qualitative spectrum analysis is a convenient, sensitive and, when properly applied, trustworthy method of determining most of the elements present in a specimen of material, but that it is no method for the careless or inexperienced. This needs particular emphasis because it is often applied without adequate precautions, and results are announced as established which in fact are incorrect. It is no exaggeration to say that in my experience more than half of the spectrographic analyses which have been published during the last thirty years are untrustworthy By far the commonest error is the announcement of absent elements as present; it is comparatively rare for an element to be missed. Only after the strictest attention to details—which, so far as I know them, are given here—is it possible to say with confidence that the results obtained are accurate.

CHAPTER

8

QUANTITATIVE SPECTRUM ANALYSIS

THE SOLUTION OF THE GENERAL PROBLEM of quantitative spectrum analysis is still only at its beginning, although numerous attempts, extending over many years, have been made to devise a practicable method. Several characteristics of the spectrum of a substance are affected by the amount of that substance in the source of light. For instance, the intensity, breadth, and number of the lines, the appearance of some of them as reversed lines or otherwise, as well as the effect of an easily ionised element on the relative strengths of neutral and enhanced lines of other elements in the source (see, for example, p. 88), are all criteria which, in theory, may be used to give a measure of the amount of a particular constituent in a mixture. The difficulty is that so many other factors intervene that a direct correlation between any of these effects and the amount of the substance causing it has so far not been obtained in the most general case. In special cases, however (e g. when the problem is to determine the variations of a minor constituent in a substance of otherwise constant composition), sufficient accuracy and trustworthiness can be attained for many purposes, and the speed of the spectrographic method, especially for routine work, then gives it a great advantage over chemical processes.

The effect used in all practicable methods up to the present is the strength of the lines. The general procedure is to obtain a set of standard spectra of mixtures containing various known amounts of the substance under test. The spectra will show the lines of that substance varying in strength, while the lines of the main constituents appear constant in strength. (See, for example, Plate XVIIIA.) The spectrum of the specimen under test is then compared with this standard set and the amount of the substance of interest is determined by seeing which of the set it matches. This procedure is particularly applicable to metallurgical work, in which the electrodes are themselves rods of the metal under examination. Provided that the minor constituent is uniformly distributed throughout the rods, either arc or spark spectra may be used, but if it is distributed in scattered, small pieces, the arc is necessary to give trustworthy average results.

In this process all the conditions—state of adjustment of spectrograph, character and arrangement of light source, kind of photographic plate, time of exposure, etc.—must be kept as constant as possible so that variations in the relative strengths of the lines can arise only from differences in the amount of the substance concerned. Also it is advisable that the comparison should normally be made between two particular lines, one for each element, and that these should be as near together as possible in the spectrum, since the properties of the photographic plate vary with wave-length. A variation of the method which has sometimes been adopted, when the most abundant element present has a large number of lines, is to note which of its lines appears equal in strength to a neighbouring line of the minor constituent for each step in the standard series. Thus, as the percentage of the minor constituent goes up through the series 0·1, 0·2, . . . 0·5, say, its lines a, b, . . . e, may be found respectively equal in strength to the near lines a', b' . . . e' of the major constituent. This has the slight advantage that equality of intensity is rather easier to judge than a particular ratio of unequal intensities, and, moreover, the result is less dependent on accidental variations of time of exposure since, in theory at least, two lines of equal intensity will appear equal whatever the length of exposure. Eye estimates of the intensities are often sufficiently accurate, but the sensitivity of the method sometimes warrants the employment of a microphotometer, of which various types are obtainable.

The General Problem. The foregoing method is obviously purely empirical. When we attempt to extend it to the general case—e.g. to the determination of the percentage of an element Z in any mixture at all—it breaks down. There is, of course, no direct correlation, even in the simplest case, between the spectrum and the amount of a particular substance, but only a correlation between the spectrum and the relative amounts of one substance and another in the specimen. This, however, involves no practical difficulty because we can always add to the specimen a known proportion of some element not already in it, and then, by measuring the amount of the substance of interest with respect to that, deduce its percentage in the original mixture. The difficulty in the general case, however, is that the relative strengths of the lines in question vary so much with the other constituents of the mixture and with the general conditions of excitation that no set of standard spectra, like that in Plate XVIIIA, can be obtained.

In earlier days, when the mechanism of spectrum production was largely unknown, these vagaries had simply to be accepted as insuperable barriers to a general method of quantitative analysis based on line intensities. We know enough now, however, to be able to state precisely all the factors that determine the intensity of a spectrum line, and the problem is then reduced to that of standardising all of them except the one which we want to measure, namely, the percentage of the constituent in question in the source of light. In Fig. 36 a table is given showing

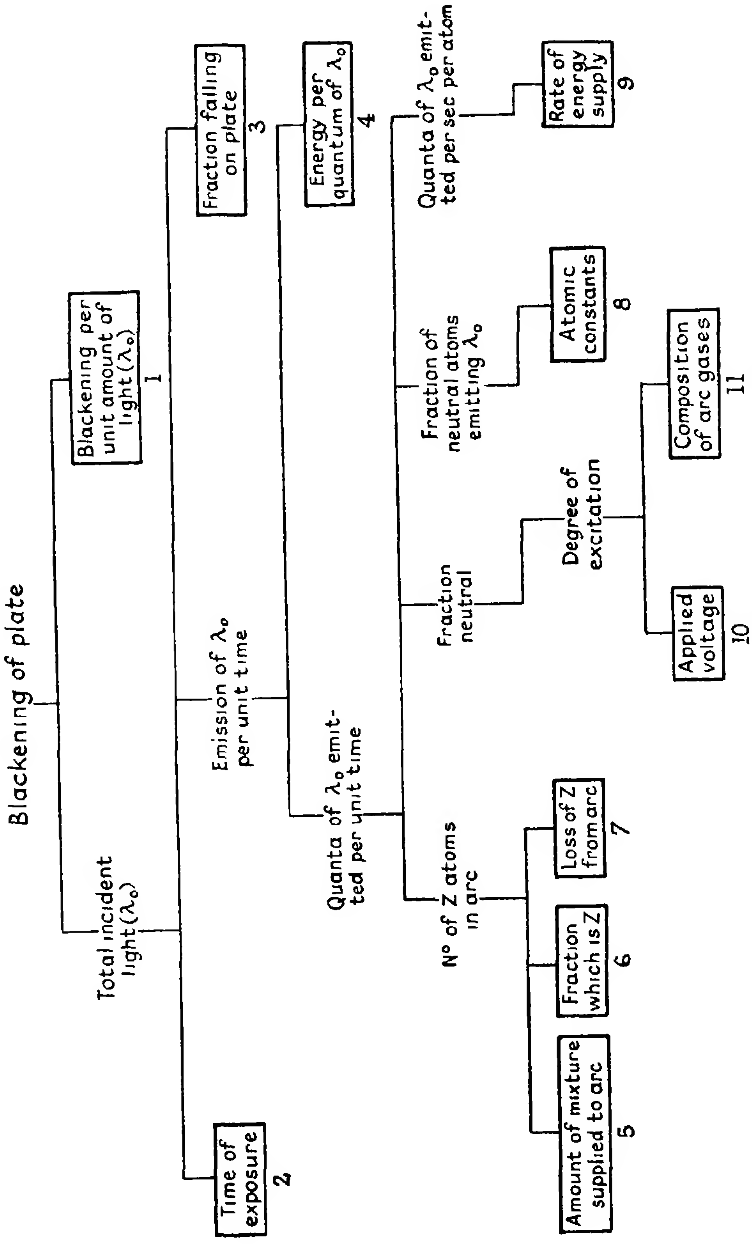

FIG. 36.—Analysis of factors contributing to intensity of photograph of spectrum line.

the various conditions that affect the blackening of the plate, which is the observable phenomenon from which we wish to deduce the percentage of the element present.

The way in which this table has been constructed is as follows. Each entry, beginning with "blackening of plate," is analysed in the line below into all the factors that determine it. The way in which they determine it is immaterial; the essential point is that when they are fixed, their effect is uniquely fixed. Thus, since the blackening of the plate per unit amount of the light in question is a definite quantity, it follows that if the number of such units in the light which has formed the line—i.e. the "total incident light (λ_0)"—is fixed (not necessarily known), the blackening of the plate is uniquely determined. It is not, of course, the product of those two quantities, because the relation between blackening and amount of light is not linear, but that does not matter; if the two factors are fixed, the blackening is fixed. The same is true for each subsequent step in the table, and when a factor is reached which we have a reasonable chance of controlling practically, it is enclosed in a frame. We have then simply to consider the framed factors, and if we can keep them all constant except that (No. 6) which we want to determine, we shall obtain a direct correlation between the blackening of the plate and the percentage of the constituent in the mixture, and the general problem of quantitative analysis will be solved.

Before coming to the practical considerations it is advisable to say a little about the successive steps of the table. Of the first two products of the analysis, the blackening per unit amount of the wave-length in question is framed, since this can be made the subject of an independent investigation. The total amount of the incident light, however, is analysed into the time of exposure, the emission of the wave-length in question in each unit of that time, and the fraction of the amount emitted which falls on the plate. It is obvious that if these are fixed, the total amount of light falling on the plate is fixed. The time of exposure and the fraction of the emitted light which falls on the plate are clearly under our control, and we have, therefore, only to analyse the amount of the wave-length in question emitted per unit time. This is determined by the number of quanta emitted per unit time and the energy in each quantum. The latter is, of course, hn (see p 12), and is, therefore, directly controlled by natural causes, and the former is determined if we fix the number of atoms of the element Z in the arc, the fraction of these which remain neutral (it is assumed here that the line in question is a line of the neutral atom), the fraction of neutral atoms which emit the wave-length in question, and finally, the number of quanta of this wave-length emitted per second per atom. None of these factors can be controlled directly, so we analyse them further, taking them for convenience in the reverse order. The number of quanta of a particular wave-length emitted per second per atom is controllable only if we have a steady source of light. We thus come to our first stipulation for the successful solution of our problem: *the source must be steady,* emitting in each second the same amount of energy as it receives. We can then fix (as already said, we need not determine it) the quantity emitted by fixing the rate of supply of energy to the arc. Next, the fraction of neutral atoms which emit the wave-length in question is a quantity which, for given physical conditions, is determined by the probabilities of transition of the electron from orbit to orbit, and this again is controlled for us by nature. The fraction of the atoms which remain neutral depends on what we may call the "degree of excitation" in the arc; this we must analyse further. Finally, the number of atoms of the element in question in the arc depends on the amount of the mixture which we originally inserted, on the fraction of this mixture which consists of the element, and on the loss of the element from the arc during its running. Each of these factors will call for consideration. We are thus left with the degree of excitation. This I have analysed into "applied voltage" and "composition of arc gases." The effect of the former factor is obvious, and that of the latter may be understood from the consideration, previously mentioned, that the degree to which an element is ionised depends on both the energy available for ionising it and the facilities for recombination of the ions with free electrons. The effect of the general composition of the arc gases is that it influences the number of free electrons (see p. 88).

We have now to consider the eleven factors which have been framed and numbered in the table. Although in principle the table allows us, if we can satisfactorily control these factors, to determine the absolute amount of the element in question introduced into the arc, the procedure for controlling them is simplified if we consider two elements with lines of roughly equal intensity close together in the spectrum, and determine the ratio of the amounts of these elements. As has been explained, we can easily convert this to absolute measure by making one of the elements a voluntary addition in known proportion. In that case, factor No. 1 becomes entirely a matter of plate characteristics. Unit amount of light of each of the wave-lengths will blacken the plate by the same amount, and although this amount varies as the exposure proceeds, it will vary similarly for each wave-length. We can therefore control factor No. 1 by always using the same type of plate.

Factor No. 2 (time of exposure) can be standardised at whatever value we find convenient. No. 3, the fraction of the emitted light which falls on the plate, is entirely a matter of geometry. With the same spectrograph and the same condensing lens kept at a fixed position, this fraction is fixed. No. 4, the energy per quantum, as has already been remarked, is fixed by nature, as is also No. 8. We can easily standardise No. 5, making it low enough to include the smallest amounts of substance which we are likely to have to deal with, and Nos. 9 and 10 also are obviously easy to control. This leaves Nos. 6, 7 and 11. Of these 6 is what we want to determine, and we are therefore left with the two most troublesome factors, 7 and 11, to consider.

Let us take 11 first. Strictly speaking, of course, the standardisation of this factor is impossible, because it is of the essence of our problem that the arc gases shall include whatever substances we are presented with for analysis, and it may therefore vary in any manner whatsoever from specimen to specimen. We can, however, largely overcome this difficulty by making the whole of the specimen we are examining but a small fraction of the complete substance inserted in the arc. For example (a purely imaginary case), we can stipulate that 0·01 gm. of the specimen be taken on every occasion and mixed with 0 5 gm. of NaCl. The effect of variation of the specimen will then be very slight; we shall effectively have an arc of constant composition every time, and the sensitivity of the method is such that the lines we are interested in will usually appear in spite of the smallness of the amount of substance.

No. 7, the loss from the arc, constitutes the most difficult part of the problem. By "loss" is meant any process by which the element in question is prevented from being in a position to radiate the line we are interested in. Thus the substance may pass out into the air, it may combine with another element in the arc or in the air to form a molecule, or it may get into the outer parts of the arc and act in a reverse way by absorbing the light from the centre of the arc. Any of these processes constitutes a loss in the sense implied in the table, and they are all clearly beyond our power to control. It is, however, probable—and this is confirmed by experience--that their effect is fairly small, and that when we are dealing with minor constituents and determining relative instead of absolute amounts, they do not constitute a fatal barrier to a practicable method.

The sort of procedure to which we are led is therefore this. Adopt a standard configuration for the instrument and source of light, a standard photographic plate, time of exposure, and total amount of substance, and a standard current and voltage across the arc. Let the mixture contain one constituent whose relative amount is known, and choose a line of this constituent that is near to, and roughly of the same strength as, a line of the element to be estimated. Maintain a steady arc throughout the exposure, and arrange that the general composition of the arc gases is constant. The ratio of the intensities of the two chosen lines should then depend only on the relative amounts of the corresponding elements in the mixture inserted in the arc.

The Foster Arc. The initial steps in putting this programme into practice have been taken by Foster. He has shown that if graphite poles are used and shaped as shown in Fig. 87, the lower (the anode) being filled with a mixture of powdered graphite and any one of a number of salts (e.g. the chlorides of the alkalis or the alkaline earths), an arc which is very steady can be run for about a minute—giving ample time for the exposure. When the arc is first struck it wanders about the rim of the anode cup until the anode gets hot enough to distil the vapours of the salt upwards into the arc; it then settles down to a very steady state in which the vapour of the salt appears to enter the arc at a uniform rate. When it is exhausted the arc becomes unsteady again. If, then, the mixture under analysis is placed in a thin layer near the centre of the cup, as indicated by the shaded strip in Fig. 87, with the mixture of graphite and salt above and below, the steady state begins before the central layer is hot enough to lose its contents appreciably by evaporation. The exposure can then begin and be continued until the end of the steady state, if necessary, though the mixture will probably all have been evaporated and passed into the arc before that time. In this way the arc is made both steady and approximately of constant general composition, whatever the composition of the specimen.

The arc is rather sensitive to the proportions in which the powdered graphite and the impregnating salt are mixed. Foster recommends deposition of the salt from solution on to the powdered graphite, and subsequent drying. This ensures intimate mixing, but such deposition is not essential if the same degree of uniformity of the mixture can be attained otherwise. From 0·2 to 1·0 c.c. of a solution of 10 gm. NaCl (or chemically equivalent amounts of other metals in their respective salts) in one litre of distilled water was added to 0·09 gm. of powdered graphite in Foster's experiments. More work is needed before the method can be said to be completely satisfactory for all mixtures, but a very promising start has been made on a very complex problem. Foster's paper, appearing in *Proc. Phys. Soc.*, **53**, 594 (1941), should be consulted for details of the dependence of the arc on variations in the conditions.

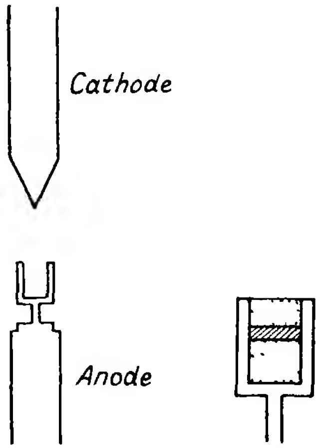

Fig. 37.—The Foster arc for quantitative spectrum analysis

A very convenient and sensitive method of ensuring that a constant degree of excitation has been attained might be mentioned. V and Ti, which show many lines of both neutral and ionised atoms in the arc, are common impurities in graphite, and a close pair of lines of either element, one neutral and one enhanced, shows very readily, by the relative intensities, whether the degree of ionisation is constant or not. In Plate XV, already referred to (p. 88), the lines of neutral and ionised

V at 2923·62 and 2924·64, 2924·02 are shown for three different arcs, one of which contained more Na—and consequently more free electrons—than the others. This, of course, is not a method of *keeping* the degree of excitation constant but of indicating whether it is constant or not.

One result of this work is the possibility of a much more definite determination than has so far been made of the sensitivity of spectrographic analysis. The minimum amount of a substance that can be detected depends so much on the conditions of excitation and the kind and quantity of the other substances that are associated with it that no useful statement can at present be made about it. With the establishment of a standard arc, however, trustworthy figures should be possible. Foster found that the smallest amount of Ag detectable was in the neighbourhood of 10^{-9} gm., and it would be well worth while to make a systematic investigation of the other elements in order to determine the corresponding figure for them.

APPENDIX

Table I

ATOMIC NUMBERS AND WEIGHTS

Atomic No.	Element	Symbol	Atomic Weight	Atomic No	Element	Symbol	Atomic Weight
1	Hydrogen	H	1.008	47	Silver	Ag	107.880
2	Helium	He	4.003	48	Cadmium	Cd	112.41
3	Lithium	Li	6.940	49	Indium	In	114.76
4	Beryllium	Be	9.02	50	Tin	Sn	118.70
5	Boron	B	10.82	51	Antimony	Sb	121.76
6	Carbon	C	12.010	52	Tellurium	Te	127.61
7	Nitrogen	N	14.008	53	Iodine	I	126.92
8	Oxygen	O	16.000	54	Xenon	Xe	131.3
9	Fluorine	F	19.00	55	Caesium	Cs	132.91
10	Neon	Ne	20.183	56	Barium	Ba	137.36
11	Sodium	Na	22.997	57	Lanthanum	La	138.92
12	Magnesium	Mg	24.32	58	Cerium	Ce	140.13
13	Aluminium	Al	26.97	59	Praseodymium	Pr	140.92
14	Silicon	Si	28.06	60	Neodymium	Nd	144.27
15	Phosphorus	P	30.98	61			
16	Sulphur	S	32.066	62	Samarium	Sm	150.43
17	Chlorine	Cl	35.457	63	Europium	Eu	152.0
18	Argon	A	39.944	64	Gadolinium	Gd	156.9
19	Potassium	K	39.096	65	Terbium	Tb	159.2
20	Calcium	Ca	40.08	66	Dysprosium	Dy	162.46
21	Scandium	Sc	45.10	67	Holmium	Ho	164.94
22	Titanium	Ti	47.90	68	Erbium	Er	167.2
23	Vanadium	V	50.95	69	Thulium	Tm	169.4
24	Chromium	Cr	52.01	70	Ytterbium	Yb	173.04
25	Manganese	Mn	54.93	71	Lutecium	Lu	174.99
26	Iron	Fe	55.85	72	Hafnium	Hf	178.6
27	Cobalt	Co	58.94	73	Tantalum	Ta	180.88
28	Nickel	Ni	58.69	74	Tungsten	W	183.92
29	Copper	Cu	63.54	75	Rhenium	Re	186.31
30	Zinc	Zn	65.38	76	Osmium	Os	190.2
31	Gallium	Ga	69.72	77	Iridium	Ir	193.1
32	Germanium	Ge	72.60	78	Platinum	Pt	195.23
33	Arsenic	As	74.91	79	Gold	Au	197.2
34	Selenium	Se	78.96	80	Mercury	Hg	200.61
35	Bromine	Br	79.916	81	Thallium	Tl	204.39
36	Krypton	Kr	83.7	82	Lead	Pb	207.21
37	Rubidium	Rb	85.48	83	Bismuth	Bi	209.00
38	Strontium	Sr	87.63	84	Polonium	Po	
39	Yttrium	Y	88.92	85			
40	Zirconium	Zr	91.22	86	Radon	Rn	222
41	Niobium	Nb	92.91	87			
42	Molybdenum	Mo	95.95	88	Radium	Ra	226.05
43				89	Actinium	Ac	
44	Ruthenium	Ru	101.7	90	Thorium	Th	232.12
45	Rhodium	Rh	102.91	91	Protoactinium	Pa	231
46	Palladium	Pd	106.7	92	Uranium	U	238.07

TABLE II

WAVE-LENGTHS OF IRON ARC LINES, TOGETHER WITH THOSE OF A FEW OTHER LINES FREQUENTLY OCCURRING IN THE IRON ARC SPECTRUM, AS GIVEN BY BURNS (*LICK OBSERVATORY BULLETIN No.* 247, 1913)

λ	Intensity	λ	Intensity	λ	Intensity
8824 254	1	7491 678	2	7189 17	1
8688 040	2	61 584	1	87 349	5
61 920	1	54 02	1	81 93	1
8566 21	2	47 43	1	81 22	2
14 11	2	45 783	1	80 020	1
8468 427	2	43 022	1	76 886	1
8387 785	2	40 98	1	75 937	1
65 59	1	18 680	1	64 480	4
40 06	1	11 196	3	58 502	1
32 01	2	01 707	1	55 64	1
27 080	3	7389 432	3	53 66	5
8264 80	1	86 402	2	51 495	1
48 16	1	82 99	1	45 317	1
47 45	2	75 57	1	42 522	1
32 94	1	53 528	1	32 999	2
32 36	1	51 56	1	30 956	4
20 42	3	51 160	1	12 182	1
07 85	1	33 62	1	07 486	1
8199 00	1	20 72	2	7095 447	2
8085 220	2	11 112	2	90 417	3
46 088	2	07 957	2	86 76	1
28 37	2	06 61	1	83 396	1
7998 98	2	7295 00	1	71 88	1
45 889	2	93 093	3	68 422	3
37 182	2	92 856	1	67 44	1
7882 243	2	88 782	3	60 94	1
7780 594	1	85 286	1	38 818	1
74 22	1	84 853	1	38 271	3
71 99	1	82 39	1	27 60	1
48 289	2	61 54	2	24 649	2
10 40	1	54 649	2	24 084	1
7664 303	2	44 86	2	23 49	1
61 24	1	44 00	1	23 003	8
20 581	1	39 904	2	16 436	3
7586 060	3	28 820	5	16 075	2
83 803	2	23 678	2	11 364	2
68 932	2	22 88	1	10 362	1
46 173	1	21 22	1	08 014	2
41 63	1	19·698	2	00·633	1
31 181	2	12 47	1	6099 928	3
19 84	1	07 430	4	88 541	2
11 059	4	07 128	2	78 864	3
07·31	1	00 19	1	77·445	1
7498 56	1	7195 250	8	76 934	1
95 099	3	94 50	1	76 306	1

λ	Intensity	λ	Intensity	λ	Intensity
6975 46	1	6713 14	3	6451 58	2
71 95	1	10 31	1	50 99	1
60 334	1	05·139	3	38 79	1
51 278	3	03 570	2	36 43	1
47 501	1	6699 14	1	30 859	5
45 215	4	78 001	5	28 80	1
33 632	2	67 73	1	28 079	1
30 64	1	63 452	4	24 000	1
16 710	3	63 26	1	21 361	4
11 52	1	53 88	1	19 988	3
02 80	2	46 98	1	11 674	5
6898 31	1	46 44	1	10 80	1
85 77	3	33 772	3	08 014	4
80 65	1	27 563	3	00 335	2
75 98	1	25 04	1	00 021	5
75 45	1	09 56	1	6393 609	5
62 481	2	09 124	4	92 534	1
61 93	2	08 03	2	87 215	1
60 29	1	05 39	1	85 61	1
58 173	3	04 67	1	83 32	1
57 25	2	6597 607	3	80 751	3
55 74	1	93 881	3	64 717	1
55 183	4	92 928	5	64 384	1
54 82	1	91 32	2	62 889	2
43 685	4	81 22	2	60 44	1
42 668	2	75 028	3	58 684	3
41 302	4	74 238	2	55 038	3
39 828	2	73 10	1	44 159	2
38 86	2	69 233	5	38 896	1
33 24	1	66 80	1	36 844	4
28 614	3	64 30	1	35 341	4
10 28	4	49 23	1	30 86	1
06 859	2	46 251	5	22 696	3
04 27	2	33 97	3	18 027	4
04 020	2	29 04	1	15 814	2
6796 11	2	28 53	1	15 317	3
93 26	1	24 16	1	11 506	1
86 88	2	18 380	3	06 06	1
83 71	1	16 08	1	03 46	1
77 44	1	09 56	1	02 512	3
55 609	2	08 72	1	01 524	5
52 734	3	07 95	1	6297 803	3
50 163	4	01 681	2	95 254	1
45·11	1	6498 950	2	90 968	3
39 54	1	96 462	3	83 05	1
38 08	1	95 796	2	80 622	2
33 171	3	94 993	5	78 56	1
32 06	1	81 881	3	76 958	1
29 02	1	80 45	1	70 229	2
26 668	3	77·36	1	69 72	1
25 39	2	75 685	3	65 145	3
17·556	2	74 61	1	62 75	1
16 24	2	69·216	4	61 018	1
15 410	3	62 787	4	60 56	1
13·76	1	56 89	1	56 371	3

λ	Intensity	λ	Intensity	λ	Intensity
6255·955	1	6102 185	3	5927 798	2
54 266	3	6096 689	1	26 20	1
52 567	4	95 53	1	23 06	1
51 42	1	95 116	1	20 520	2
49 52	1	93 66	1	17 80	1
46 344	4	93 090	1	16 250	3
45 84	1	89 567	1	14 16	6
43 86	1	85 267	1	13 04	1
41 707	1	82 718	1	12 83	2
40 652	2	79 02	1	11 20	1
37 21	1	78 482	3	10 59	1
36 644	1	65 496	4	08 40	1
32 667	2	62 89	1	08 24	2
30 732	5	55 991	3	05 677	2
29 234	1	42 085	2	02 52	1
27 259	1	32 67	1	5895 48	1
26 77	1	27 061	2	83 842	4
21 40	1	24 062	4	80 00	2
20 78	1	21 820	Mn	79·773	2
19 290	3	20 177	2	77 99	2
17 288	1	20 06	2	75 38	1
15 151	2	18 02	1	73 211	2
13 440	3	16 659	Mn	72 918	1
12 04	1	13 518	Mn	71 27	1
10 796	1	08 583	3	71 04	1
09 59	1	07 965	2	69 759	1
08 426	1	05 53	1	62 351	4
07 262	1	05 15	1	59 612	3
03 92	1	03 038	3	59 20	1
00 322	2	5999 950	1	57 134	1
6191 568	5	97 808	1	56 084	2
88 75	1	88 24	1	55 126	1
88 037	2	87 061	2	54 45	1
84 53	1	84 809	3	53 18	1
84 12	1	83 708	2	45 88	2
83 75	1	76 803	2	44 144	1
80 512	1	75 350	2	42 478	2
80 216	2	69 54	2	37 94	1
78 846	2	63 91	1	37 709	1
70 499	2	63 25	1	37 29	1
65 370	2	62 93	1	36 57	1
63 560	1	56 700	3	35 28	1
57 733	2	52 749	4	34·78	1
51 630	2	52 39	1	34 05	1
47 85		49 35	2	32 86	1
44 40	1	46·60	1	32 074	1
37·704	4	40 972	2	31 69	1
37 005	2	39 21	2	30 80	1
36 624	4	38 760	1	30 58	1
34·06	1	38 43	2	29 550	1
27·919	2	37 12	1	28·48	1
16 25	1	34 679	4	26·57	1
12·720	1	33·08	1	25·695	2
09 818	1	31·72	1	24·84	1
03·196	2	30·177	5	16·36	3

λ	Intensity	λ	Intensity	λ	Intensity
5815 16	1	5655 179	2	5497 521	4
14 80	1	53 91	1	94 468	1
11 93	1	52 32	1	93 508	1
09 249	2	50 71	1	87 78	3
06 727	2	50 01	1	87 10	1
04 06	1	49 66	1	83 111	1
5798 194	2	43 99	1	81 454	Mn
96 10	1	41 464	2	81 252	2
95 69	1	38 278	3	80 872	2
93 932	2	37 41	1	78 48	1
93 34	1	36 708	1	76 582	4
91·044	2	35 85	1	76 296	2
89 643	2	33·970	2	73 913	8
85 29	1	30 37	1	72 720	1
84 69	1	24 563	5	66 993	1
82 15	1	24 056	1	66 417	3
80 83	1	21 28	1	64 286	1
80 621	2	20 527	1	63 27	4
78 47	1	19 60	1	62 964	2
75 095	3	18 646	1	55 617	6
63 015	4	15 663	6	55 435	2
62 434	1	13 308	2	46 922	6
60 351	1	02 965	3	45 040	2
56 78	1	02 788	2	36 594	2
54 41	1	00 242	1	34 527	6
53 145	3	5598 306	3	29 701	6
52 035	2	94 661	2	26 367	1
48 64	1	87 582	1	24 057	4
47 95	1	86 772	6	21 543	1
41 861	2	84 768	1	18 842	1
31 775	3	76 106	4	15 189	4
17 848	3	73 10	1	10 900	3
15 107	1	72 857	5	09 125	1
14 155	1	69 631	5	05 780	6
12 150	2	67 401	2	04 131	3
11 867	2	65 703	3	03 823	1
09 895	3	63 609	3	00 504	2
08 109	1	62 712	2	5398 285	1
07 068	1	60 230	1	97 135	6
05 988	2	57 954	1	93 185	4
05 48	1	54 879	3	91 643	1
04 72	1	53 586	1	91 493	1
01·555	3	46 512	1	89 463	2
5693 638	2	43 951	2	86 341	1
91 509	1	43 184	2	83 866	5
86·532	3	38 54	1	79 578	2
86 25	1	35 423	2	73 704	1
79 028	2	32 752	1	71 496	7
77·05	1	25 552	2	69 960	4
67·533	2	22 46	2	67 455	3
62·94	1	12 277	1	65 408	2
62·533	3	06 785	4	64 859	3
58 836	4	05 889	Mn	62 744	1
58·542	1	03 08	1	60 753	1
55·506	2	01 471	4	58 386	2

λ	Intensity	λ	Intensity	λ	Intensity
5343·460	1	5225 583	2	5079 742	3
41 031	5	23 191	1	79 228	3
39 949	8	17 405	4	79 002	1
32 906	2	16 277	5	74·750	2
32 673	1	15 195	4	68 784	4
30 000	2	08 610	4	67·162	1
28 539	4	08 429	Cr	65 201	2
28 044	7	06 040	Cr	65 016	3
26 154	1	04 585	2	51 643	4
24 196	6	02 342	5	49 830	5
23 210	1	5198 843	1	48 454	2
22 049	2	98 717	4	41 763	4
21 106	1	96 100	2	41 079	3
20 048	1	95 472	4	40 902	2
17 394	1	94 950	5	39 266	2
16 620	1	92 361	8	32 846	1
07 362	2	91 475	7	29 623	1
02 315	5	87 922	2	28 135	2
5298 789	1	71 601	7	27 212	1
93 973	1	69 029	2	27 144	2
89·09	1	68 904	3	22 255	4
88 533	2	67 492	8	21 894	1
86 805	1	66 288	3	18 437	2
83 634	7	65 432	2	14 960	4
81 804	5	62 312	5	12 073	4
80 364	1	59 066	2	10 852	1
80 067	1	51 916	3	07 312	2
78 31	1	50 845	4	06 134	5
76 012	1	48 260	2	05 729	4
73 379	2	48 061	2	02 815	2
73 178	3	42 934	3	01 881	5
70 357	8	42 540	3	4994 133	3
69 538	10	41 750	2	91 288	2
68 630	1	39 481	8	88 970	2
66 569	8	39 269	6	85 562	3
63 874	1	37 394	3	85 267	3
63 321	5	33 676	5	83 858	4
59 747	1	31 477	2	83 274	3
59 007	1	27 364	3	82 524	4
54 956	2	25 137	2	78 614	2
53 479	2	23 727	4	73 112	2
51 971	1	22 150	1	72 108	1
50 650	3	21 646	2	70 496	2
50 212	1	15 260	1	69 942	2
47 052	2	10 414	4	68 709	1
43 798	1	09·662	1	67 890	2
42 495	3	07 645	4	66 104	5
36 189	1	07 454	3	57 612	10
35 392	2	06 441	1	57 311	7
32 954	8	05 547	Cu	52 646	1
30 852 (?)	2	5098 706	4	50 121	1
29 84	2	98 594	2	46 401	2
28 408	1	96·992	3	39·689	8
27 187	8	90 787	8	39·253	1
26 876	5	88 344	4	38·828	5

λ	Intensity	λ	Intensity	λ	Intensity
4938 183	1	4799 412	1	4710 283	3
34 023	1	98 736	1	09 091	2
33 348	1	98 269	1	08 972	1
30 331	1	91 250	1	07 485	2
27 875	1	89 655	3	07 287	5
24 775	3	88 761	2	05 460	1
20 521	10	87·84	1	04 955	3
19 008	8	86 810	3	01 051	1
15 605	1	85 963	1	00 201	2
10 567	1	83 434	Mn	4691·416	4
10 325	1	79 438	1	90 145	2
10 032	2	76 34	1	89 497	1
07 745	1	76 075	1	88 208	1
03 325	5	72 818	3	87 394	1
4891 510	9	71 703	1	83 566	2
90 770	7	68 397	1	82 110	1
88 651	7	68 334	1	81 46	1
86 342	1	66 422	Mn	80 475	1
85 443	2	65 863	Mn	80 302	2
82 168	2	65 485	1	79 229	1
81 722	2	62 373	Mn	78 856	5
78 226	5	61 528	Mn	73 171	3
72 154	6	59 98	1	69 184	3
71 333	8	57 581	2	68 153	4
63 655	2	56 10	1	67 460	4
59 757	5	55 86	1	63 185	1
55 688	2	54 047	Mn	61 978	2
54 89	1	51 10	1	61 539	2
48 898	1	49 93	1	57 598	1
45 656	2	45 804	3	54 637	3
44 016	2	45 12	1	54 502	4
43 156	2	41 583	3	47 440	4
42 78	1	41 092	1	46 172	Cr
40 329	1	40 344	1	43 467	3
39 546	2	38 205	1	38 020	4
38 519	2	37 632	1	37 522	4
35 866	2	36 788	5	35 853	2
34 511	1	35 844	2	32 919	3
32 732	2	34 101	1	30 128	3
24 162	1	33 594	3	29 327	1
23 524	Mn	31 488	1	25 061	4
17 784	1	30 90	1	19 295	4
13 11	1	29 699	1	18 763	2
11 04	1	29 016	1	15 568	2
09 94	1	28 549	2	14 214	1
09 14	1	27 464	Mn	13 217	3
08 69	1	27 410	2	11 290	4
08 155	1	26 165	1	07 665	4
07·729	1	25 94	1	05 246	2
04 529	1	21 000	1	04 596	2
02 887	2	14 367	1	03 956	1
01 01	1	14 182	1	02 946	4
00·652	2	14 074	1	02 009	2
00 14	1	12 104	1	00 939	1
4799 891	1	11 478	1	4599 903	2

λ	Intensity	λ	Intensity	λ	Intensity
4598 138	2	4521 841	1	4451 592	Mn
96·062	2	20 238	2	50 324	2
95 368	2	19 578	1	47 727	5
94 959	2	17 530	2	47 137	2
92 658	4	15 337	1	46 853	2
87 186	2	14 190	2	45 476	1
84 826	2	08 287	2	43 199	3
84 732	1	04 846	2	42 838	2
83 843	2	02 592	1	42 349	5
81 529	2	02 219	Mn	41 963	1
80 602	1	4498 903	Mn	40 972	2
79 825	1	95 965	1	40 840	1
79 344	1	95 586	1	40 479	1
74 730	2	95 386	1	39 886	2
74 240	1	94 571	5	39 643	1
68 842	1	92 693	1	38 355	2
68 789	1	90 768	2	36 931	2
66 990	1	90 088	2	36 357	Mn
66 525	2	89 744	3	35 154	2
65 684	2	88 920	2	33 808	2
65 324	2	88 134	2	33 222	2
64 832	1	85 674	2	32 575	2
64 715	1	84 238	3	30 622	4
60 114	2	82 750	2	30 197	2
58 110	1	82 262	4	27 313	5
56 941	1	82 176	3	25 662	1
56 128	3	81 621	2	24 194	1
55 904	1	80 143	2	23 858	2
54 467	1	79 608	2	23 145	1
52 551	2	76 023	7	22 882	1
50 824	2	72 713	2	22 570	4
49 477	2	70 141	Mn	19·534	2
47 855	3	69 390	4	18 432	1
47 027	2	66 939	2	15·127	8
42 720	1	66 557	5	14 739	2
42 422	2	66 183	1	10 717	2
41 332	1	64 773	2	09 908	1
38 764	1	64 684	Mn	09 121	2
37 684	1	62 011	3	08 420	4
33 148	1	61 658	4	07 716	2
31 642	2	61 205	2	04 752	8
31 44	1	61 096	Mn	01 447	2
31 155	5	59 128	5	01 304	3
29 684	2	58 760	1	00 350	1
29 562	1	58 268	Mn	4395 514	1
28 624	7	58 101	2	95 288	2
28·239	2	57 555	Mn	90 957	3
27 796	1	56 904	1	90 460	1
26 567	2	56 335	1	89 251	2
25 875	1	55·827	Mn	88 422	2
25 154	8	55 320	Mn	87·899	2
24 103	2	55·087	2	85 260	1
23·899	2	54 674	1	84·682	1
22 686	1	54 387	3	83 548	10
22·580	1	53·011	Mn	82·777	2

λ	Intensity	λ	Intensity	λ	Intensity
4377 796	1	4286 682	1	4232 724	1
76 782	1	86 440	1	31 700	1
75 934	5	85 832	1	31 525	1
74 495	1	85 448	2	29 752	1
73 568	2	82 406	6	29 515	1
72 994	1	81 096	Mn	27 445	7
71 558	1	79 872	2	26 732	Ca
69 777	3	79 480	1	26 425	2
67 910	1	78 228	1	25·955	2
67 584	2	78 128	1	25·464	4
65 902	1	76 670	1	24 509	2
60 818	1	74 801	2	24 172	3
58 506	2	71 764	8	22 225	5
52 740	4	71 171	7	20 343	2
51 769	Cr	68 752	2	19 364	5
51·553	3	67 831	2	17 559	2
48 946	1	66 968	2	16 185	4
47·854	1	65 918	Mn	15 975	1
47 239	1	65 256	2	15 424	2
46 561	2	64 208	2	13 649	2
44 513	Cr	60 489	10	10 362	6
43 704	2	60 135	2	08 605	2
43 278	2	59 988	2	07 127	2
38 270	2	58 950	1	06 696	2
37 052	5	58 611	1	05 542	2
30 962	1	58 386	1	03 985	3
27 100	2	56 212	2	03 570	1
26 762	2	55 852	1	02 755	1
25 770	9	55 499	1	02 032	7
24 961	1	54 938	1	00 922	2
21·798	2	54 338	2	4199 098	6
15 092	5	50 791	8	98 645	2
11 526	1	50 134	7	98 314	6
10 776	1	48 224	2	98 268	1
09 382	2	47 440	5	96 672	1
09 041	2	46 089	2	96 533	1
07·910	8	45 875	1	96 220	2
05 458	2	45 258	2	95 622	2
04 548	1	44 418	1	95 342	3
02 191	2	43 786	1	94 903	1
00 828	1	43 368	2	91 678	2
4299 254	7	42 728	2	91 446	6
98 043	2	42·588	1	87 812	6
94 939	1	41 112	1	87 052	6
94 132	6	40 370	2	84 894	4
92 293	1	39 846	2	84 491	1
91·472	1	39 728	Mn	83 621	1
90·869	1	38 828	4	83 025	1
90·384	2	38 037	1	82 790	2
89 724	Cr	37·163	2	82 385	2
88·962	1	35·958	8	81·759	6
88·150	2	35 289	Mn	78 868	1
87·579	1	35 143	Mn	78 048	1
86 976	1	33 614	6	77·598	2
86·892	1	33 163	1	76·567	2

λ	Intensity	λ	Intensity	λ	Intensity
4175 640	4	4127 930	1	4078 362	3
74 917	2	27 810	2	76 812	1
73 925	2	27 616	4	76 641	5
73·475	1	26 186	2	76 498	1
73 320	2	25 886	1	76 226	1
72 748	2	25 634	1	75 940	1
72 641	1	23 759	1	74 793	3
72 128	3	23 736	1	72 518	1
71 904	2	22 520	2	71·748	7
71 699	2	21 809	2	70 780	2
70 906	2	21 326	1	70 279	1
70 046	1	20 213	2	67 987	5
69 777	1	19 400	1	67 279	3
68 942	1	18 904	1	66 983	4
68 625	1	18 555	6	65 402	1
67 960	1	17 872	1	63 604	8
67 862	2	14 957	1	63 295	2
65 420	1	14 454	4	62 541	4
63 676	1	12 980	2	61 958	1
61 488	1	12 371	1	61 116	1
61 080	1	12 35	1	60·781	1
60 561	1	09 810	4	59 726	1
58 810	2	09 072	1	58 937	Mn
57 805	3	07 499	5	58 766	1
56 805	4	06 437	1	58 230	2
56 670	1	06 266	1	57 356	1
56 460	1	04 135	2	55 555	Mn
54 819	4	01 684	1	55 046	1
54 504	4	01 272	1	54 883	1
54 109	1	00 745	2	54 833	1
53 920	4	4098 189	3	53 272	1
53 393	1	97 096	1	52 664	1
52 176	2	96 118	1	52 466	1
51 957	1	95 980	3	52 312	1
50 277	2	92 512	1	51 929	2
49 368	2	92 294	1	49 336	1
47 675	4	91 562	1	48 758	Mn
46 071	2	90 984	1	47 315	1
45 209	1	90 085	1	46 629	1
44 625	1	89 224	1	45 822	8
43 874	7	88 567	1	45 130	1
43 420	5	87 102	1	44 617	2
42 628	1	85 314	3	43 901	2
41 862	1	85 012	2	41 366	Mn
40 441	1	84 508	4	41 288	1
39 934	1	83 777	1	40 646	1
37 002	3	83 638	Mn	38 817	1
36 526	1	83 554	1	37 725	1
34 684	5	82·947	Mn	35 729	Mn
34 433	1	82 122	1	34 489	Mn
34 343	1	80·886	1	33 072	Mn
33 870	2	80 226	2	32 636	1
32 905	8	79 847	2	31 968	2
32 064	7	79 424	Mn	31 243	1
31 601	1	79 248	2	30·759	Mn+Fe

λ	Intensity	λ	Intensity	λ	Intensity
4030 508	3	3974 766	1	3933 607	2
30 104	2	74 394	1	32 921	1
29·640	2	73 916	1	32 635	3
26 441	1	73 656	1	31 128	2
24 745	2	72 920	1	30 304	7
24 104	1	71 328	4	29 215	1
21 872	5	70 394	2	29 123	1
21 622	1	70 261	1	28 095	1
20 400	1	69 633	1	27 925	6
18 282	2	69 263	7	26 001	1
18 108	2	68 472	Ca	25 945	3
17 154	3	67 966	1	25 650	2
17 096	1	67 426	4	25 201	1
16 432	1	66 814	1	22 917	6
14 536	4	66 626	5	20 849	1
13 825	2	66 532	1	20 261	6
13 798	1	66 069	5	19 068	2
13 644	1	65 523	1	18 645	4
11 416	1	65 446	1	18 420	2
10 950	1	64 524	2	18 318	2
09 718	5	63 119	2	17 185	5
07 274	3	62 353	1	16 736	3
07 233	1	61 534	1	14 273	1
06 768	1	61 148	1	13 635	2
06 631	1	60 287	1	10 847	2
06 314	2	57 038	2	09 834	2
05 250	7	56 682	6	09 669	1
04 98	1	56 461	4	07 938	3
04 836	1	55 962	1	07 468	1
03 770	1	55 366	2	06 752	1
02 665	1	53 863	1	06 484	5
01 667	3	53 158	2	03 903	3
00 464	1	52 704	1	02 950	7
00 262	1	52 606	4	00 524	1
3998 059	5	51 165	4	3899 711	6
97 398	6	49 956	4	99 030	1
96 970	1	48 779	4	98 013	4
95 989	1	48 112	3	97 892	4
95 312	1	47 537	2	97 454	1
95 215	1	47 393	1	95 659	5
94 120	1	47 004	2	94 014	2
93 402	1	45 123	1	93 918	1
90 380	1	44 896	1	93 395	4
89 861	2	44 750	1	93 316	1
86 178	3	44 651	1	92 898	1
85 394	1	43 346	1	91 933	4
83 964	5	42 446	3	90 844	2
81 776	3	42 383	1	88 825	2
81 106	1	41 292	2	88 520	7
78 466	1	40 885	4	87 053	6
77 747	5	40 044	1	86 287	7
76 866	1	38 022	1	85 514	3
76 622	2	37 334	2	85 154	1
76 564	1	35 817	4	84 365	2
76·392	1	33 663	Ca	83 288	2

λ	Intensity	λ	Intensity	λ	Intensity
3878 726	2	3827 574	1	3787 170	1
78 663	4	26 842	1	86 678	3
78 578	6	25 886	8	86 177	2
78 024	6	25 408	1	85 948	5
76 044	1	24 444	6	85 713	1
74 053	1	24 306	2	82 618	1
73 950	1	24 080	1	82 456	1
73 766	4	23 514	Mn	82 128	1
72 923	1	21 837	2	81 946	1
72 506	6	21 182	6	81 190	1
72 196	1	20 430	8	79 503	1
71·752	2	16 343	2	79 444	2
69 590	1	15 844	7	79 424	1
69 563	2	14 525	2	78 700	1
68 243	1	13 891	2	78 515	1
67 925	1	13 639	2	77 452	1
67 221	3	13 062	2	77 069	1
65 526	6	12 966	6	76 456	2
64 110	1	11 894	2	75 856	1
63 745	1	10 759	2	74 826	2
61 342	2	09 153	1	73 693	2
59 918	7	09 043	1	73·364	1
59·215	5	08 732	2	70 405	1
56 373	6	08 283	1	70 305	1
55 866	1	07 541	4	69 995	1
55·329	1	06 702	6	68 028	1
53·462	1	06 384	1	67 194	6
52 577	3	06 222	2	66 665	1
50 993	1	05 346	6	66 092	1
50 820	5	04 014	2	65 541	6
50 513	1	02 282	1	63 792	6
49 970	6	01 967	2	62 205	1
49 667	1	01 811	1	61 410	1
46 949	1	01 681	2	60 583	3
46 806	5	3799 548	6	60 051	5
46 412	2	98 512	6	59 155	1
46 001	1	98 259	1	58 234	7
45 699	1	97 954	1	57·460	1
45 473	1	97 516	5	56 940	3
43 259	5	95 534	1	56 071	1
41 052	6	95 004	6	54 503	2
40 443	6	94 341	3	53 614	5
39 614	2	93 874	1	53·141	1
39 259	5	93 486	1	52 418	1
37 136	1	93 354	1	51 821	1
36 839	3	92 834	1	51·091	1
34 227	7	92·157	2	50 677	1
33·863	1	91·511	1	49 487	8
33 812	4	90·759	1	48 959	3
30 866	1	90·660	1	48·492	1
30 761	1	90·094	4	48 264	6
29 458	1	89·577	1	46 927	2
29 147	1	89·439	1	46 479	1
28 510	1	89 181	1	45 900	6
27·826	6	87 880	6	45·568	7

TABLE II

λ	Intensity	λ	Intensity	λ	Intensity
3744 095	2	3702 488	1	3657 148	2
43 471	4	02·032	1	56 227	2
43 364	2	01 083	6	55 470	4
43 061	1	00 772	1	53 763	2
42 937	1	3699 186	1	51 512	1
42 623	1	98 606	1	51 473	6
40 262	1	97 510	1	50·282	4
40 061	1	97 436	2	50 026	3
39 542	1	95 507	1	49 509	6
39 317	1	95 054	3	49 308	3
39 113	1	93 999	6	47 845	6
38·310	4	93 021	1	47 430	3
37 185	7	92 645	1	45 825	4
35 329	3	90 728	2	45 494	2
34 869	9	89 897	1	45 090	2
33 319	6	89 456	6	43 716	2
32 398	6	88 877	1	43 624	2
31 374	1	88 476	1	40 392	6
30 947	1	87 657	2	38 209	6
30 390	3	87 458	6	37 862	4
28 666	1	87 101	1	37 251	2
27 810	1	86 258	1	36 994	2
27 622	6	85 995	5	36 650	2
27 095	2	84 110	5	36 186	2
26 922	3	83 798	1	34 336	5
25 495	1	83 616	1	33 837	4
24 380	6	83 056	4	32 977	2
22 565	6	82 235	6	32 554	3
22 025	1	82 209	1	32 040	6
21 928	1	81 774	1	31 464	6
21 606	1	80 801	2	31 093	5
21 512	1	80 694	1	30 352	3
21 396	1	79 915	5	28 094	2
21 278	1	78 862	2	25 148	6
21 189	1	78 046	1	23 794	Mn
19 938	8	77 907	1	23 446	2
18 410	2	77 817	1	23 260	1
16 450	6	77 630	6	23 186	5
15 916	2	77 477	2	22 005	6
11 408	1	77 309	1	21 718	2
11·227	2	76 879	1	21 463	6
09 535	1	76 588	1	19 392	Ni
09 250	6	76 313	4	18 769	6
08 602	1	74 768	2	18 388	3
07 923	5	70 810	2	17 789	6
07 828	8	70 085	3	17 320	3
07·048	3	70 035	2	16·583	4
05·567	6	69 525	6	14 563	2
04·462	5	69 158	3	12 936	2
04 336	1	67 909	2	12 082	4
04·208	1	67 280	4	10 705	2
04 010	1	66 781	2	10 151	5
03·824	1	64 555	2	08·860	6
03·702	1	63 458	2	08 154	3
03·556	1	59 521	5	06 682	5

λ	Intensity	λ	Intensity	λ	Intensity
3005 60	1	3548 024	Mn	3478 382	1
05 454	5	47 190	2	77·850	2
05 830	Cr	45 638	5	77 007	1
03 818	3	43 680	4	76 860	2
03 203	5	42 243	2	76 705	5
02 515	2	42 079	6	76 336	2
3599 628	3	41 090	6	75 867	1
95 294	2	40 714	2	75 653	4
94 627	5	40 132	4	75 454	6
89 453	3	37 890	4	74 436	2
89 105	4	37 731	4	73 674	1
88 918	2	37 495	2	73 497	1
88 622	3	36 552	6	73 303	2
87 749	2	33 196	5	71 914	1
87 424	2	33 004	4	71 34	3
87 253	2	30 382	4	71 27	3
86 989	6	29 816	4	69 834	2
86 115	5	27 795	4	69 604	1
85 708	5	26 672	5	69 390	1
85 322	6	26 470	4	69 012	2
85 193	2	26 379	3	68 849	4
84 960	5	26 167	5	66 897	2
84 788	2	26 069	2	66 501	2
84 662	5	26 016	4	66 279	1
83 324	2	24 537	Ni	65 864	6
82 202	4	24 244	4	64 914	1
81·646	2	24 077	4	63 305	2
81 197	8	21 837	2	62 808	1
76 762	4	21 264	5	62 354	2
75 983	2	16 410	3	61 656	Ni
75 375	4	15 056	Ni	59 922	4
75 248	2	13 822	5	59 740	1
73 894	4	10 443	2	59 429	2
73 842	3	08 492	4	58 465	Ni
73 403	2	06 502	5	58 310	3
71 998	7	05 065	2	57 512	1
71 228	2	04 866	2	57 090	3
70 243	7	00 570	2	56 248	1
70 102	7	3497 842	5	55 235	1
68 980	4	97 137	1	53 025	2
68 828	2	97 112	4	52 279	4
67 045	4	95 290	4	51 920	6
66 377	Ni	92 960	Ni	51 796	1
65 584	4	90 577	6	51 618	2
65 383	6	89 672	4	50 334	6
60 705	2	85 344	6	49 447	1
59 514	2	83 408	1	49 172	1
58 522	5	83 012	4	48 869	1
56 880	6	82 165	2	48·786	1
		81 855	1	48 478	1
54 924	8				
54 121	4	81 558	1	47·989	1
53 741	5	80 341	2	47 283	6
52 840	4	79 683	1	46 960	1
52 112	2	78 788	1	46 791	1
49 873	8	78 623	2	46·262	Ni

λ	Intensity	λ	Intensity	λ	Intensity
3445 783	2	3406 446	2	3378 024	2
45 155	4	05 582	1	76 745	1
44 392	1	04 903	1	76 513	2
43·883	6	04 755	1	75 322	1
43·645	1	04 356	6	74 463	2
42 979	1	04 301	2	74 221	1
42 676	2	02 262	4	73 874	1
42 364	4	01 523	4	72 866	1
41 995	Mn	3399 62	1	72 359	1
40 992	6	99 339	6	72 081	3
40 614	7	99 230	1	71 068	1
39 050	1	99 048	1	70 787	6
38 306	3	98 226	1	69 555	Ni | Fe
37 958	2	97 642	2	68 983	1
37 631	1	97 560	1	68 172	1
37 045	2	97 221	1	67 161	1
36 045	1	96 982	3	66 870	3
34 029	1	96 386	1	66 790	3
33 049	2	96 029	1	64 639	1
32 023	1	95 958	1	64 276	1
31 827	2	95 382	1	63 815	1
31 596	1	95 080	1	63 418	1
28 746	2	94 590	4	62 285	1
28 200	6	94 085	1	61 959	1
27 127	6	93 915	1	60 935	1
26 994	2	93 609	1	59 814	2
26 646	6	93 382	1	59 496	3
26 393	4	92 992	Ni	58 911	1
25 021	4	92 658	5	56 695	1
24 290	6	92 308	4	56 412	3
23 998	1	92 018	3	56 332	1
22 665	4	91 051	Ni	55 517	1
22 503	2	89 748	3	55 235	4
19 706	1	89 268	1	55 126	1
19 157	1	88 966	1	54 953	1
18 514	5	88 628	2	54 380	1
18 179	2	88 174	1	54 068	3
17 847	6	87 624	2	53 268	1
17 265	1	87 410	4	52 929	1
17 162	1	85 444	1	51 750	3
16 688	1	85 231	1	51 529	3
16 299	1	83 985	5	50 284	2
15 537	4	83 86	1	49 739	1
13 948	1	83 699	4	47 932	4
13 140	7	83 387	1	47 507	1
12 844	1	83 01	1	46 942	2
12·643	1	82 410	3	45 679	1
12 347	1	81 340	2	44 988	1
11 356	2	80 885	1	43 784	1
11 184	1	80 578	Ni	43 678	1
10 905	1	80 115	5	43 243	1
10·175	2	80 004	1	42 298	3
10 047	1	79 825	2	42 225	3
07 468	7	79 024	4	41 912	4
06 807	4	78 682	4	40 879	1

λ	Intensity	λ	Intensity	λ	Intensity
3340 570	4	3303 476	1	3263 378	2
39 691	1	02 865	1	62 346	1
39 588	1	01 927	1	62 284	2
39 202	3	01 421	1	62 009	2
38 643	3	01·227	2	61 332	2
37 671	4	3299 511	1	60 276	2
36·262	3	99 079	1	60·258	1
35 776	3	98 137	5	60 004	4
35 513	1	97 883	1	59 062	2
35 403	1	96 806	1	58 786	1
34 278	1	95 825	1	58 423	Mn
34·223	2	93 146	1	57 603	4
31·778	2	92 599	5	57 471	1
31 616	2	92 029	5	57 244	2
30 676	1	90 995	4	57 129	1
30 316	1	90·722	2	56 701	2
29 970	1	90 037	1	56 142	Mn
29 532	2	89 442	2	55 898	2
29 050	2	88 972	3	54 734	2
28 871	4	88 660	2	54 372	4
28 765	1	87 680	1	54 261	1
27 961	1	87·117	1	53 954	2
27 498	2	86 763	8	53 839	1
25 468	4	86 463	2	53 610	4
24 796	1	86 026	2	52 928	4
24 541	4	85 425	3	52 748	1
24 372	2	84 597	4	52 440	2
23 741	4	83·552	1	52 260	1
23 631	1	83 430	1	51 238	5
22 498	3	82 898	4	50 770	Ni
20·800	2	82 725	1	50 634	3
20 650	2	81 302	2	50 400	2
19 258	2	80 763	1	49 204	2
17·126	4	80 268	5	49 037	1
15 670	Ni	79 743	2	48 520	Mn
14 746	6	78 741	3	48 215	6
14·450	2	78 112	1	47 554	Cu
14 070	1	77 358	2	47 297	3
13·723	1	76 477	3	47 220	2
12 707	1	75 848	1	46 973	4
12 232	1	75 685	1	46 492	2
11·451	1	74 452	2	46·015	3
10 496	3	73 965	Cu	45·984	2
10·347	3	71 693	2	44 186	8
07·711	1	71 498	2	43 788	Mn
07 238	4	71·013	6	43·406	2
07 148	1	69 964	1	43 118	1
07 015	1	69 240	1	42 268	1
06 614	1	68·246	4	40 409	1
06·495	1	67 762	1	40·027	1
06 357	8	67·257	2	39 680	1
05·980	8	65·629	6	39 449	8
05·189	1	65 057	3	39 029	1
03·574	2	64·716	2	38·404	1
03·551	1	64 522	4	37·429	1

λ	Intensity	λ	Intensity	λ	Intensity
3287 234	1	3212 000	4	3170 346	2
86 785	Mn	11 872	2	67 907	1
86 281	5	11 693	4	67 856	2
85·888	1	11 494	4	66 440	4
85 178	1	10 834	5	65 858	3
34·623	5	10 458	2	65 005	2
33 976	6	10 245	4	63 874	1
33 304	1	10 212	1	61 945	5
33 061	5	09 328	4	61 370	2
32 944	Ni	09 115	1	60 650	6
32 808	1	08 640	1	60 342	2
31 599	1	08 484	4	60 200	2
80 976	6	07 709	1	57 877	4
30 726	Mn	07 649	1	57 037	4
30 210	4	07 092	2	56 269	4
30 003	3	05 396	7	55 293	2
29 595	2	02 562	3	54 510	2
29 389	3	00 790	2	54 202	4
29 129	4	00 484	6	53 208	4
28 915	4	3199 526	6	51·867	1
28 262	4	97 00	2	51 341	6
28 099	Mn	96 937	4	50 301	2
28 003	2	96 147	2	47 792	1
27 814	4	96 086	2	45 057	2
27·756	4	94 422	4	44 488	4
27 067	2	93 811	3	43 982	6
26 727	1	93 314	4	43 242	2
26 487	1	93 214	4	42 888	4
26 189	1	92 806	5	42 445	4
25 790	8	91 666	5	40 385	4
24 930	1	90 825	2	39 908	2
24 208	1	90 658	2	34 109	5
24 155	1	88 837	5	32 514	2
23 853	1	88 586	4	29 334	4
23 273	1	86 750	3	26 172	4
22 070	6	84 903	4	25 663	6
21 936	2	84 631	1	20 874	2
19 817	4	83 126	1	20 435	4
19 582	5	82 988	2	19 495	4
17 872	1	82 076	3	16 632	5
17 389	4	81 528	4	12 079	2
16 948	1	80 764	4	11 823	1
15 943	5	80 220	8	10 844	2
15 687	8	79 538	2	10 285	2
15 482	2	79 498	1	02 871	1
15 288	1	78 970	3	01 878	Ni
14 624	1	78 545	2	01 558	Ni
14 411	1	78 014	6	01 003	2
14 396	1	76 366	2	00·838	2
14 044	8	75·446	6	00 668	4
13 771	1	75·042	1	00 305	4
13·594	2	73 663	3	3099 968	4
13·320	4	72 067	3	99 898	4
12·436	3	71·659	1	98 191	3
12 184	1	71·353	4	95 270	2

λ	Intensity	λ	Intensity	λ	Intensity
3093 888	2	3021 562	2	2968 484	2
93 806	2	21 076	6	66 902	6
93 360	2	20 643	6	65 816	2
92 785	1	20 495	5	65 258	5
91 581	4	19 291	1	65 040	3
90 209	1	18 988	5	64 632	2
83 745	4	17 630	5	60 303	2
80 118	1	16·200	2	59 996	4
79 994	1	16 170	2	57 494	2
78 436	3	15 925	3	57 370	5
78 020	3	14 919	2	54 659	3
77 172	2	14 176	2	53 943	5
75 725	5	12 456	2	53 778	3
74 442	1	12 004	Ni	53 490	3
74 157	2	11 484	4	50 250	6
73 982	1	09 575	5	49 206	5
68 180	4	09 098	3	48 439	4
67 952	1	08 142	5	47 876	5
67 250	5	07 284	4	47 661	4
67 123	4	07 146	4	47 366	2
67 008	1	05 306	2	45 070	2
66 487	3	04 119	2	44 400	4
63 939	2	03 624	Ni	41 313	8
60 990	3	03 034	4	40 592	3
60 545	1	02 651	2	39 307	Mn
59 090	5	02 488	Ni	37 809	6
57 451	5	00 951	5	36 903	7
55·268	4	00 453	4	33 052	Mn
53·070	4	2999 516	5	29 618	2
50 820	Ni	96 391	4	29 118	4
48 466	2	94 50	2	29 006	7
47 608	6	94 434	6	26 584	5
47 047	1	91 648	4	25 890	3
46 929	1	90 394	4	25 358	3
45 594	1	88 473	2	23 852	4
45 082	4	87 293	5	23 441	2
42 672	5	86 655	1	23 289	4
42 025	4	86 460	3	22 62	1
41 745	4	86 313	2	20 693	4
41 639	3	85 552	4	19 849	2
40 430	4	84 834	4	18 354	3
39 322	2	84 785	1	18 027	5
37 934	Ni	83 571	4	14 305	2
37 782	2	81 856	4	12 257	2
37 392	5	81 448	4	12 161	8
33·104	1	80 535	3	09 500	2
31 641	5	79 356	2	08 864	2
31 216	4	76 130	4	07 518	3
30·150	4	73·286	4	06 411	2
29 237	2	73 137	4	04·168	2
26 468	6	72·275	2	01 919	4
25 846	5	70 518	4	01 382	4
25 638	4	70 107	4	2899 418	4
25 283	2	69 482	4	98 351	2
24 035	5	69 364	3	95 036	4

λ	Intensity	λ	Intensity	λ	Intensity
2894 506	4	2832 433	6	2767 518	7
93·882	2	31 559	3	66 910	4
93 763	2	28 808	4	66 659	2
92 485	3	27 894	4	64 327	4
91 904	2	25 687	4	63 107	4
89 991	2	25 556	6	62 774	3
87 808	4	23 276	7	62 029	5
86 318	2	20 807	2	61 809	4
83 748	2	19 302	2	61 788	5
83 726	3	19 28	1	59 816	4
80 757	3	17 506	3	57 864	2
80 577	2	15 507	2	57 316	4
78 762	2	13 288	9	56 332	5
77 303	5	08 329	2	56 270	8
75 337	1	07 244	2	55·736	8
75 308	3	06 985	7	54·428	3
74 176	7	04 865	2	54 032	4
73 403	2	04 523	7	53 688	4
72 379	1	03 614	2	53 290	4
72 338	4	01 082	Mn	50 874	4
69 313	6	2799 297	1	50 145	6
67 88	2	99 152	2	49 487	3
67 565	2	98 268	Mn	49 324	7
67 313	2	97 777	4	49 182	4
66 629	4	95 542	Mg(?)	47 558	2
65 191	3	95 008	2	46 988	7
63 866	5	94 819	Mn	46 486	7
63 434	4	94 706	2	44 531	5
62 496	3	93 888	2	44 072	8
58 898	4	92 402	2	43 566	4
58 341	3	91 792	3	43 199	6
57 993	2	91 461	2	42 408	6
57 809	2	89 806	3	42 258	4
55 673	2	89 480	2	42 021	4
53 771	3	88 108	6	41 833	2
53 685	2	87 938	4	39 551	9
51 798	8	84 349	2	38 19	1
48 714	4	83 696	3	37 833	3
48 047	1	81 840	4	37 643	2
46 830	2	80 698	3	37 312	6
45 709	2	79 304	3	36 970	4
45 596	4	78 847	4	35 611	3
45 55	1	78 226	6	35 480	8
43 974	7	78 075	3	34 619	2
43 928	2	74 733	4	34 271	4
43 629	5	73 234	4	34 010	4
42 558	2	72 511	2	33 580	9
40 648	2	72 112	6	30 984	3
40 422	4	72 083	4	30 740	4
39 531	2	70 694	2	28 972	2
38 118	6	69 671	8	28 902	3
35 949	2	69 356	3	28 825	4
35 710	3	69 300	4	28 026	4
35·455	4	68 938	2	27 542	5
34 750	2	68 110	2	27 389	3

λ	Intensity	λ	Intensity	λ	Intensity
2726 243	3	2679 066	6	2606 839	5
26 064	4	75 287	2	05 687	6
24·958	4	78 219	2	04 766	2
24 892	3	69 498	4	2599 577	3
23 582	6	67 918	2	99·405	6
20 910	7	66 970	3	98·380	7
20 202	3	66 818	4	94 161	2
19 426	4	66 644	3	94 046	2
19 037	7	66 405	3	93 732	Mn
18 445	4	64 670	3	93 525	2
17 794	3	64·042	3	92 796	4
17 375	2	62 320	2	91 554	4
16 259	2	62 066	3	91 264	2
16 226	3	61 317	2	88 010	5
15 326	2	61 200	2	87 958	3
14 875	4	60 406	2	85 886	7
14 419	6	56 798	2	84 544	4
14 067	2	56 154	3	83 754	2
11 848	3	51 718	3	82·590	4
11 662	5	47 568	3	82·310	4
11 460	2	45 431	2	80 074	2
10 552	4	44 008	4	79 855	2
10 000	2	41 654	3	79 275	2
09 063	3	36 489	3	77 930	4
08 580	4	35 818	4	76 869	4
07 456	2	34 782	2	76 699	4
06 590	5	32 604	2	76 111	6
06 07	1	32 248	4	75 755	4
06 020	3	31 617	2	74 374	3
03 995	3	31·332	6	72 762	2
02 455	2	31 053	6	70 860	3
01 912	2	30 082	3	70 536	3
2699 114	4	29 600	5	69 751	3
97 028	3	28 303	6	69 605	3
96 290	5	25 676	8	68 872	2
95 998	4	25 499	4	66 921	4
95 609	2	23 544	4	64·764	2
95 542	3	23 378	2	64 566	2
95 044	3	21 677	6	63 820	2
94 544	4	20·704	3	63 485	5
92 842	2	20 419	3	62 543	5
92 656	2	19·081	3	49 616	6
92 612	3	18 719	3	46·86	2
02·255	2	18 027	4	45·979	3
90 074	3	17 627	6	44 716	4
89 838	4	15 429	2	43 927	5
89 421	1	14 508	3	42 105	5
89·220	5	13 835	8	40·976	6
84 863	2	12 787	3	37·180	6
84 759	3	11 885	8	35 610	6
84 073	2	11·086	2	33·80	2
83 948	1	10 759	3	30 70	2
82·218	2	09·233	2	29 832	6
81 591	4	08·584	3	29 80	2
80·460	3	07·099	7	29·187	6

λ	Intensity	λ	Intensity	λ	Intensity
2527·44	4	2479 782	4	2404 888	6
25 03	2	79 48	2	04 435	4
24 291	6	76 67	2	2399 244	6
23 661	4	74 818	5	95 628	8
22 855	4	73 159	4	95 423	4
19 64	2	72 910	4	89 979	4
18 107	6	72 875	5	88 631	6
17 663	4	72 351	5	84 39	2
12 366	4	68 885	5	83 253	4
10 837	6	67 74	2	88 06	2
07 904	4	65 155	5	82 039	8
01 70	2	62 652	6	81 85	2
01 135	3	62 191	6	80 763	4
2496 539	5	57 602	6	79 276	4
91 162	4	53 478	4	75 193	4
90 659	4	47 717	4	73 733	6
89 750	6	43 871	4	73 624	4
88 148	4	42 574	4		
87 371	4	40 11	2		
87 069	4	39 746	4		
86 693	4	38 19	2		
86 380	4	13 313	6		
84 188	6	11 071	6		
83·543	4	10 526	6		
83 277	5	06 663	6		

TABLE III

PRISMATIC SPECTRA

Calculation of Constants

Interpolation Formula: $\lambda=\lambda_0+\frac{C}{(s+s_0)}$

$$(s_1+s_0)=\frac{(\lambda_2-\lambda_3)(s_2-s_1)(s_3-s_1)}{(\lambda_1-\lambda_2)(s_3-s_2)-(\lambda_2-\lambda_3)(s_2-s_1)}$$

$$C=\frac{(\lambda_1-\lambda_2)(s_1+s_0)(s_2+s_0)}{(s_2-s_1)}\qquad \lambda_0-\lambda_1-\frac{C}{(s_1+s_0)}$$

Reference Lines $\begin{cases}\lambda_1=2881\cdot578\\ \lambda_2=2825\ 560\\ \lambda_3=2772\ 109\end{cases}$

$s_1=0$
$s_2=13657$
$s_3=27626$

	logs		antilogs	
$\lambda_1-\lambda_2=56\cdot018$	1 748 3276	Add		
$s_3-s_2=13969$	4 145 1658			
	5 893 4920		782515 35	Subtr.
$\lambda_2-\lambda_3=53\ 451$	1 727 9558	Add		
$s_2-s_1=13657$	4 135 3553			
	5 863 3111	Add	729980 17	
$s_3-s_1=27626$	4 441 3180		52585 18	$=d$
	10 304 6291	Subtr		
log $d=$	4·720 4502			

Add	log (s_1+s_0)	5 584 1789
	log (s_2+s_0)	5 599 3612
	log $(\lambda_1-\lambda_2)$	1 748 3276
		12 931 8677
Subtr.	log (s_2-s_1)	4·135 3553
Subtr.	log C	8·796 5124
	log (s_1+s_0)	5 584 1789
	log $(\lambda_1-\lambda_0)$	3·212 3335
Subtr.	log C	8·796 5124
	log (s_3+s_0)	5 614 3604
	log $(\lambda_3-\lambda_0)$	3 182 1520

$(s_1+s_0)=383865$ } Subtr.
$s_1=0$
$s_0=383865$ } Add
$s_2=13657$
$(s_2+s_0)=397522$ } Add
$(s_3-s_2)=13969$
$(s_3+s_0)=411491$
$\lambda_1=2881\ 578$ } Subtr.
$(\lambda_1-\lambda_0)=1630\cdot548$
$\lambda_0=1251\ 030$ } Add
$(\lambda_3-\lambda_0)=1521\cdot080$
$\lambda_3=2772\cdot110$ (Check)

$$\lambda=1251\cdot030+\frac{[8\ 796\ 5124]}{s+383865}$$

Table IV

PRISMATIC SPECTRA

Calculation of Wave-lengths

(For explanation see pp 69—71)

$s_0 = 341209$, $\log C = 8\ 760\ 4063$, $\lambda_0 = 2255\ 978$

Line λ_{obs}	Average Reading	Reduced Reading s	$s+s_0$	$\log(s+s_0)$	$\log C - \log(s+s_0)$	$\frac{C}{s+s_0}$	$\lambda_{calc} = \lambda_0 + \frac{C}{s+s_0}$	$\lambda_{obs} - \lambda_{calc}$	λ_{obs}	Identification
3944 032	6647	$0 = s_1$								
(6)	8762	2115	343324	5 535 7042	3 224 7021	1677 653	3933 631	+ 033	3933 664	Ca II
3930 304	9452	2805	4014	536 5761	223 8302	74 288	30 266	+ *038*		
27 925	9945	3298	4507	537 1980	223 2083	71 892	27 870	+ *055*		
20 261	11532	4885	6094	539 1941	221 2122	64 227	20 205	+ *056*		
(4)	13299	6652	7861	541 4058	219 0005	55 772	11 750	+ 060	3911 810	Sc
(3)	14206	7559	8768	542 5366	217 8697	51 467	07 445	+ 060	07 505	Sc
3899 711	15861	9214	350423	544 5926	215 8137	43 667	3899 645	+ *066*		
95 659	16723	10076	1285	545 6596	214 7467	39 634	95 612	+ *047*		
(2)	17062	10415	1624	546 0785	214 3278	38 053	94 031	+ 059	3894 090	Co
(1)	17638	10991	2200	546 7894	213 6169	35 374	91 352	+ 058	91 410	Zr
3886 287	18741	12094	3303	548 1473	212 2590	30 268	86 246	+ *041*		
(1)	19389	12742	3951	548 9431	211 4632	27 284	83 262	+ 054	83 316	CN (band-head)
3878 578	20421	13774	4983	550 2076	210 1987	22 552	78 530	+ *048*		
(1)	21433	14786	5995	551 4439	208 9624	17 940	73 918	+ 049	73 967	Co
(2)	21616	14969	6178	551 6671	208 7392	17 109	73 087	+ 049	73 136	Co
(2)	23609	16962	8171	554 0904	206 3159	08 110	64 088	+ 042	64 130	Mo
3859 913	24548	17901	9110	555 2275	205 1788	03 906	59 884	+ *029*		
(1)	24909	18262	9471	555 6639	2[illegible]7424	02 295	58 278	+ 033	58 311	Ni
3856 873	25342	18695	9904	556 1866	204 2197	00 368	56 346	+ *027*		
(0)	26947	20300	361509	558 1191	202 2872	1593 262	49 240	+ 031	49 271	Zr
(1)	27808	21161	2370	559 1522	201 2541	89 477	45 455	+ 028	45 483	Co
(1)	29993	23346	4555	561 7631	198 6432	79 949	35 927	+ 019	35 946	Zr
3834 227	30395	23748	4957	562 2417	198 1646	78 209	34 187	+ *040*		
24 444	32664	26017	7226	564 9334	195 4729	68 458	24 436	+ *008*		
20 480	33605	$26958 = s_2$								
15 844	34687	28040	9249	567 3193	193 0870	59 865	15 843	− *001*		
06 702	36861	30214	371423	569 8688	190 5375	50 735	06 713	− *011*		
(2)	38895	32248	3457	572 2406	188 1657	42 288	3798 266	− 014	3798 252	Mo
3763 792	47429	40782	381991	582 0531	178 3532	07 833	63 811	− *019*		
58 234	48833	42186	3395	583 6465	176 7598	02 311	58 289	− *055*		
49 487	51083	44436	5645	586 1877	174 2186	1493 546	49 524	− *037*		
45 900	52013	45366	6575	587 2338	173 1725	89 953	45 931	− *031*		
34 869	54897	48250	9459	590 4618	169 9445	78 919	34 897	− *028*		
19 938	58878	$52231 = s_3$								

TABLE V

RAIES ULTIMES OF THE ELEMENTS

(The intensity numbers under "Harrison" are taken from the *Massachusetts Institute of Technology Wave-Length Tables*, and those under "Hilger" from Messrs Adam Hilger's list of the lines shown in the arc spectrum of their "R.U. powder." A blank space indicates that the line is not in the list under that heading given by the author concerned Wave-lengths have been given the values recorded in the Massachusetts Institute Tables whenever possible The symbol "R" indicates that the line is often reversed)

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
A	8115 311	-		5000	
	7503 867	—		700	
	7067 217	-		400	
	6965 430	—		400	
Ag	5465 487	1000R	500R		
	5209 067	1500R	1000R		
	3382 891	1000R	700R		10
	3280 683	2000R	1000R		10
	2437 791	60	500		
	2246 412	25	300		
Al	6243 36	-	100		
	6231 76	—	30		
	3961 527	3000	2000		7
	3944 032	2000	1000		5
	3092 713	1000	1000		3
	3082 155	800	800		3
	2816 179	10	100		
	2669 166	3	100		
	2631 553	—	40		
	2575 100				0
	2567 987				0
	2373 132				1
	2367 062				0
As	2898 71	25	40		2
	2860 452	50	50		3
	2780 197	75R	75		3
	2744 991				2
	2492 91				2
	2456 53	100	8		2
	2381 18				2
	2370 77	50	3		2
	2369 67	40	--		2
	2349 84	250R	18		4
	2288 12	250R	5		3
Au	2802 19	—	200		
	2675 95	250R	100		2
	2427 95	400R	100		2
B	3451 41	5	30		
	2497·738	500	400		5
	2496 778	300	300		4

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Ba	5777 665	500R	100R		
	5535 551	1000R	200R		8
	5519 115	200R	60R		
	5424 616	100R	30R		
	4934 086	400	400		5
	4554 042	1000R	200		15
	4130 664	50	60		
	3891 785	18	25		
	3071 591	100R	50R		
	2335 269	60R	100R		
	2304 235	60R	80R		
Be	3321 343	1000	30		2
	3321 086	100	-		2
	3321 013	50	-		
	3131 072	200	150		2
	3130 416	200	200		3
	2650 94*				0
	2650 781	25	—		
	2650 31*				0
	2494 87*				0
	2494 44*				0
	2348 610	2000R	50		5
Bi	4722 552	1000	100		
	3067 716	3000R	2000		5
	2989 029	250	100		
	2938 298	300	300		
	2897 975	500R	500R		2
	2809 625	200	100		
	2780 521	200	100		
	2276 578	100R	40		
	2061 70	300R	100		
Br	4816 71	—	—	300	
	4785 50	—	—	400	
	4704 86	—	—	250	
C	4267 27	- -	500		
	4267 02	- -	350		
	2837 602	—	40		
	2836 710	—	200		
	2478 573	400		400	2
	2296 89	—	200		
Ca	4456 620				25†
	4454 781	200			
	4434 960	150	-		20
	4425 441	100	—		15
	4318 652				12
	to				
	4283 010				12
	4226 728	500R	50		50
	3968 468	500R	500R		40
	3933 666	600R	600R		40
	3179 332	100	400		
	3158 869	100	300		

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* These wave-lengths, given by Hilger, appear to be inaccurate see p. 99

† Possibly given in error for 4454 781, a much more sensitive line.

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Cd	6438 470	2000	1000		
	5085 824				1
	4799 918				1
	3610 510	1000	500		3
	3467 656				2
	3466 201	1000	500		3
	3403 653	800	500		2
	3261 057	300	300		5
	2748 58	5	200		
	2573 09	3	150		
	2312 84	1	200		
	2288 018	1500R	300R		2
	2265 017	25	300		
	2144 382	50	200R		
Ce	4186 599	80	25		
	4165 606	40	6		
	4040 762	70	5		
	4012 388	60	20		
Cl	4819 46	—		200	
	4810 06	—		200	
	4794 54	—		250	
Co	3529 813	1000R	30		
	3465 800	2000R	25		
	3453 505	3000R	200		3
	3405 120	2000R	150		1
	2519 822	40	200		
	2407 254				0
	2388 918	10	35		
	2378 622	25	50		
	2363 787	25	50		
	2307 857	25	50		
	2286 156	40	300		
Cr	5208 436	500R	100		
	5206 039	500R	200		
	5204 518	400R	100		
	4289 721	3000R	800		2
	4274 803	4000R	800		2
	4254 346	5000R	1000		2
	3605 333				2
	3593 488				2
	3578 687				3
	2860 934	60	100		
	2855 676	60	200		
	2849 838	80	150		
	2843 252	125	400		
	2835 633	100	400		
Cs	8943 50	2000R	—		
	8521 10	5000R	—		
	4593 177	1000R	50		1
	4555 355	2000R	100		3
Cu	5218 202	700	—		
	5153 235	600	—		
	5105 541	500	—		
	3273 962	3000R	1500R		15
	3247 540	5000R	2000R		20

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Cu (*contd.*)	2246 995	30	500		
	2192 260	25	500		
	2135 976	25	500		
Dy	4211 719	200	15		
	4167 966	50	12		
	4077 974	150	100		
	4045 983	150	12		
	4000 454	400	300		
Er	3906 316	25	12		
	3692 652	20	12		
	3499 104	18	15		
Eu	4205 046	200R	50		
	4129 737	150R	50R		
F	6902 46	—		500	
	6856 02	—		1000	
	5291 (band)	200			Present
Fe	3749 487				1
	3748 264	500	200		1
	3745·903	150	100		
	3745 564	500	500		1
	3737 133	1000	600		
	3734 867				2
	3719 935	1000R	700		2
	3647 844				1
	3617 788				1
	3581 195				2
	3570 097				2
	3565 381				1
	3490 575				1
	3475 454				2
	3457 086				2
	3440 610				2
	3047 605				2
	3021 073				1
	3020 640				2
	2983 572				0
	2973 237				0
	2966 900				0
	2742 408				1
	2719 025				1
	2631 051				0
	2613 823				1
	2527 433				0
	2522 848				2
	2488 148				2
	2483 270				3
	2413 309	60	100		
	2410·517	50	70		
	2404 882	50	100		
	2395 625	50	100		
	2382 039	40	100R		
Ga	4172 056	2000R	1000R		
	4032 982	1000R	500R		
	2943 637	10	20		
	2874·244	10	15		

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Gd	3768 405	20	20		
	3646 196	200	150		
Ge	4226 570	200	50		
	3269 494	300	300		
	3039 064	1000	1000		2
	2754 592				2
	2709 626	30	20		2
	2691 344				1
	2651 575	30	20		1
	2651 178	40	20		2
	2592 537				1
H	6562 79	—		3000	
	4861 327	—		500	
He	5875 618	—		1000	
	4685 75	—		300	
	3888 646	—		1000	
Hf	4093 161	25	20		
	3134 718	80	125		
	3072 877	80	18		
	2940 772	60	12		
	2916 481	50	15		
	2904 408	30	6		
	2898 259	50	12		
	2820 224	40	100		
	2773 357	25	60		
	2641 406	40	125		
	2516 881	35	100		
	2513 028	25	70		
Hg	5460 740	-		2000	
	4358 35	3000	500		
	4046 561	200	300		
	3663 276	500	400		
	3654 833	—		200	
	3650 146	200	500		
	2536 519	2000R	1000R		2
Ho	3891 02	200	40		
	3748 17	60	40		
	2936 77	—	1000R		
I	5464 61	—		900	
	5161 188	—		300	
	2062 38			900	
In	4511 323	5000R	4000R		6
	4101 773	2000R	1000R		4
	3258 564	500R	800R		2
	3256 090	1500R	600R		5
	3039 356	1000R	500R		2
Ir	3513 645	100	100		1
	3437 015	20	15		
	3220 780	100	80		1
	3133 821				1
	2924 792	25	15		
	2849 725	40	20		
	2689 712				0
	2543 971				0

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
K	7698 979	5000R	—		
	7664 907	9000R	—		
	4047 201	400	200		5
	4044 140	800	400		5
	3447 701				1
	3446 722				1
Kr	5870 916			3000	
	5570 290			2000	
La	6249 929	300	—		
	5930 648	250	—		
	5455 146	200	1		
	4429 904				1
	4333 734				1
	4123 228	500	500		2
	4086 714				2
	4077 340	600	400		
	3995 750				1
	3949 106	1000	800		4
	3337 488				3
Li	6707 844	3000R	200		20
	6103 642	2000R	300		5
	4603 00	800	—		2
	3232 61	1000R	500		1
Lu	4518 57	300	40		
	3554 43	50	150		
	3472 48	50	150		
	3397 07	50	20		
	2911 39	100	300		
	2894 84	60	200		
Mg	5183 618	500	300		30
	5172 699	200	100		25
	5167 343	100	50		20
	3838 258	300	200		25
	3832 306	250	200		20
	3829 350	100	150		15
	3096 899				30
	3092 991				15
	3091 077				10
	2852 129	300R	100R		100
	2802 695	150	300		30
	2795 53	150	300		30
Mn	4034 490	250	20		3
	4033 073	400	20		3
	4030 755	500	20		4
	2798 271				3
	2605 688	100R	500R		1
	2593 729	200R	1000R		1
	2576 104	300R	2000R		1
Mo	3902 963	1000R	500R		4
	3864 110	1000R	500R		5
	3798 252	1000R	1000R		5
	3447 123				1
	3358 124				0
	3208·834				1

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Mo (*contd*)	*3193 973*				3
	3170 347				3
	3158 165				2
	3132 594				3
	3112 124				0
	2909 116	25	40		
	2890 994	30	50		
	2871·508	100	100		
	2848·232	125	200		
	2816 154	200	300		
N	5679 56	—		500	
	5676 02	—		100	
	5666 64	—		300	
	4109 98	—		1000	
	4103 37	—		80	
	4099 94	—		150	
	4097 31	—		100	
Na	5895 923	5000R	500R		30
	5889 953	9000R	1000R		30
	5688 224	300	—		1
	5682 657	80	—		0
	3302 988	300R	150R		4
	3302 323	600R	300R		4
Nb	4137 095	100	60		
	4123 810	200	125		1
	4100 923	300	200		1
	4079 729	500	200		2
	4058 938	1000	400		3
	3358 417				2
	3225 479	150	800		
	3194 977	30	300		
	3163 402	15	8		
	3130 786	100	100		
	3094 183	100	1000		
Nd	4303 573	100	40		
	4177 321	15	25		
	3951 154	40	30		
Ne	6402 246	—		2000	
	5852 488	—		2000	
	5400 562	—		2000	
Ni	3524 541	1000R	100		2
	3515 054	1000R	50		0
	3492 956	1000R	100		
	3446 263				1
	3414 765	1000R	50		2
	2287 084	100	500		
	2270 213	100	400		
	2264 457	150	400		
	2253 86	100	300		
O	7775·433	—		100	
	7774 138	--		300	
	7771 928	--		1000	

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Os	4420 468	400R	100		1
	4260 854				1
	3267 945	400R	80		2
	3262 290	500R	50		1
	3058 66	500R	500		2
	3030 695				1
	3018 039				1
	2909 061	500R	400		3
	2838 626				1
	2637 133				0
	2488 548				2
P	2554 93	60		20	1
	2553 28	80		20	2
	2535 65	100		30	2
	2534 01	50		20	1
Pb	5608 8	—		40	
	4057 820	2000R	300R		10
	3739 947				2
	3683 471	300	50		8
	3671 503				1
	3639 580	300	50		6
	3572 734				2
	2873 316				4
	2833 069	500R	80R		5
	2823 189				2
	2663 166				3
	2614 178	200	80		4
	2577 263				1
	2476 379				2
	2393 794				1
	2203 505	50	5000R		
	2169 994	1000R	1000R		
Pd	3634 695	2000R	1000R		1
	3609 548	1000R	700R		1
	3516 943	1000R	500R		2
	3481 152				2
	3460 774*				2
	3421 24	2000R	1000R		3
	3404 580	2000R	1000R		4
	3242 703				3
	2854 581	4	500		
	2658 722	20	300		
	2505 739	3	30		
	2498 784	4	150		
	2488 921	10	30		
Pr	4225 827	50	40		
	4189 518	100	50		
	4179 422	200	40		
	4062 817	150	50		
Pt	3064 712	2000R	300R		2
	3042 687				1
	2997 967	1000R	200		1
	2929 794	800R	200		1
	2830 295	1000R	600		1
	2719 038				1
	2705 894				0

* Hilger gives this as 3461 75—evidently a misprint.

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Pt	2702 899				1
(*contd*)	2659 454	2000R	500R		2
	2650 857				1
	2628 029				0
Ra	4825 91	- -		800	
	4682 28	—		800	
	3814 42	—		2000	
Rb	7947 60	5000R			
	7800 227	9000R	—		
	4215 556	1000R	300		4
	4201 851	2000R	500		4
Re	4889 17	2000			
	3460 47	1000			
Rh	4374 80				1
	3692 357	500	150		1
	3657 987	500	200		0
	3596 194				00
	3434 893	1000	200		2
	3396 85	1000	500		
	3323 092	1000	200		0
Rn	7450 00	-		600	
	7055 42	—		400	
Ru	3728 030				2
	3726 926				2
	3661 353				1
	3634 929				1
	3596 179	30	100		0
	3593 022				1
	3498 942	500R	200		4
	3436 737	300R	150		2
	3428 634				1
	3428 309				1
	3417 353				0
	2976 586	60	200		
	2965 546	60	200		
	2945 668	60	300		
	2712 410	80	300		
	2692 065	8	200		
	2678 758	100	300		
S	9237 49	—		200	
	9228 11	—		200	
	9212 91	—		200	
	4696 25	—		15	
	4695 45	—		30	
	4694 13	—		500	
Sb	3267 502	150	150		2
	3232 499	150	250		1
	3029 807				0
	2877 915	250	150		4
	2769 939				1
	2598 062	200	100		4
	2528 535	300R	200		4
	2311 469	150R	50		3
	2175 890	300	40		
	2068 38	300R	3		

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Sc	4246 829				1
	4023 688	100	25		2
	4020 399	50	20		1
	3911 810	150	30		2
	3907 476	125	25		1
	3642 785	60	50		0
	3630 740	50	70		
	3613 836	40	70		
	3580 927				1
	3572 523				1
Se	4742 25	—		500	
	4739 03	—		800	
	4730 78	—		1000	
	2062 788	—		800	
	2039 851	—		1000	
Si	3905 528	20	15		1
	2881 578	500	400		8
	2528 516	400	500		4
	2524 118				4
	2519 207				4
	2516 123	500	500		5
	2514 331				4
	2506 899	300	200		4
	2435 159				2
Sm	4434 321	200	200		
	4424 342	300	300		
	4390 865	150	150		
Sn	4524·741	500	50		
	3330 594				2
	3262 328	400	300		4
	3175 019	500	400		3
	3034 121	200	150		3
	3009 147	300	200		1
	2863 327	300R	300R		4
	2839 989	300R	300R		4
	2706 510				3
	2661 248				0
	2546 552				1
	2429 495				2
	2354 845				2
Sr	4962 263	40			
	4872 493	25	—		
	4832 075	200	8		
	4607 331	1000R	50R		10
	4305 447	40	—		
	4215·524	300	400		6
	4077 714	400	500		10
	3474 887	80	50		
	3464 57	200	200		
	3380 711	150	200		
Ta	3406·664	70	18		
	3318 840	125	85		1
	3311 162	800	70		1
	3103 251				0
	2714 674				2

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Ta (*contd.*)	2656 61				1
	2653 274				1
	2647 472				1
Tb	3874 18	200	200		
	3848 75	100	200		
	3561 74	200	200		
	3509 17	200	200		
Te	2769 67	—		30	
	2530 70	—		30	
	2385 76	600		800	
	2383 25	500		800	
	2142 75	60R	—		
Th	4019 137	8	8		
	3601 040	8	10		
	3538 75	--	50		
	3290 59	—	40		
Ti	5007 213	200	40		
	4999 510	200	80		
	4991 066	200	100		
	4981 733	300	125		
	4536 053				1
	to				
	4533 244				1
	3998 640				2
	3989 763				1
	3981 764				0
	3958 213				1
	3956 343				0
	3653 496	500	200		1
	3642 675	800	125		1
	3635 463	200	100		1
	3383 761	70	300R		
	3377 585				1
	3372 800	80	400R		2
	3371 454				2
	3370 439				1
	3361 213	100	600R		2
	3354 635				1
	3349 406				2
	3349 035	125	800R		1
	3341 875				3
	3322 937				0
	3241 986				0
	3239 038				1
	3236 573				1
	3234 516				1
	3199 915				1
Tl	5350 46	5000R	2000R		7
	3775 72	3000R	1000R		6
	3529·43				4
	3519 24	2000R	1000R		6
	3229 75	2000	800		
	2918 32	400R	200R		1
	2767 87	400R	300R		3

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Tm	3761 917	200	120		
	3761 333	250	150		
	3462 21	200	100		
U	4241 669	40	50		
	3672 579	8	15		
	3552 172	8	12		
V	4594 108				0
	4460 292				1
	4408 511				1
	4389 974	80R	60R		Present
	4384 722	125R	125R		Present
	4379 238	200R	200R		2
	4134 488				0
	4132 017				1
	4128 071				2
	4116 703				1
	4111 785				2
	4105 167				1
	4099 796				1
	3185 396	500R	400R		2
	3183 982	500R	400R		2
	3183 406	200R	100R		1
	3125 284	80	200R		
	3118 383	70	200R		
	3110 706	70	300R		0
	3102 299	70	300R		1
	3093 108	100R	400R		
	3066 375				1
	3060 460				1
	2908 817				1
W	4302 108	60	60		
	4294 614	50	50		0
	4008 753	45	45		1
	3613 790	10	30		
	3215 560	10	9		
	2589 167	15	25		
	2397 091	18	30		
Xe	4671 226	—		2000	
	4624 276	—		1000	
	4500 977	—		500	
Y	4674 848	80	100		
	4643 695	50	100		0
	4374 935				1
	4142 839				2
	4102 376				3
	3982 595				0
	3788·697	30	30		
	3774 332	12	100		2
	3710 290	80	150		2
	3633 123	50	100		0
	3620 941				1
	3600 734	100	300		
	3327 875				1
	3242 280	60	100		2
	3216 682				1

Element	*Raies Ultimes*	Harrison			Hilger
		Arc	Spark	Discharge Tube	Arc
Yb	3987 994	1000R	500R		
	3694 203	500R	1000R		
	3289 37	500R	1000R		
Zn	6362 347	1000	500		20
	4810 534	400	300		50
	4722 159	400	300		50
	4680 138	300	200		30
	3345 572				30
	3345 020	800	300		30
	3302 941				25
	3302 588	800	300		25
	3282 333	500R	300		20
	2557 958	10	300		
	2502 001	20	400		
	2138 56	800R	500		
	2061 91	100	100		
	2025 51	200	200		
Zr	4772 312	100	-		
	4739 478	100	-		
	4710 075	60	—		
	4687 803	125	–		
	3601 193	400	15		
	3572 473	60	80		1
	3547 682	200	12		
	3519 605	100	10		
	3496 210	100	100		2
	3481 146				0
	3438 230	250	200		2
	3391 975	300	400		2

TABLE VI

INSPECTION LIST

Visible Region

6707 844	Li	4511 323	In	4044 140	K
6298 327	Rb	4379 238	V	34 190	Mn
06 300		4294 614	W	33 073	
5895 923	Na	54 346	Cr	30 755	
89 953		26 728	Ca	23 688	Sc
5535 551	Ba	15 556	Rb	08 753	W
5350 46	Tl	15 524	SrII	3968 468	CaII
5291	F	01 851	Rb	61 527	Al
4934 086	BaII	4172 056	Ga	49 106	LaII
4810 534	Zn	02 376	Y	44 032	Al
4722 159		01 773	In	33 666	CaII
4680 138		4077 714	SrII	11 810	Sc
07 331	Sr	58 938	Nb	07 476	
4555 355	Cs	57 820	Pb	02 963	Mo
54 042	BaII	47 201	K	3775 72	Tl

Ultra-violet Region

3498 942	Ru	3282 333	Zn	3067 716	Bi	2833 069	Pb
96 210	ZrII	80 683	Ag	64 712	Pt	01 064	Mn
60 47	Re	73 962	Cu	39 064	Ge	2798 271	
53 505	Co	61 057	Cd	21 073	Fe	94 817	
38 230	ZrII	47 540	Cu	20 640		80 197	As
34 893	Rh	42 703	Pd	2944 175	Ga	73 357	HfII
14 765	Ni	3193 973	Mo	43 637		14 674	Ta
04 580	Pd	75 019	Sn	09 061	Os	2675 95	Au
3382 891	Ag	70 347	Mo	2881 578	Si	59 454	Pt
45 572	Zn	33 321	Ir	77 915	Sb	2598 062	Sb
45 020		32 594	Mo	74 244	Ga	36 519	Hg
37 488	LaII	31 072	BeII	60 452	As	35 65	P
02 941	Zn	30 416		52 129	Mg	2427 95	Au
02 588		3075 901	Zn	39 989	Sn	2138 56	Zn

TABLE VII

IDENTIFICATIONS OF LINES APPEARING ON PLATES I TO V (VISIBLE REGION)

(For explanation see pp 92–95; the symbol "n" in the "Intensity" column indicates that the line is "nebulous.")

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
6791 05	4	*Sr*																				
17 685	5	*Ca*																				
07 844	25	*Li*																				
6693 88	7		Ba																			
75 268	7		Ba																			
43 540	5			Sr																		
17 259	7			Sr																		
6595 32	14		Ba																			
78 513	0				La																	
72 781	1	*Ca*																				
50 255	6	*Sr*																				
46 791	3			Sr																		
43 151	1					La																
27 314	18		Ba																			
03 995	12			Sr																		
6499·650	16						Ca															Blend
98 762			Ba																			
96 901	12								BaII													
93 780	11						Ca															
82 912	14	*Ba*																				
71 660	8						Ca															
62 566	18						Ca															
55 988	3				La																	
50 854	12		Ba																			
39 073	20						Ca															

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
6435 000	1	*Y*																				
08 473	14			Sr																		
6394 234	4					La																
88 239	3									Sr												Blend
86 501										Sr												
80 746	4									Sr												
69 962	1	*Sr*																				
41 683	10		Ba																			
05 671	3	*Sc*																				
6292 827	1										V											
85 165	1										V											
74 654	0										V											
61 099	1											Ti										
58 703	2											Ti										Blend
58 103												Ti										
51 823	0										V											
49 929	3					La																
43 105	6										V											
30 736	1										V											
6162 172	50												Ca									Blend
60 760														Na								
54 229	25													Na								
41 716	14								Ba II													
22 218	14												Ca									
10 785	14														Ba							
03 642	16	*Li*																				Blend
02 721													Ca									
6091 174	6	*Ti*																				
63 118	9														Ba							
19 474	7														Ba							

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
5997 091	6														Ba							
71 701	6														Ba							
5895·923	250R															Na						
89 953	500R															Na						
26 295	10	*Ba*																				
5777 665	10																Ba					
27 029	6	*V*																				
5688 224	300																	Na				
82 657	150																	Na				
27 641	6																		V			
24 598	4																		V			
02 836	8																			Ca		
01 264	8																			Ca		
5598 474	12																			Ca		
94·454	14																			Ca		
90 110	7																			Ca		
88 748	16																			Ca		
81 969	10																			Ca		
70 450	2																				Mo	
40 052	6		*Sr*																			
35 551	25	*Ba*																				Blend
34 807			Sr																			
33 046	5																				Mo	
27 540	1			Y																		
21 88	10		Sr																			
20 496	0				Sc																	
19 115	10n																Ba					
14·215	0				Sc																	
06 491	6																				Mo	
04 17	10		Sr																			

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
5501·340	6						La															
5486·12	7		Sr																			
84 618	1					Sc																
81·989	0					Sc																
80 840	14		Sr																			
66·472	5			Y																		
65 487	1	*Ag*																				
55·146	7						La															
50 842	8		Sr																			
46 920	0							Fe														
29 699	0							Fe														
24 616	12n																Ba					
15 263	1								V													
09 791	6									Cr												
05 778	1							Fe														
01 933	0								V													
5397 131	1							Fe														
92 075	1	*Sc*																				
85 137	0	*V*																				
71 493	2							Fe														
57 873	2	*La*																				
56 100	3										Sc											
53 485	1	*Co*																				
50 46	12											Tl										Forms doublet with [3775 72
49 474	9	*Ca*																				Blend
49 294											Sc											
48 319	2									Cr												
45 807	4									Cr												
44 170	1	*Nb*																				
43 388	0												Co									Blend
42 708													Co									

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
5341 065	3	*Mn*																				
29 823	3n	*Sr*																				
28 050	4							Fe														
5298 269	3									Cr												
96 686	2									Cr												
75 53	4													Re								
70 276	18														Ca							Blend
69 541								Fe														
65 722	12									Cr												Blend
65 562															Ca							
64 240	8														Ca							Blend
64 152										Cr												
62 248	10														Ca							
61 704	7														Ca							
59 990	1	*Ti*																				?
56 903	12															Sr						
53 458	6	*La*																				
47 564	0									Cr												
40 872	4																V					
38 551	8															Sr						
34 274	6	*La*																				Blend
34 070																	V					
29 270	7															Sr						
25 113	7															Sr						
22 199	7															Sr						
19 706	0																	Ti				
11 870	6																		La			
10 389	6																	Ti				
08·436	9																			**Cr**		

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
5206 039	8																			Cr		
04 518	7																			Cr		
5194 832	1	*V*																				
92 975	6n																	Ti				
88 850	8n	*Ca*																				
83 618	6																				Mg	
77 311	6																		La			
73 748	4																	Ti				
72 699	5																				Mg	
67 343	5																				Mg	
58 693	4						La															
53 645	50		Na																			
49 090	25		Na																			
45 422	6																		La			
28 530	1	*V*																				
20 425	0	*Ti*																				
16 967	2	*Mo*																				?
06 233	3																		La			
05 541	7	*Cu*																				
01 121	1			Sc																		
5099 228	3			Sc																		
96 716	2			Sc																		
95 299	1				Nb																	
89 888	1						Sc															
87 148	0						Sc															
86 951	4			Sc																		
85 824	6					Cd																Blend
85 547				Sc																		
83 713	6			Sc																		
81 554	6			Sc																		

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
5078 964	0				Nb																	
75 814	1			Sc																		
70 249	3			Sc																		
64 655	6							Ti														
56 461	3																		La			
52 874	1	*Ti*																				
50 569	3																		La			
46 884	2																		La			
41 625	7n	*Ca*																				
39 953	4							Ti														
38 402	2								Ti													
36 468	3								Ti													
35 907	4								Ti													
24 842	1									Ti												
22 866	1									Ti												
20 027	1									Ti												
16 166	1									Ti												
14 241	6									Ti												Blend
14 189								Ti														
07 213	6									Ti												
4999 510	7									Ti												
82 845	300										Na											
78 585	150										Na											
67 944	7											Sr										
62 263	14											Sr										
49 769	6	*La*																				
34 086	25													BaII								
25 652	1														V							
21 783	1															LaII						
20·971	1															LaII						

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4904 289	0														V							
02 898	1																	Ba				
01 862	1	*La*																				
00 121	4	*Y*																				
4892 663	10n																Sr					Blend
91 980																	Sr					
89 17	7n													Re								
85 085	1	*Ti*																				
83 693	1	Y II																				
81 557	8																			V		
78 132	10n	*Ca*																				
76 325	12												Sr									
75 478	7																			V		
72 493	12											Sr										
69 19	10n																Sr					Blend
68 700																	Sr					
64 737	7																			V		
59 847	4																		Y			
58 1	0	*ScO*																				Band-head
55 045	8																Sr					
52 692	5																		Y			
51 485	7																			V		
50 817	2																				La	
45 675	4																		Y			
43 828	1	*W*																				?
40 874	3	*Ti*																				
39 866	5																		Y			
32 427	16																			V		Occurs in two multiplets
32 075												Sr	Sr									
31 645																				V		

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4827 450	6																			V		
23 516	7		Mn																			
15 629	6			Zr																		
11 881	14												Sr									Blend
10 534					Zn																	
07 530	5						V															
05 870	1			Zr																		
4799 918	6					Cd																
96 918	4						V															
91 419	1	*Re*																				
86 507	5						V															
84 320	10												Sr									
83 420	7n		Mn																			
79 347	3	*Sc*																				
76 363	4						V															
72 312	5			Zr																		
66 894	6n																				La	Blend
66 634							V															
66 430								Mn														
62 376	5							Mn														
51 891	40								Na													
48 016	20								Na													
43 814	6									Sc												
41 922	10												Sr									
41·018	3									Sc												
39 478	6			Zr																		
37 642	5									Sc												
34 094	5									Sc												
32 329	1	*Zr*																				
29 226	3									Sc												

Table VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4728 769	2									Sc												
26 450	8n	*Ba*																				
22 278	10												Sr									Blend
22 159					Zn																	
10 075	6			Zr																		
00 436	1																	Ba				
4691 622	7										Ba											
87 803	10			Zr																		
81 916	3	*Ti*																				
74 848	4											Y										
68 597	200												Na									
64 858	100												Na									
52 158	3													Cr								
46 174	5													Cr								
43 695	6											Y										
39 667	0														Ti							Blend
39 366															Ti							
33 985	0															*Zr*						
29 342	0														Ti							
26 188	1													Cr								
23 094	1														Ti							
19 771	5																	V				
17 270	2														Ti							
16 137	2													Cr								
13 373	1													Cr								
07 331	35	*Sr*																				
00 752	1													Cr								
4599 751	4	*Ba*																				
94 108	10																	V				
91 394	2													Cr								

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
4586 357	16n																	V				Blend
85 871																	Ca					
81 402	10n																Ca					
80 401	7																	V				
79 667	10																		Ba			
78 730	7n																				V	Blend
78·558																	Ca					
77 174	8																	V				
75 515	4															Zr						
73 855	10										Ba											
73 075	0	*Nb*																				
71·783	6																				V	
70·027	6																			La		Blend
69·644			Cr																			
69 530			Cr																			
67 909	6																			La		
60 714	6																				V	
55·489	6			Ti																		
54 042	25													Ba II								
49 502	1																			La		
48 767	1			Ti																		
45 393	6																				V	
36·053	6			Ti																		Blend
35·922				Ti																		
35·575	6			Ti																		
34·782	6			Ti																		
33 244	7			Ti																		
31 348	4	*Sr*																				
29·586	1				V																	
27 812	6			Ti																		

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
4524 741	1	*Sn*																				
24·216	0				V																	
23 237	7n										Ba											
18 032	4			Ti																		
12 738	4			Ti																		
05 934	7										Ba											
4497 724	40					Na																
94 266	20					Na																
88 889	1	*V*																				
74 714	1	*V*																				
69 710	5							V														
62 363	6							V														
60·292	10									V												
59 760	7									V												
57 479	6									V												
56 612	3								Ca													
55 887	12								Ca													
54 781	18								Ca													
52 008	6							V														
49 148	0	*Ti*																				
48 0	1						LaO															Band-head
44 207	7									V												
43 069	1n	*Mo*																				?
41 683	7									V												
37 837	8									V												
35 688	10								Ca													
34 960	16								Ca													
33 0	1						LaO															Band-head
31·898	10										Ba											
29·796	6											V										

Table VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4428 515	6									V												
28 2	3						LaO															Band-head
27 312	4	*Fe*																				
27 101	3	*Ti*																				
26 005	6											V										
25 441	12								Ca													
23 1	4						LaO															Band-head
21 578	7											V										
19 935	3									V												
18 2	5						LaO															Band-head
16 474	7											V										
15 125	5												Fe									
08 511	10											V										
08 204	7											V										
07·637	8											V										
06 641	9											V										
04 752	7												Fe									
02 551	8n																		Ba			
00 575	8											V										
4395 228	10											V										
89 974	11											V										
87 6	0															LaO						Band-head
84·977	12														Cr							Blend. Vanadium line occurs in two multiplets
84 722												V		V								
83 547	7												Fe									
81 640	1	*Mo*																				
79 238	14											V										
75 8	2															LaO						Band-head
74 80	4	*Rh*																				
72 0	2															LaO						Band-head

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
4371 279	1														Cr							
68 042	2													V								
61 815	2n	*W*																				?
59 631	3														Cr							
55 943	1													V								
54 804	0	*La*																				
52 872	8													V								
51 770	6														Cr							
51 051	3														Cr							
50 375	1n										Ba											
47 892	5	*Zr*																				
44 507	6														Cr							
41 013	7													V								
39 718	3														Cr							
39 450	5														Cr							
37 566	4														Cr							
33 734	2	*La*II																				
32 823	7													V								
30 024	7													V								
25 765	7																Fe					
18 652	16																	Ca				
14 801	4	*Ti*																				
09 795	5													V								
07 906	16																Fe					Blend
07 741																		Ca				
06 214	3													V								
05 916	7																		Ti			
02 527	20																	Ca				Blend
02 108																				W		
01 088	6																		Ti			

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
4300 565	6																		Ti			
4298 986	14																	Ca				Blend
98 665																			Ti			
98 029	4		V																			Blend
97 681			V																			
96 107	2		V																			
95 756	2																		Ti			
94 614	6																				W	
93 210	0			Mo																		
91 816	4		V																			
90 937	1																		Ti			
89·721	10				Cr																	
89 364	12																	Ca				
87·405	1																		Ti			
86 009	2																		Ti			
84 055	4					V																
83 010	14																	Ca				
80 261	7							La														
77 242	2			Mo																		
76 958	6					V																
74 803	10				Cr																	
71 764	8																Fe					
71 554	3					V																
69 392	1	*W*																				
68·643	7					V																
62·161	0					V																
54 346	12				Cr																	
50 790	4																Fe					
46 829	8	*ScII*																				
41·687	3								Zr													

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4241·202	4								Zr													
40·339	4								Zr													
39 314	5								Zr													
38 879	0									LaII												
35 943	6										Y											
35·290	2	*Mn*																				
32 586	1	*Mo*																				
27 758									Zr													
26 728	50	*Ca*																				Blend
26 570		*Ge*																				
15 556	20											Rb										Blend
15 524														SrII								
13 865	1								Zr													
12 950	2	*Pd*																				
12 063	1	*Ru*																				
11 728	6	*Ti*																				
09 857	4												V									
02 031	7n																Fe					Blend
01 851												Rb										
4199 902	2	*Ru*																				
99 099	2	*Fe*																				
96 547	1									LaII												
94 762	5	*Zr*																				
91 558	1												V									
90 884	1	*Nb*																				
89 841	4												V									
88 321	2	*Mo*																				
87 316	7							La														
86 777	4														Zr							
82 591	4												V									

Table VII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4179 419	5															V						
77·486	2	*La*																				
74 133	7																Y					
72 056	16																	Ga				
68 126	5																		Nb			
67 507	6																			Y		
66 365	0								Zr													
65·184	1																				Sc	
64 660	5																		Nb			
63 657	5																		Nb			
60 264	2	*La*																				
59·686	1															V						
53 910	0	*Fe*																				
52·576	6																		Nb			
52 355	1																				Sc	
51·955	1		LaII																			
50 962	2	*Ti*																				
43 871	6			Fe																		
43 549	1	*Mo*																				
43 046	2	*Ti*																				?
42 839	8										Y											
40 304	0																				Sc	
39 707	2																		Nb			
37·095	6																		Nb			Blend
37·025									La													
34 488	10			V																		
32 431	8	*Ba*																				
32 060	10			Fe																		Blend
32·017				V																		
30·664	5n				BaII																	

TABLE VII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4128 304	8										Y											
28 071	9			V																		
23 810	4																		Nb			
23 566	9			V																		
21 319	7					Co																
20 538	4										V											
19 457	5										V											
18 773	6					Co																Blend
18 643											V											
16 703	10			V																		Blend
16 470				V																		
15 185	12			V																		
13 518	4			V																		
12 714	2	*Ti*																				
11 785	14			V																		
10 535	0	*Co*																				
09 786	10			V							V											Occurs in two multiplets
07 495	0														Zr							
05 167	10			V																		
04 877	3										La											
03 850	In																					?
02 376	11																			Y		
02 159	4										V											
00 923	6																		Nb			
4099 796	10			V																		
95 486	7										V											
92 694	8			V																		
90 579	7										V											
89 612	4										La											
86 714	4	*LaII*																				

TABLE VII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
4083·713	7																Y					Blend
83 628							Mn															
82 944	5						Mn															
82 896	8							Sc														
81 215	6									Zr												
80 600	3	*Ru*																				
79 729	6																		Nb			
79·422	3						Mn															
79·241	4						Mn															
77 714	20													SrII								Blend
77 866																				Y		
74·364	6																				W	
72 704	6									Zr												
71 740	7			Fe																		
69 882	1	*Mo*																				
65·580	1											La										
64 783	4										La											
64·155	5									Zr												
63 597	7			Fe																		
62 076	0	*Mo*																				
60·321	6										La											
58 938	8																		Nb			Blend
58 930							Mn															
57·820	14												Pb									In multiplet with 2833·069 in Table VIII
55 543	7						Mn															
55·030	4									Zr												
54·555	7							Sc														
53·837	1	*Ti*II																				?
51·352	4																		V			
50·963	0																		V			

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
4048 755	6						Mn															
47·792	7													Sc								
47 632	5																Y					
47·201	6														K							
45 815	8			Fe																		
44·140	7														K							
43 576	3	*Zr*																				
42 911	1	*LaII*																				
41 361	7						Mn															
39 834	4										Y											
37·214	5								La													
35·728	6						Mn															
34 490	14															Mn						
33 073	18															Mn						Blend
32·982																		Ga				
31·692	1		LaII																			
30·755	16															Mn						
30·039	1									Zr												
27·205	1									Zr												
24·918	0									Zr												
24·573	3																Ti					
23·688	10													Sc								
20 399	9													Sc								
18 102	6						Mn															
15 393	5																	La				
09·717	1	*Fe*																				
08·928	4																Ti					
08 753	7																				W	
08·020	5	*Mn*																				
05 246	6			Fe																		

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3998 730	8								V													Blend
98·640																	Ti					
97 92	4																			Ba		
96 607	7													Sc								
95 664	6																			Ba		
95 310	7	*Co*																				
93 404	10n																			Ba		
92·801	6								V													
91·123	1																		Cr			
90 566	6								V													
89 763	7																Ti					
88 518	1		LaII																			
87 994	7	*Yb*																				
83 907	2																		Cr			
82 484	3	*Ti*																				
81 764	7																Ti					
76 665	3																		Cr			
73 707	8n																				Ca	
69 748	1																		Cr			
69 261	6			Fe																		
68 468	20		CaII																			
64 272	4																Ti					
63 690	5																		Cr			
62 852	5																Ti					
61 527	10			Al																		
58 865	1	*Rh*																				
58·642	0	*Pd*																				
58 218	7				Ti																	
57 053	7n																				Ca	
56 343	7				Ti																	

TABLE VII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3953 680	1											La										
52 917	1					Co																
49 106	1									LaII												
48 901	6n																				Ca	
48 674	6				Ti																	
47 775	5					Ti																
44 032	10			Al																		
37 876	6n																			Ba		
35 725	10n																			Ba		
33 666	18		CaII																			
31 340	1	*V*																				?
30 299	6								Fe													
30 023	1	*V*																				
29 875	2				Ti																	
29 530	4							Zr														
28 636	1										Cr											
27 922	6								Fe													
27 558	4																	La				
25 947	3	*Fe*																				
25 240	4																V					
24 529	5				Ti																	
22 914	6								Fe													
22 431	4														V							
21·792	3											Zr										
21 424	1					Ti																
21 022	1										Cr											
20 260	6								Fe													
19 159	5										Cr											
14 335	4												Ti									
12 207	1														V			V				Occurs in two multiplets

TABLE VII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3911 810	10														Sc							
09 917	8																			Ba		Blend
09 894																				V		
08 755	2										Cr											
07 476	9														Sc							
06 748	1														V			V				Occurs in two multiplets
06 482	1								Fe													
04·785	5	*Ti*																				
02·963	9									Mo												Blend
02 948											Fe											
02 250	9																			V		
3899·709	6								Fe													
95 658	6								Fe													
94 982	0											Co										
94 081	7													Co								
92·859	7																			V		
91 785	2				BaII																	
91 383	6	*Zr*																				
90 318	3											Zr										
90 184	7																V					
89 316	7	*Ba*																				
88 517	4										Fe											
87 051	5														Fe							
86 284	7								Fe													
85 425	4							Zr														
83 4	6																CN					Band-head
81·874	5											Co										
78·575	6								Fe													
78·021	5														Fe							
77·595	3	*Zr*																				

TABLE VII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3876 086	7																V					
75 902	4																			V		
75 256	2												Ti									
75 075	8																			V		
73 955	6											Co										
73 115	7											Co										
72 504	4														Fe							
71 631	1	*LaII*																				
71·3	2																CN					Band-head
71 078	2	*V*																				
67 975	3																			W		
67 602	4																			V		
65 526	4														Fe							
64 862	7																			V		
64·110	8									Mo												
63 874	4											Zr										
62 826	0	*Ti*																				
62 223	1																V					
59 913	8								Fe													
58 301	5	*Ni*																				
56 373	6								Fe													
55 841	8						V															
55 370	6																			V		
49 969	2														Fe							
49 254	3	*Zr*																				
49 013	0	*LaII*																				
47 331	5																			V		
45·471	6													Co								
44·438	5																			V		
43 983	0																Mn					

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3842 050	1	*Co*																				
41·082	5																Mn					Blend
41 051											Fe											
40 752	8						V															
40 439	5														Fe							
38 258	5n															Mg						
35·964	5											Zr										
34·364	1																Mn					
34 225	6														Fe							
33 862	3																Mn					
32 306	4n															Mg						
29 350	3															Mg						
28 559	7						V															
27 825	5										Fe											
25 884	7														Fe							
24 444	6								Fe													
23 893	1																Mn					
23 513	4																Mn					
23 213	4																				V	
22 888	4																				V	
22 009	5						V															
21 487	3																				V	
20 429	7														Fe							
19 963	3																				V	
18 244	6						V															
15·842	6										Fe											
13 492	6						V														V	Occurs in two multiplets
09 597	3																				V	Blend
09 592																	Mn					
08 521	5						V															

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3807 505	3																				V	
07 144	1	*Ni*																				
06 719	5																Mn					
03 474	5																				V	
02 923	0	*Nb*																				
00 996	4																		Sn			In multiplet with 3330 594 in Table VIII
3799 912	4																				V	
99 549	1																	Fe				
99 347	4																			Ru		
98 901	3																			Ru		
98 513	4																	Fe				
98 252	8									Mo												
95 004	6																	Fe				Blend Vanadium line occurs in two multiplets
94 964							V														V	
90 324	1n																				V	Blend
90·215																	Mn					
86 055	0																			Ru		
80 538	2											Zr										
78 684	0																				V	
75 72	10n											Tl										Forms doublet with [5350 46
67 194	4																	Fe				
63 790	5																	Fe				
58 235	6																	Fe				
52 860	4		Ti																			
49 487	6																	Fe				
48 264	5				Fe																	
45 903	4				Fe																	
45 564	6				Fe																	
41 062	3		Ti																			
37 133	7				Fe																	

TABLE VII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3734 867	8																	Fe				
33 319	1				Fe																	
22 564	1				Fe																	
19·935	7				Fe																	
05 567	3				Fe																	
05 035	2							V														
04·699	5							V														
03 584	6							V														

Table VIII

IDENTIFICATIONS OF LINES APPEARING ON PLATES VII and VIII (ULTRA-VIOLET REGION)

(For explanation see pp 92–95; the symbol "n" in the "Intensity" column indicates that the line is "nebulous.")

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3558 518	5		Fe																			
56 597	3				ZrII																	
55·755	1	*Th*																				
53·082	6	*Pd*																				
52 721	3					Co																
51 951	2						ZrII															
50·595	4							Co														Blend
50 460		*Zr*																				
49 543	3	*Rh*																				
49 011	3	*YII*																				
48 185	3								Ni	Ni												Occurs in two multiplets
47 682	6										Zr											
43 948	3											Rh										
42 623	1	*ZrII*																				
39·369	2												Ru									
38 142	1	*Rh*																				
37 466	4	*Re*																				
36 557	3	*Fe*																				
35·729	3	*ScII*																				
35 301	4													Nb								
34 529	1	*Th*																				
33 676	5														V							
33 358	5															Co						Blend
33 217		*Zr*																				

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3532 121	3																Mn					Blend
31 998																	Mn					
31 848																	Mn					
29 813	8																	Co				Blend
29 735															V							
29·033	4															Co						
28 024	6																		Rh			
26 849	8							Co														
26·169	2		Fe																			Blend
26 042				Fe																		
24 541	10																			Ni		
23 434	4																				Co	
23 021	1	*Hf*																				
21 567	4		Co																			
21 264	1		Fe																			
20 081	3							Co														
19 605	8										Zr											
19·24	3			Tl																		
18 349	4				Co																	
17 301	0					V II																
16 943	6	*Pd*																				
15 549	1	*Be*																				?
15 054	10						Ni															
14·488	2												Ru									
13 933	1							Ni														
13 480	4															Co						
12 641	6																				Co	
10 426	6					Co																Blend
10 338																				Ni		
09 843	4																	Co				
09 323	6								Zr													

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3507 960	1													Nb								
07 316	3									Rh												
06 843	1										V											
06 315	10																				Co	
05 690	1										V											Blend
05 669							ZrII															
04 439	1					VII																
02 624	8					Co																Blend
02 524										Rh												
02 279	12																				Co	
01 116	16	*Ba*																				
00 852	3											Ni										
00 041	1																					?
3499 576	0				ZrII																	
98 942	8												Ru									
98 629	1	*Nb*																				
97 843	3			Fe																		
97 491	2	*Hf*																				
96 681	1	*Co*																				
96 210	4						ZrII															
95 687	5																	Co				
93 526	1	*Th*																				
92 956	10																			Ni		
91 321	1					Co																
90 736	6		Co																			Blend
90 575				Fe																		
89 772	1	*Pd*																				
89 402	6				Co																	
86 520	1	*Th*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3485 888	1							Ni														Blend
85 867											V											
85·267	1	*Pt*																				
83 774	3											Ni										
83·410	3												Co									
82 809	3								*Zr*													Possibly blended with line of greater wave-length
81 152	6													Pd								Blend
81·146															ZrII							
80 530	1	*Ti*																				
79 392	3														ZrII							
78 906	4											Rh										
76 704	4			Fe																		
75 454	6			Fe																		
74 780	3									Rh												
74 022	6							Co					Co									Occurs in two multiplets
72 545	5								Ni													
71 189	4								Zr													
70 657	3																		Rh			
69 926	1	*Th*																				
69 486	3n															Ni						
67 502	3									Ni												
66 647	1	*Th*																				Blend
66 536		*Th*																				
66 201	1	*Cd*																				
65 863	8			Fe																		Blend
65 800																Co						
64 722	6																Re					
64 37	3	*Yb*																				
62 803	6												Co									
62 040	3																		Rh			
61·652	8							Ni														

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3461 176	3	*Co*																				
60 774	6													Pd								
60 47	8																Re					
59 918	1	*Fe*																				
58 934	1	*Zr* II																				
58 474	8						Ni															
57 494	1	*Ti*																				
57·152	1	*V* II																				
56·387	1	*Mo*																				
55 908	2	*Zr*																				
55 234	3					Co																
54 551	1																					?
54 004	3																					?
53 505	10																	Co				
52 890	4							Ni														
51 808	5																Re					
49 441	4																	Co				
49 170	5																	Co				
47 701	0																	K				
47 365	3	*Zr*																				
47 123	2	*Mo*																				
46 722	1																	K				
46 263	6								Ni													
45 151	1	*Fe*																				
43 878	3			Fe																		
43 641	6																	Co				
42 926	3					Co																
41 396	4	*Pd*																				
40 991	4			Fe																		
40 610	5			Fe																		

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3438 230	3						Zr II															
37 280	4									Ni												
36 737	4												Ru									
35 555	3																		Sc			
34 893	6									Rh												
34 045	1	*Mo*																				
33 558	5	*Pd*					Ni															Blend
33 449																						
33·040	4												Co									
31 575	3					Co																
30 532	1																			Zr II		
29 483	1																		Sc			
29 000	1	*Th*																				
28 309	3	*Ru*																				
27·449	1	*Nb*																				
27·0	4n	*Na*																				
25 070	1	*V*																				
24·604	2	*Re*																				
23 991	1	*Th*																				
23 711	4								Ni													
22·660	1	*Fe*																				
21 24	6																				Pd	
19 659	1	*Zr*																				
19·175	1	*Hf*																				
18·519	1	*Mo*																				
17·843	0	*Fe*																				
17·353	2	*Ru*																				
17·160	4												Co									
15·205	1																					?
14·765	8						Ni															

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3413 939	1							Ni														
13 478	2		Ni																			
13 019	1	*Th*																				
12 633	4					Co																
12 339	5			Co																		
10 248	1																			Zr II		
09 177	4												Co									
08 750	1	*Th*																				
08 134	1	*Pt*																				
07 461	1	*Fe*																				
06 837	1				V																	
05 937	1					Mo																
05 561	1	*Th*																				
05 120	7												Co									
04 580	6													Pd								
04 342	1					Mo																
02 571	2				V																	
01 739	1	*Ru*																				
00 395	2				V																	
3399 696	1	*Rh*																				
99 299	2	*Re*																				
98 548	2	*Th*																				
97 580	1						V															
96 85	4																		Rh			
95 375	3			Co																		
94 575	1							Ti II														
92 992	6								Ni													
91 975	5						Zr II															
91 050	4		Ni																			
90 403	1	*Co*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3389 439	1	*Ru*																				
88 612	1	*La*																				
88 173	3												Co									
87 837	1							Ti II														
85·946	4								Ti													
85 664	1									Ti												
85·224	2																	Co				
84·616	2					Mo																
83 761	2							Ti II														
82 891	14										Ag											
81 498	1	*Co*																				
80 910	4											La II										
80 574	5	*Ni*																				
80 280	0							Ti II														
79 966	1	*Mo*																				
79 216	½									Ti												
77 625	5						V															Blend
77·585									Ti													
77·894	1						V															
76 329	0	*La II*																				
76 057	1						V															
74 925	2												Nb									
74·221	2							Ni														
73 417	1	*Zr II*																				?
73·001	4																				Pd	
72·800	4							Ti II														
72·151	4													Sc II								
71·454	6									Ti												
70·439	4								Ti													
69 573	5											Ni										

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3368·946	3													ScII								
67·109	3																	Co				Blend
66 956													Nb									
66·333	4n																	Sr				Blend
66·168																Ni						
65·766	1	*Ni*																				
65 553	1						V															
63 776	1	*Mo*																				
61 935	3n													ScII								Blend
61·918															Ca							
61 556	2						Ni															
61·270	4													ScII								Blend
61·263									Ti													
61·213								TiII														
60 990	1									Ti												
60 455	1	*Zr*																				
59 895	1	*Rh*																				
59 679	1													ScII								
58 417	3															Nb						
58 124	2					Mo																
57 264	0																ZrII					
56 352	2						V															
56 091	1																ZrII					
54·635	6									Ti												
54 377	1												Co									
53 734	4	*ScII*																				
51·246	4n																	Sr				Blend
50 89																			Rb			
50 209															Ca							
49 406	4							TiII														

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3349 059	4															Nb						Blend
49 035																				Ti II		
48 72	1																		Rb			
46 935	1	*Co*																				
46 742	1n	*Cr*																				
45 860	1	*W* II																				
44 746	1					Mo																
44 560	3											La II										
44 513	1														Ca							
43 709	4															Nb						
42 224	3	*La*																				
41 974	6															Nb						Blend. Lines of Ti I and Ti II coincident
41 875										Ti										Ti II		
40·555	1																Zr II					Blend
40 344																					Ti II	
39 552	2	*Ru*																				
38 545	1																		Rh			
37 844	1	*Cu*																				
37 488	5											La II										
35 195	1																				Ti II	
34 605	1	*Th*																				
34 137	3												Co									
33 605	0	*Cr*																				?
33·129	1	*Th*																				
32 729	3	*Hf*																				
31·672	1	*W*																				?
30 594	4																		Sn			In multiplet with 3800 996 in Table VII
30 475	3	*Th*																				
29 988	5																	Sr				Blend
29 855		*V*																				

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3329 456	1																				TiII	
27 875	4	YII																				
25 132	1	*Th*																				
23 949	1	*Mo*																				
23 092	5		Rh																			Blend
22 937																					TiII	
22 231	4																	Sr				Blend
22 199		*Co*																				
21 343	3			Be																		
21 086	2			Be																		Blend
21 013				Be																		
20 257	3	*Ni*																				
19 025	2n					ZrII																Blend
18 840		*Ta*																				
15 663	4				Ni																	
14 423	4						Ti															
12 865	3	*Hf*																				
12 600	1							Nb														
10 274	1	*Hf*																				
09 501	2						Ti															
02 988	35R								Na													
02 323	30R								Na													
3298 139	3									V												
92 075	2	*Ti*																				
91 676	1									V												
90 823	1	*Mo*																				
89 37	3	YbII																				
89 015	2	*Mo*																				
87 249	1																				Pd	
86 755	2	*Fe*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3285 668	1							Nb														
84·713	2					ZrII																
84 860	1	*V*																				
83 573	2		Rh																			
83 311	3									V												
82 732	1											Zr										
80·683	18										Ag											
79·265	3																ZrII					
77 672	1	*Nb*																				
76 124	4										VII											
73 962	12												Cu									
73 619	6													Sc								
73 047	4																ZrII					
72 080	1														TiII							
71 652															TiII							Blend
71 637	5									V												
71 612												Rh										
71·125	4										VII											
71·118	1	*Ni*																				
69 904	7													Sc								
69 657	3n	*Zr*																				Blend
69 494		*Ge*																				
67 702	3										VII											
67·502	1															Sb						
67 002	1	*Th*																				
65 67	3											LaII										
64·711	2																	Mn				
63·238	5									V												
62·671	1	*Th*																				
62 328	7	*Sn*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3261·605	1														Ti II							
61 057	5	*Cd*																				
60 231	3																		Mn			
60 111	2	*Zr*																				
59 549	1	*Re*																				
58 780	4																Pd					
58·413	3																		Mn			
57 369	2	*Th*																				
56 137	4																		Mn			
55 678	5													Sc								
54 778	1																			V		
54 250	3		Ti II																			
52 948	4																		Mn			Blend
52 914			Ti II																			
51 911	2		Ti II																			
51 640	3	*Pd*																				
51 135	0																		Mn			
50 777	1	*Y* II																				
50 392	2											*Zr*										
49 566	3																			V		
49 351	1																				La II	
48 602	4														Ti II							Blend
48 516																			Mn			
47 540	18												Cu									
45 120	3	*La* II																				
44 450	0	*Th*																				
43 780	4																		Mn			
43 058	4				Ni																	
42 703	6																				Pd	
42 280	4			Y II																		

Table VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3241 986	3		TiII																			
41 046	2					ZrII													Mn			
40 616	1																	Mn				
40 399	0																					
39 436	0	*Fe*																				
39 038	4		TiII																			
38 118	1n	*Th*																				Blend
37 874		*V*II																				?
37 075	1	*Mo*																				
36 778	4																		Mn			
36 573	3		TiII																			
34 516	4		TiII																			
34 124	5											Zr										
33 190	1					V																
32 963	4	*Ni*																				
32 499	0															Sb						
32 055	1	*Os*																				
31 693	3																ZrII					
30 719	4																		Mn			
29 75	1	*Tl*																				
29 193	2		TiII																			
28 090	6																		Mn			
26·106	1							V														Blend
26 034																			Mn			
25 789	1				Fe																	
25 478	1						NbII															
25 020	1	*Ni*																				
24 761	1	*Mn*																				
22 842	2		TiII																			
21 911	1	*W*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3221 652	2															Ni						
20 780	2	*Ir*																				
18 869	2					V																
17 830	1	*Ni*																				
17 503	0								K													
17 060	2		TiII																			Blend
17 017									K													
16 682	4			YII																		
15 813	2									La												
15 560	3										W											
15 073	2	*Mo*																				
14 243	4n											Ti										Blend
14 189																	ZrII					
12 884	2																		Mn			
12 434	5												V									
12 013	4											Zr										
10 097	1													V								
08 834	5														Mo							
07 410	6							V														
05 883	1	*Mo*																				Blend
05 848		*Ti*																				
05 582	4												V									
05 262	0													V								
04 895	1	*Zr*																				
04 040	1															Pt						
03 828	3											Ti										
03 323	4			YII																		
02 381	7							V														
00 270	2			YII																		
3199 915	8											Ti										

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3198 841	1	*W*																				
98 012	6							V														
97 113	2																Ni					
96 930	2				Fe																	
95 615	3			Y II																		
94 977	0						Nb II															
94 234	1	*Os*																				?
93 973	10																	Mo				
93 228	1	*Fe*																				
92·586	1	*Th*																				
91·994	6											Ti										
91 214	4											Zr										
90 678	3																		V II			
88·513	2																		V II			
87·708	2																		V II			
87 493	1																			Nb		
86 454	6											Ti										
85 396	12							V														
83·982	10							V														
88 406	8							V														
82 858	0																				Zr II	
81 275	1n		Ca II																			
80·947	2	*Ta*																				
80 226	3				Fe																	
79 332	6n		Ca II																			
78 244	2	*Th*																				
77 273	0	*Co*																				
75 987	1n									La												
75·019	8			Sn																		
73·427	1	*Th*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3172·942	4	*Hf*																				?
70 620	3																	Mo				
70·347	6																					
69 767	0						Co															
68 521	3				TiII																	
65 97	3							ZrII														
64 39	2	*Hf*																				
63·756	1	*Cr*																				
63·402	2						NbII															
62 570	4				TiII																	
61·774	1				TiII																	
61·205	1				TiII																	
59 823	3	*Hf*																				
58 869 }	5n		CaII																			} Blend
58 775 }									Co													
58 165	5														Mo							
57·823	4	*Zr*																			Zr	Singlet and multiplet lines [coincident
56 626	3	*Hf*																				
56·248	0	*Os*																				
54 794	3	*Co*																				
51·870	1																			Nb		
49 313	1									Co												
48 820	2					Zr																
48 414	1	*Hf*																				
47 064	3								Co													
45 719	0										Ni											
42 762	1																				LaII	
42 444	0	*Cu*																				
41 809	0	*Sn*																				
41 537	1	*Ti*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3140 312	1	*Cu*																				
39 943	2									Co												
39 801	1	*Zr*																				
39 386	2											Pt										
38 678	2							ZrII														
37 327	2								Co													
36 958	3												Zr									
36 218	2	*Th*																				
34·108	5													Ni								
33·328	3n														VII							Blend
33 321		*Ir*																				
32 878	3	*Ru*																				?
32 594	6																	Mo				
32 066	3					Zr																Blend
32 058																CrII						
31·814	2	*Hf*																				
31 110	3					Zr																
30·786	1						NbII															
30 267	3n														VII							
29 761	1							ZrII														
29·176	1																				ZrII	
26 215	3														VII							
25 284	4														VII							
24·978	1															CrII						
23 074	2	*Ti*																				
22 781	3	*Au*																				
21·415	2									Co												
21·145	2														VII							
20·741	4					Zr																
19 725	2	*Ti*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3118·383	4														VII							
16 848	2	*Cu*																				
14 124	4	*Pd*															Ni					Blend
14·040																						
13·506	1					Zr																
12 124	4														Mo							
10·706	5														VII							
10 021	0						Co															
09 436	1																La					
08 374	1																	Zr				
06 576	1	*Zr*II																				
05 469	2																		Ni			
04 589	0	*La*II																				
03 226	2																					?
02 299	5														VII							
01 879	5	*Ni*																				
01 554	6													Ni								
00 666	3																			Fe		
00 304	3																			Fe		
3099 971	3																			Fe		Blend
99 897																				Fe		
99 230	1							ZrII														
99 115	2	*Ni*																				
98·196	1								Co													
97·118	3										Ni											
96 023	1																La					
95·823	2																				Zr	
94·799	3n																				Zr	Possibly blended with line [of smaller wave-length
94 183	1						NbII															
93 792	0		V																			

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3093 108	5														VII							
92 842	6			Al																		Blend
92 713				Al																		
91 578	2																			Fe		Blend
91 52				V																		
91 437	1			V																		
90 437	1												Zr									
89 595	2								Co													
89 130	3		V																			
88 025	4					TiII																
87·065	1		V																			
86·777	3																			Co		
85 615	2	*Mo*																				
85·344	1	*Zr*																				
83·742	3																			Fe		
82 618	3								Co													
82 155	8			Al																	V	Blend
82 109																						
80·755	4																	Ni				
80 330	1		V																			
78·645	3					TiII																
77 720	2	*Os*																				
75·721	3																			Fe		
75 269	3n	*V*																				Blend
75·224						TiII																
74·791	2	*Hf*																				
74 374	2	*Mo*																				
74 08	1	*Os*																				
73·823	5			V																	V	Occurs in two multiplets
72·877	4	*Hf*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3072 344	3																			Co		
71 591	6	*Ba*																				
70 266	0	*Mn*																				
69 645	4			V																		
69 237	0	*Ta*																				
68 890	1	*Ir*																				
67 716	7	*Bi*																				
67 244	1n																			Fe		Blend
67 2					OH																	Band-head
66 375	8																				V	
65 306	3																				Pd	
65 042	1	*Mo*																				
64 712	5											Pt										Blend
64 623																		Ni				
64 279	2	*Mo*																				
63 6	3n				OH																	Band-head
61 819	4																			Co		
60 460	6																				V	
59 086	5						Fe															
58 66	1	*Os*																				
57 638	5																	Ni				
57 446	4																			Fe		
57 016	3	*Hf*																				
56 615	1	*Nb*																				?
56 334	6																				V	
55 263	1							Fe														
54 316	4													Ni								
53 880	3								Cr													
53 65	5																				V	
52 194	3			V																		

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3050 819	6													Ni								
49 691	2	*W*																				
48 888	2																			Co		
48 096	1	*Nb*																				
47 821	1	*Mo*																				?
47 605	5						Fe															
47 035	2									Mn												
46 452	1										W											
45 829	1																				Zr	
45 593	1									Mn												
45 369	0	*Y*																				
44 936	4																				V	
44 567	1	*Mn*																				
44 005	5																			Co		
43 555	4																				V	
43 124	4																				V	
42 665	3	*Pt*																				
41 866 }	3n											W										} Blend
41 701 }		*Mo*																				
40 846	3										Cr											
39 780	0								Cr													
39 064	5	*Ge*																				
37 935	4													Ni								
37 388	4						Fe															
37·044	3										Cr											
36 450	0	*Pt*																				
34 190 }	6								Cr													} Blend
34·121 }				Sn																		
31 870	0										Ni											
31 639	0												Fe									

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
3031 353	0										Cr											
30 769	2														Sc							
30 450	0	*Re*																				
30 245	4										Cr											
29 807	1															Sb						
29 515	5													Zr								
29 164	1								Cr													
27 910	3																Pd					
26 461	1												Fe									
25 842	4						Fe															
24 920	1															W						
24 635	1	*Bi*																				
24 350	4								Cr													
24 033	3																Fe					
22 749	1	*Mn*																				
22 281	1																	Y				
21 78	1	*V*																				
21 558	6										Cr											
21 073	5						Fe															
20 673	6										Cr											Blend
20 640							Fe															
20 489	3						Fe															
19 350	5														Sc							
19 143	0										Ni											
18 821	1								Cr													
18 496	2								Cr													
18 314	3	*Hf*																				
17 569	6										Cr											Blend
17 546																				Co		
16 784	3																			VII		Blend
16 78		*Hf*																				

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3016 454	2	*Mn*																				
16 185	2												Fe									Blend
16 16																			V			
15 364	5														Sc							
15 194	4										Cr											
14·915	5										Cr											
14·760	3										Cr											
13·713	3								Cr													
13 030	1								Cr													
12 537	2	*Ta*																				
12·004	5	*Ni*																				
11 748	4													Zr								
09 570	3												Fe									
09·205	7																				Ca	Blend
09 147				Sn																		
08 139	5						Fe															
07 281	1																Fe					
07 145	1							Fe														
06·858	7																				Ca	
05·497	3	*Zr*																				
05 370	0																	Zr				
05·062	4		Cr																			
03·629	5																	Ni				
03 031	1												Fe									
02·728	1			Ti																		
02·491	6																	Ni				
01 205	1																			VII		
00 951	7						Fe															Blended with next two lines
00 890			Cr																			

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
3000·868	7			Ti																		Blended with previous two lines
00 863																					Ca	
2999 641	5																				Ca	
99 512	4												Fe									
99 238	1																		V			
98 787	3				Cr																	
97 967	5	*Pt*																				
97 314	6																				Ca	
96 580	4		Cr																			
94·964	5					Ru																Blend
94 958																					Ca	
94 460	6	*Ni*																				Blend
94 429							Fe															
94 069	1				Cr																	
93 611	2	*W*																				
93 342	0	*Bi*																				
92 595	4													Ni								
92 372	1	*Re*																				
91 886	4		Cr																			
90 948	1																		V			
89 588	3	*Co*																				
89 029	4	*Bi*																				Blend
88 952							Sc															
88 649	3				Cr																	
88 234	1	*Th*																				
87 648	0	*Si*																				
87·292	1												Fe									
87 162	3																			Co		
86 788	1	*Th*																				
86 473	6		Cr																			

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2985 905	4		Cr																			
85 849	3		Cr																			
85 389	4													Zr								
84 256	3																	Y				
84 131	2																		Ni			
83 818	1	*Th*																				
83 572	6						Fe															
83 306	1			Ti																		
81 651	4																	Ni				
81 448	4			Ti																		Blend
81 446																	Fe					
80·810	6	*Hf*																				Blend
80 791			Cr																			
80 752							Sc															
79 858	2	*W*																				
79 280	1	*Hf*																				
77 539	5								V													
76 520	1							Vii														
75 483	4		Cr																			
75 056	1	*V*																				
74 593	3																	Y				
74 006	4						Sc															
73 536	1	*Th*																				
73 237	6									Fe												
73 134	3									Fe												
71·112	4		Cr																			
70 881	1			Ti																		
70·105	4									Fe							Fe					Occurs in two multiplets
69 477	1												Fe									
69 189	2													Zr								

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2968 378	1							V II														
67 642	4		Cr																			
67 225	2										Ti											
66 900	6									Fe												
65 86	3						Sc															
65 545	1	*Ta*																				
65 264	4									Fe												
64 968	1											Y										
64 876	4	*Hf*																				
64 515	1	*W*																				
63 322	2	*Ta*																				
62 772	5								V													
61 024	3	*Os*																				
60 870	3	*Zr*																				
59 992	1	*Fe*																				
58 018	3	*Hf*																				
57 365	5									Fe												Blend
57 33									V													
56 797	2										Ti											
56 131	6										Ti											
55 799	3															V						
54 332	4								V													
54 205	4	*Hf*																				
53 940	5									Fe						V						Lines of Fe and V coincident
52 075	3												V II									
50 679	4	*Hf*																				
50 348	1												V II									
49 626	4															V						
49 205	3													Mn II								
48 405	1											Y										

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2948 255	5										Ti											
47 876	5									Fe												
47 384	1	*W*																				
46 981	4	*W*																				
46 527	3								V													
44 395	3	*W*																				
44 175	4														Ga							
43 914	3																	Ni				
43 637	12														Ga							
43 196	3								V													
42 352	4								V							V						Occurs in two multiplets
41 995	5										Ti											
41 369	3												VII									Blend
41·343										Fe												
41 041	1	*Mn*																				?
40 772	5	*Hf*																				
40 215	1	*Ta*																				
39 304	3													MnII								
38 666	1	*V*																				?
38 298	2	*Bi*																				
37 687	3															V						
37 316	2										Ti											
37 141	0	*W*																				
36 905	5									Fe												
35 874	4															V						
34 991	3	*W*																				
34·648	1								V													
34 401	0												VII									
34 022	0	*Mn*																				
33·548	4										Ti											

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2933 068	3													Mn II								
31 836	5	*Sr*																				
30 806	3												V II									
29·794	5	*Pt*																				
29 008	4									Fe												
28 344	4	*Ti*																				
26 256	3																V					
25 124	0	*W*																				
24 792	2	*Ir*																				
24 633	4												V II									
24 017	5												V II									
23 620	7																	V				
23 098	0																		W			
22 575	1															V						Blend
22 492																	Pd					
20 690	0																				Fe	
20 385	2		V II										V II									Occurs in two multiplets
19 992	1		V II																			
19 931	0															V						
19 344	0	*Pt*																				
19 048	2	*Y*																				
18 576	3	*Hf*																				
18 32	2	*Tl*																				
17 932	2											V										
16 481	5	*Hf*																				
16 255	2					Ru																
16 019	2											V										
15 331	3																V					
14 926	5																	V				
12 158	4									Fe												

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2911 145	3																			Cr		
10 902	3																			Cr		
10 389	3		VII																			
10 019	3		VII																			
09 061	4	*Os*																				Blend
09 052																				Cr		
08 817	4			VII																		
07·471	3												VII									
07 216	0	*Mn*																				
06 457	3		VII																			
06·134	4																	V				
05 487	2																			Cr		
04 751	4	*Hf*																				
04·408	4	*Hf*																				
04 126	3																	V				
03·698	3																V					
03 078	1		VII																			
02 046	0	*Ta*																				
2899 597	4																	V				
99 201	4																	V				
98 259	5	*Hf*																				
97 975	3	*Bi*																				
97 873	2	*Pt*																				
96 753	3																			Cr		
96 446	4	*W*																				
96 211	0		VII																			
96·008	2											W										
95 035	0																				Fe	
94·577	3																	V				
94·171	3																			Cr		

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2893 865	3	*Pt*																				
93 314	4			VII																Cr		Blend
93 254																						
92 659	3			VII																		
92 441	1			VII																		
92 265	0				*Zr*																	
91 843	1	*Ta*																				
91·642	2			VII																		
89 621	4			VII																		Blend
89 619		*Hf*																				
89 265	4																			Cr		
88 246	0						VII															
87 666	3	*Re*																				
87 135	1	*Hf*																				
86 997	3																			Cr		
86 457	2					Y																
85 045	1	*Th*																				
84 785	2			VII			VII															Occurs in two multiplets
84 295	0	*Th*																				
82 501	2			VII																		
81 578	6	*Si*																				
80 030	2			VII																		
79 393	3															W						
79 274	1																			Cr		
79·107	3	*W*																				
78 716	2	*W*																				
77 915	4							Sb														
75 983	4				*Zr*																	
74 984	4					Ru																

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2874 244	12														Ga							Blend
74 172									Fe													
73 316	5	*Pb*																				
72 336	0										Fe											
71 632	1																			Cr		
71·417	0	*Ta*																				
70 547	5														V							
69 308	3								Fe													
68 108	4										V											
66 629	4										Fe											Blend
66·594											V											
66 373	5	*Hf*																				
66 061	3	*W*																				
65 107	1									Cr II												
64 359	6														V							
63 327	8			Sn																		
62 571	0									Cr II												
61 407	0	*Ru*																				
60 851	1				*Zr*																	
60 452	3												As									
59 971	4														V							Blend
59 963															Nb							
56 027	1	*W*																				
55·221	3														V							
53 081	4R													Na								
52 828	5R													Na								
52 129	3R	*Mg*																				Blend
51·798												Fe										
51·748															V							
50 618	1															Sn						
49 838	1									Cr II												

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2849 175	3														V							
48 774	2														V							Blend
48 718											Fe											
48 523	3	*Zr*																				
48 026	3	*W*																				
46 573	2	*V*																				
45 828	2	*Hf*																				
45 595	0										Fe											
45 353	0	*Ta*																				
43 979	4											Fe										
43 632	1										Fe											
43·257	3									Cr II												
42 815	0	*Ta*																				
41 570	3																W					
39 989	10			Sn																		
38 626	1	*Os*																				
38 120	3											Fe										
37 232	6				Zr																	
36 313	0	*Mn*																				
35 633	3									Cr II												
33 628	3	*W*																				
33 276	3	*Hf*																				
33 069	8												Pb									In multiplet with 4057 820 (in Table VII
32 436	4											Fe										
31 378	5	*W*																				
30 794	0	*Mn*																				
30 295	5	*Pt*																				
29 825	1	*W*																				
26 475	1														Nb							
25 689	1	*Fe*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2825 560	4	*Fe*																				
24 448	2	*Ir*																				
24 369	2	*Cu*																				
23 276	3											Fe										
23 179	4n	*Ir*																				
22 559	2					Y																
21 293	3	*Ni*																				
20 224	1	*Hf* II																				
19 955	0	*Re*																				
19 738	1	*Hf*																				
18 771	1	*Mn*																				?
18 361	0	*Ru*																				
18 060	4	*W*																				
17 972	1	*Mn*																				
16 154	1	*Mo* II																				?
15 559	2																		Co			
14 905	4				Zr																	
13 473	1	*Mn*																				
13 288	4											Fe										
12 845	1	*Mn*																				
10 553	3	*Ru*																				
10 033	1	*Ru*																				
09 106	3	*Mn*																				
08 39	1n	*La* II																				Blend
08 384		*Mn*																				
08 054	1														Nb							
06·984	3	*Fe*																				
06 793	1	*Mn*																				
06 581	1	*Ta*																				
06 301	0	*Ta*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2806 136	1	*Mn*																				
04·521	3											Fe										
04·344	0	*Mn*																				
04 095	1	*Mn*																				
02 695	8																	MgII				
02 500	3	*Ti*																				
02·003	10	*Pb*																				
01 064	14																			Mn		
2799 924	3																		W			
99 842	4	*Mn*																				
98 653	2																				Ni	
98 271	16																			Mn		
97 702	1	*Ir*																				
96 339	2	*Ta*																				
95·53	8																	MgII				
94 817	16																			Mn		
93 390	1	*Zr*																				
92 696	3	*W*																				
92 037	2n				Zr																	
91·089	1	*Mn*																				
90 356	2n	*Mn*																				
90 143	3	*Zr*																				
89 197	1	*Mn*																				
88 105	6											Fe										
85 689	2				V																	
85 031	1															Sn						
83 783	0				V																	
82 974	5		Mg																			
82 363	0	*Nb*																				
81 835	0					Fe																

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2781 417	5		Mg																			
80·703	3n			Cr																		Blend
80 521		*Bi*																				
80·197	4												As									
79 834	6		Mg																			
79 366	3	*Hf*																				
78 845	0	*Fe*																				
78·288	4		Mg																			Blend
78·221												Fe										
76 690	5		Mg																			
75 877	3	*Ta*																				
74 480	3				W																	
74 002	3						W															
73 679	3						V															
73 203	3								Nb													
73·017	2	*Hf*																				
72·109	4																		Fe			
71·666	3	*Pt*																				
70 881	3	*W*																				
69 939	4n							Sb														Blend
69·915				Cr																		
69 741	1	*W*																				
68·937	3						V															
67 87	6			Tl																		
67 523	3					Fe																
66 912	1																	Fe				
66·540	1	*CrII*																				
64 188	2																		Co			
63 419	2	*Ru*																				
63 092	4	*Pd*																				

Table VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2762 345	2											W										
62·032	3					Fe																
61 785	2					Fe																
61 755	2n			Cr																		
60 093	1	*Y*																				
59 817	0															Fe						
58 813	2									ZrII												
58 612	2								Nb													
58 310	3	*Ta*																				
58 075	1	*Ti*																				
57 320	2					Fe																
56 741	0																					?
56 834	4																		Fe			
55 737	2	*FeII*																				
54 592	7							Ge														
54 037	0																	Fe				
53 692	1					Fe																
52·206	2									ZrII												
51·472	1	*Mo*																				?
50 144	6																		Fe			
49 829	1	*Ta*																				?
48·849	4								Nb													Probably W line of same [wave-length superposed
48 286	4			Cr																		
47 161	0	*Th*																				
46 914	1								Nb													
46 746	1																				Ni	
45 855	1									ZrII												
44 991	3												As									
44 527	3					Fe																
44 072	5																		Fe			

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2743 638	1	*Hf*																				} Blend
43 565		*Fe*																				
42 557	1										Zr II											
42 408	6																		Fe			
42 256	1					Fe																
41 068	2	*Cr*																				?
40·431	2	*Ge*																				
39·807	1												Ti									
39 383	1	*Cr*																				?
39 218	0	*Ru*																				
37 834	0	*Fe*																				?
37 314	6																		Fe			
35 726	3	*Ru*																				
35 475	4					Fe																
34 855	1										Zr II											
33 961	5	*Pt*																				
33 584	6					Fe																
33 259	3												Ti									
32 721	0											Zr II										
31 346	4									V												
29 915	0	*Pt*																				
28 021	0	*Fe*																				
26 973	0	*Ru*																				?
26 493	2										Zr II											
26 054	2															Fe						
25 466	2	*Ru*																				
25 057	1																W					
24 959	0														Fe							
24 352	4	*W*																				
23 577	5																		Fe			

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2722 998	1	*Y*																				
22 610	4									Zr II												Blend
22 558										V												
21 645	3	*Ca*																				
20 905	6																		Fe			
19 653	4													Ga								
19 038	7	*Pt*																				Blend
19 025																			Fe			
18 901	2	*W*																				
18 588	1	*Hf*																				
18 435	2	*Fe*																				
16 181	0	*Cr*																				
15 987	0	*Co*																				
15 686	1															V II						
15 470	3	*Re*																				
14 674	4	*Ta*																				
13 839	1	*Hf*																				
11 736	0																V II					
11 654	1													Fe								
11 343	4																	Sc				
10 127	2	*Ta*																				
09 626	7							Ge														
08 921	1	*W*																				
08 570	2	*Fe*																				
07 863	2n																V II					Probably blended with line of greater wave-length
06 76	3																	Sc				
06 510	7			Sn																		
06 169	1															V II						
05 894	4	*Pt*																				
05 611	4	*Hf*																				

Table VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2702·399	5	*Pt*																				
02·189	1																V II					
01·989	2														Cr							
00·986	2															V II						
00·131	1											Zr II										
00·009	1	*W*																				
2699·590	3																			W		
99·107	1														Fe							
98·730	0	*V*																				
98·428	1	*Pt*																				
98·301	3	*Ta*																				
97·745	4																			V		
96·993	4																			V		
95·849	0										Co											
95·666	2																				W	
94·233	2	*Ir*																				
92·806	0																					?
92·422	0	*Th*																				
91·844	6							Ge														
91·091	0	*W*																				
90·245	1				V II																	
89·212	3	*Fe*																				
88·042 }	4n														Cr							} Blend
87·956 }					V II																	
87·802	1	*Fe*																				?
87·151	1		Nb																			
86·518	8					V																
86·294	0	*Ru*																				
85·341	0										Co											
84·276	2	*Ta*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2681·413	4	*W*																				
80·443	6			Na																		Blend
80 335				Na																		
79 062	1													Fe								
78 675	1					V																Blend
78 632											Zr II											
77 149	3	*Pt*																				
75 95	6	*Au*																				
74 337	2	*Re*																				
72 004	1				V II																	
71 673	2					V																
71 466	3				W																	
70 643	2							Sb														
69 598	2					Ti																
68 291	2		Nb																			
66 970	0	*Fe*																				
66 818	2														Fe							
65 964	2					V																
64 958	0	*W*																				
64 786	3	*Ir*																				
63 166	5	*Pb*																				
62 835	3						W															
61 983	3n	*Ir*																				Blend
61 970						Ti																
61 423	5							V														
61 248	4								Sn													
60 393	3n						Al															
59 866	4													Ga								
59 454	5	*Pt*																				
58 722	0	*Pd* II																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2658 174	1	*Pt*																				
57 616	1									Nb												
57 381	2	*W*																				
56 61	5	*Ta*																				Blend
56 539													W									
56 225	4							V														
54 448	3		Nb																			
53 274	4	*Ta*																				
52 921	0	*V*																				
52 489	3n						Al															
51 898	4							V														
51 575	7							Ge														
51 178	8							Ge														
50 857	1	*Pt*																				Blend
50 781											Be											
50 636	4										Be											Blend
50 615											Be											
50 470	1										Be											
49 517	3									Nb												
48 635	3										Co											
47 710	3							V														
47 505	4		Nb																			
47 096	0	*W*																				
46 886	4															Pt						
46 735	1	*W*																				
46 637	5													Ti								
46 369	1	*Ta*																				
46 222	2	*Ta*																				Blend
46 186		*W*																				
45 694	0	*W*																				

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2645 259	1							V														
44 264	5													Ti								
44 000	2		Fe																			
43 160	3							V														
42 270	2							V														
41 099	4													Ti								
39 712	3	*Ir*																				
38 304	1	*Mo*																				
37·133	1	*Os*																				
36 899	2	*Ta*																				
36 673	2	*Ta*																				
35 808	3		Fe																			
35 424	0	*Zr*																				
33 127	3	*W*																				
32 700	1	*W*																				
32 418	1													Ti								
32 236	0		Fe																			
31 543	2													Ti								
30 566	0	*Mn*																				
29 850	2	*Mo*																				
28 493	0		Nb																			
28 292	0										FeII											
28 029	4	*Pt*																				
27 640	1	*Co*																				
27 440	1										Nb											
26 640	0	*Mn*																				
25 215	3	*W*																				
24 045	3	*Mn*																				
23 532	4		Fe																			
22 898	2	*Mn*																				

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2620 226	1	*W*II																				?
19 939	3														Ti							
19·567	1	*Pt*																				
18 914	0	*Mn*																				?
18 468	1																					?
18·017	2		Fe																			
16 782	1	*Mo*																				
16 479	1										Nb											
15·656	0	*Ta*																				
15 391	1	*Mo*																				
15 122	1	*W*																				
14 178	8	*Pb*																				
13 823	3										FeII											
13 653	4	*Pb*																				
13 072	4	*W*																				
11 285	5														Ti							
10 335	0	*La*II																				
09 057	0	*Ru*																				
08 627	3	*Ta*																				
08 318	1	*W*																				
07 378	2																W					
06 825	4		Fe																			
06 386	3	*W*																				
05 688	5											MnII										
05 151	4														Ti							
03·570	1	*Cr*																				
01 963	1																			W		
2599·915	4														Ti							
99·570	2		Fe																			
99·396	2										FeII											

TABLE VIII—*continued*

Wave-length	Intensity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2598 062	6							Sb							Sb							Occurs in two multiplets
96 585	0														Ti							
95 761	4															Mn						
95 261	0	*Ta*																				
94 423	1	*Sn*																				
93 729	4											MnII										
92 944	3															Mn						
92 537	6							Ge														
91 848	2																Cr					
89 167	2	*W*II																				
84 536	4		Fe																			
84 308	5															Mn						
80 837	1	*Co*																				?
80·488	3																				W	
78 738	0	*Nb*																				
77 651	1																Cr					
77 292	4												V									
76 691	3		Fe																			
76 104	5											MnII										
75 509	4															Mn						
75 100	5																	Al				
74 350	4											Co										
74 020	5												V									
73 793	0	*Ta*																				
73 544	1	*Ta*																				
72 758	4															Mn						
71 741	1																Cr					
71 592	4															Sn						
71·391	2																		ZrII			
69 469	4n	*Sr*																				

TABLE VIII—*continued*

Wave-length	Intensity	Identification 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Remarks
2568 873	1																		ZrII			
67 987	4																	Al				
67 638	1																		ZrII			
67 346	4											Co										
64 816	1												V									
64 177	1n	*Ir*																				
63 183	0																			ScII		
62 146	4											Co										Blend
62 130													V									
61 962	1												W									
60 688	1																Cr					
60 227	2																			ScII		
59 427	2	*Ta*																				
57 153	0																Cr					
56 743	2	*W*																				
56 511	2	*Re*																				
55 799	0																			ScII		
55 091	0	*W*II																				
54 93	2																				P	
53 819	2	*W*																				
53 28	4																				P	
53 062	1																Cr					
52 652	3												V									
52 359	3																			ScII		
51 347	4	*W*																				
50 373	2						W															
49·968	0												V									
49 613	5			Fe																		
49 279	1	*V*II																				
48 336	1	*Co*																				

TABLE VIII—*continued*

Wave-length	Inten-sity	Identification																				Remarks
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
2547 136	3	*W*																				
46·552	5								Sn													
45 983	6												V									Blend
45 979				Fe																		
45 339	1	*W*																				
44 253	4											Co										
43 971	3	*Ir*																				
42 101	1	*Fe*																				
41 917	2		Ti																			
40 976	5			Fe																		
35 964	4											Co										
35 65	4																				P	
30 179	1	*V*																				
29 854	1		Ti																			
29 133	3			Fe																		
28 967	4											Co										
28 535	0														Sb							
28 516	4	*Si*																				
27 433	4			Fe																		

INDEX

(*Names of Persons are in Italics*)

PLATES I–XIX

DESCRIPTION

I–V	Spectrum of *raies ultimes* mixture with iron arc comparison, region 6720–3700 A (*See* pp 92–5.) Two spectra of the mixture are shown, with different exposures, one on each side of the iron spectrum
VI	Iron arc spectrum, region 3800–3460 A
VII–VIII	Spectrum of *raies ultimes* mixture with iron arc comparison, region 3560–2520 A (*See* pp 92–5.)
IX	Iron arc spectra from centre of arc and positive and negative poles, region 2845–2325 A
X–XI	Iron arc spectrum, region 2465–2085 A
XII	Absorption spectrum of nitroso dimethyl-aniline
XIII	Flame, arc and spark spectra of thallium.
XIV (A)	Arc spectrum of graphite
(B)	A few sequences in the CN spectrum
XV	Spectra showing variations in the relative intensities of V I and V II lines in the graphite arc arising from variations in the general composition of the arc gases. (*See* p 88.)
XVI (A)	Spectrum of coal-gas flame
(B)	Absorption spectra of neodymium chloride solutions of different strengths.
XVII	Spectra showing danger of confusing Bi line at 3067.7 with a line in the band spectrum of OH. (*See* p 99.)
XVIII (A)	Example of standard spectra for special problem in quantitative spectrum analysis (*See* p. 123.)
(B)	Spectra showing danger of attributing lines of V II and Ti II in impure graphite to Be II (*See* p. 99.)
(C)	Ghosts in grating spectrum.
XIX	Spectra showing effect of salt in bringing out lines of impurities in graphite electrodes. (*See* pp 79–80.)

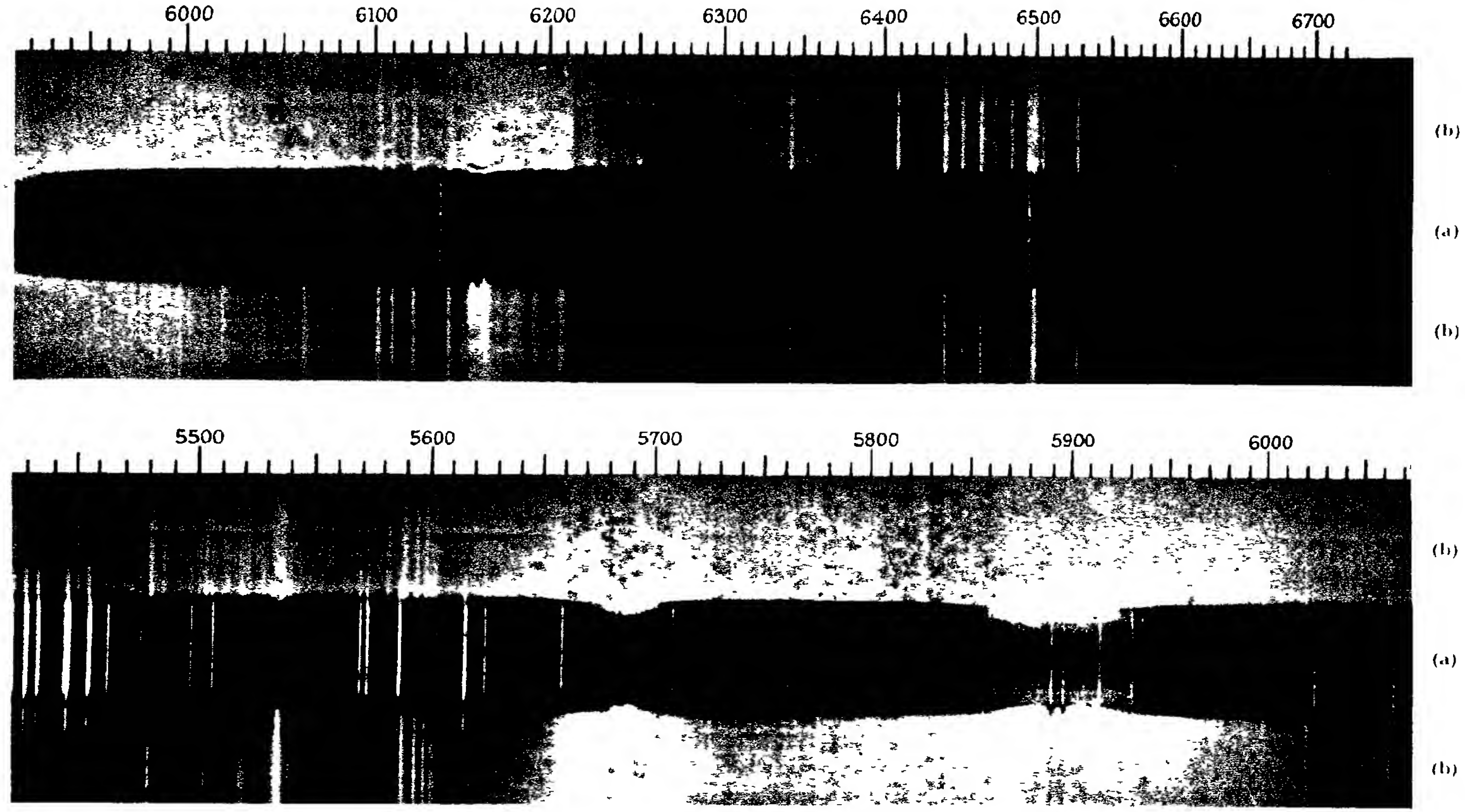


PLATE I
(a) Iron; (b) Mixture

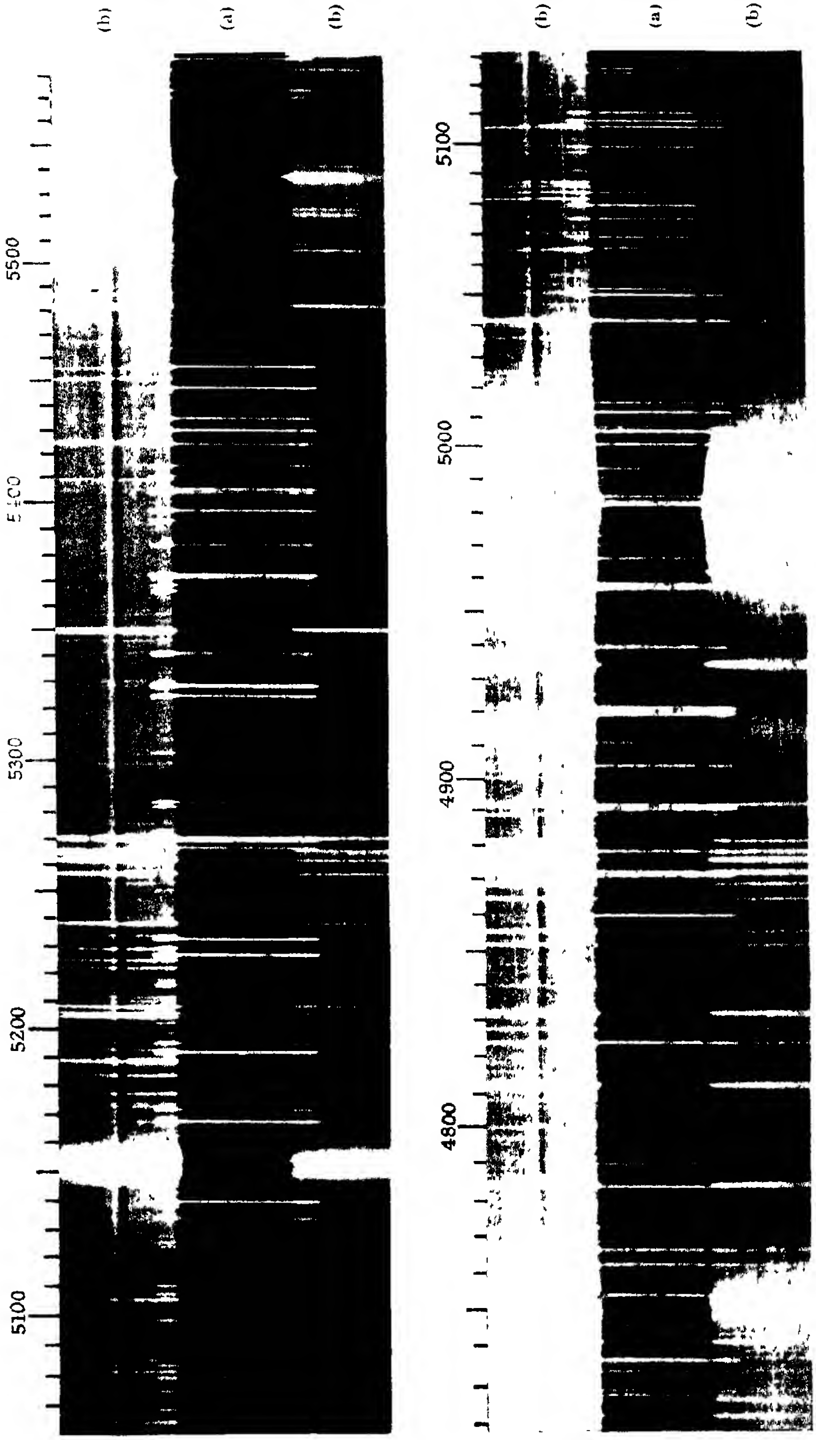


PLATE II

(a) Iron (b) Mixture

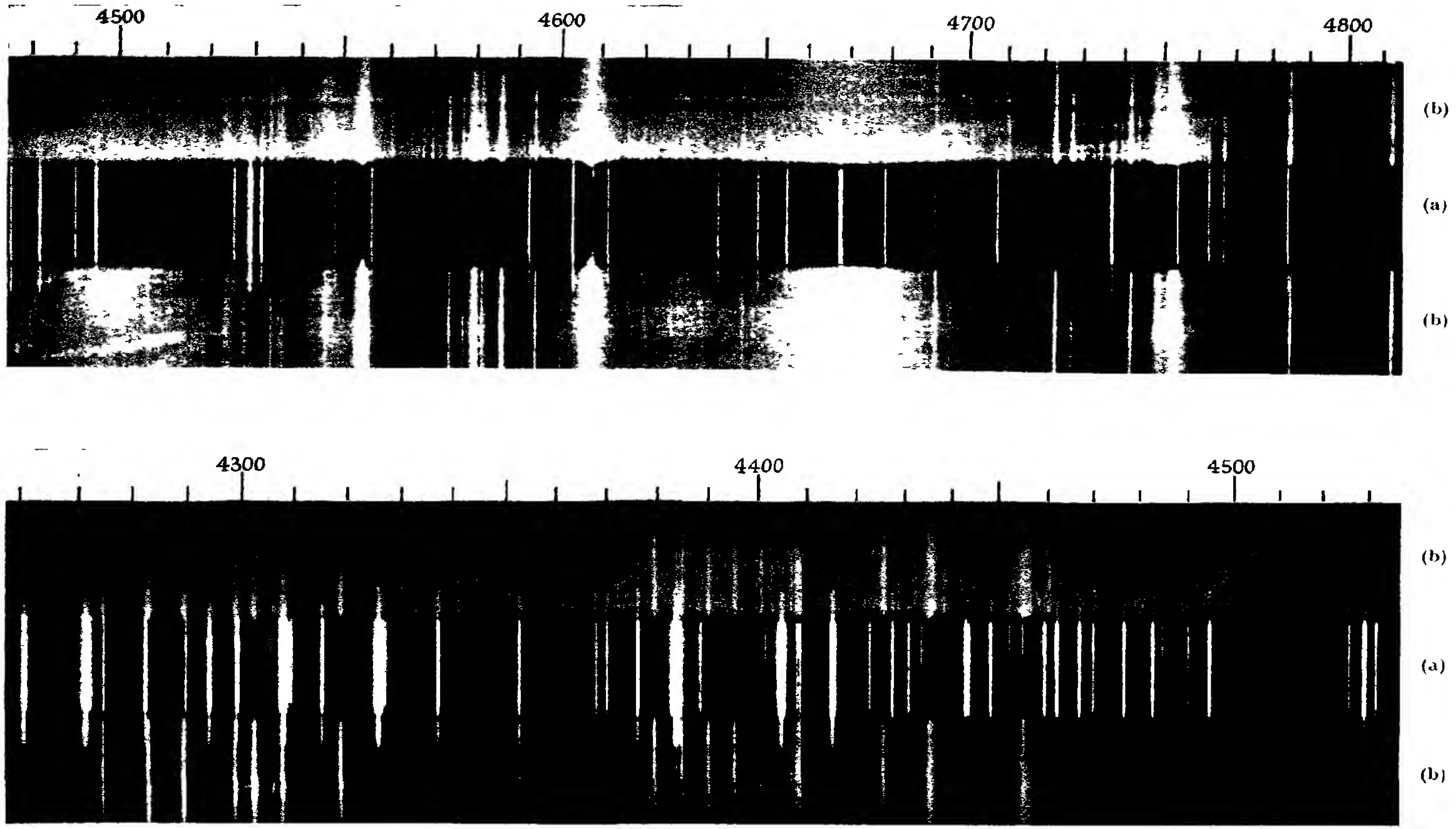


Plate III
(a) Iron (b) Mixture

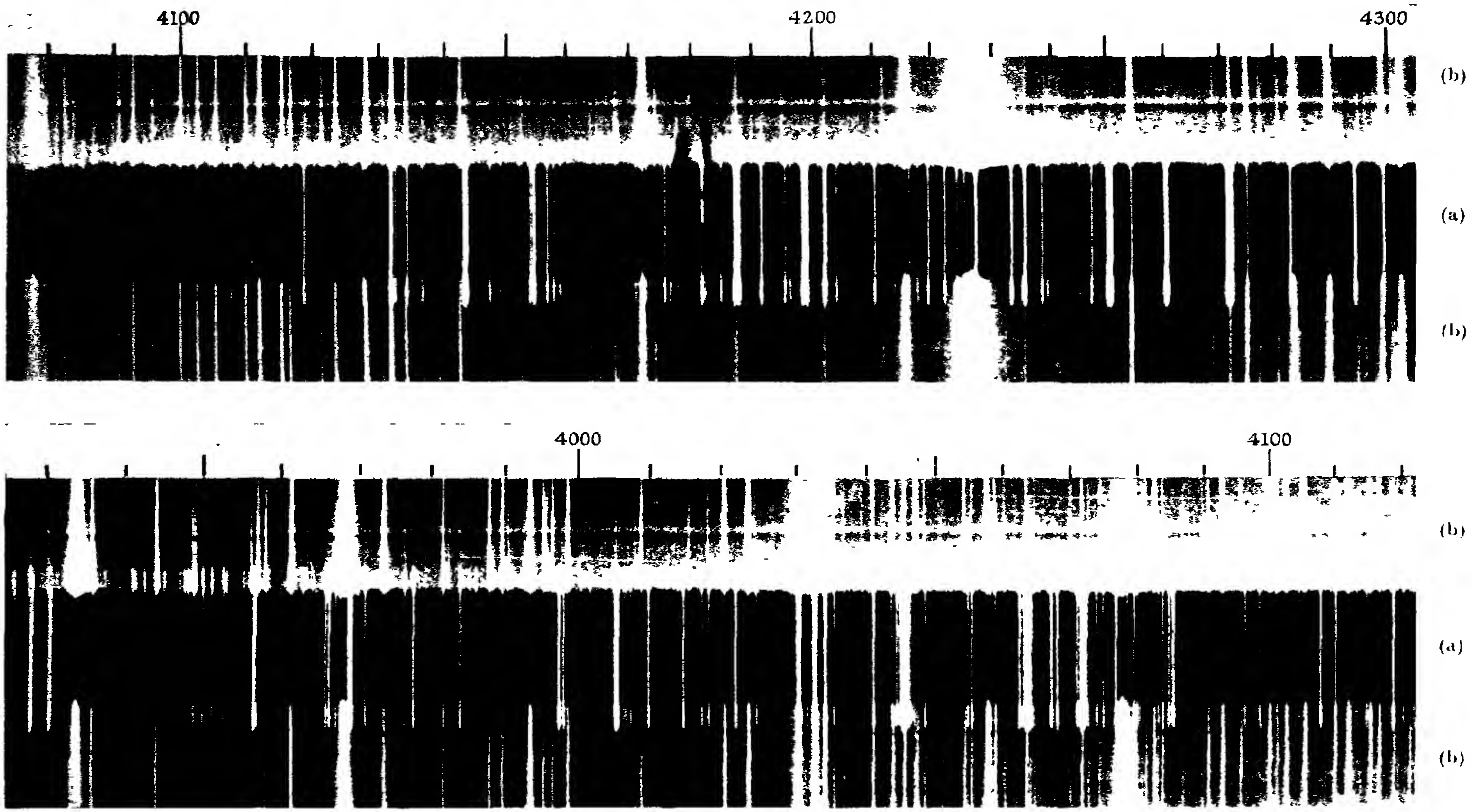


PLATE IV
(a) Iron (b) Mixture

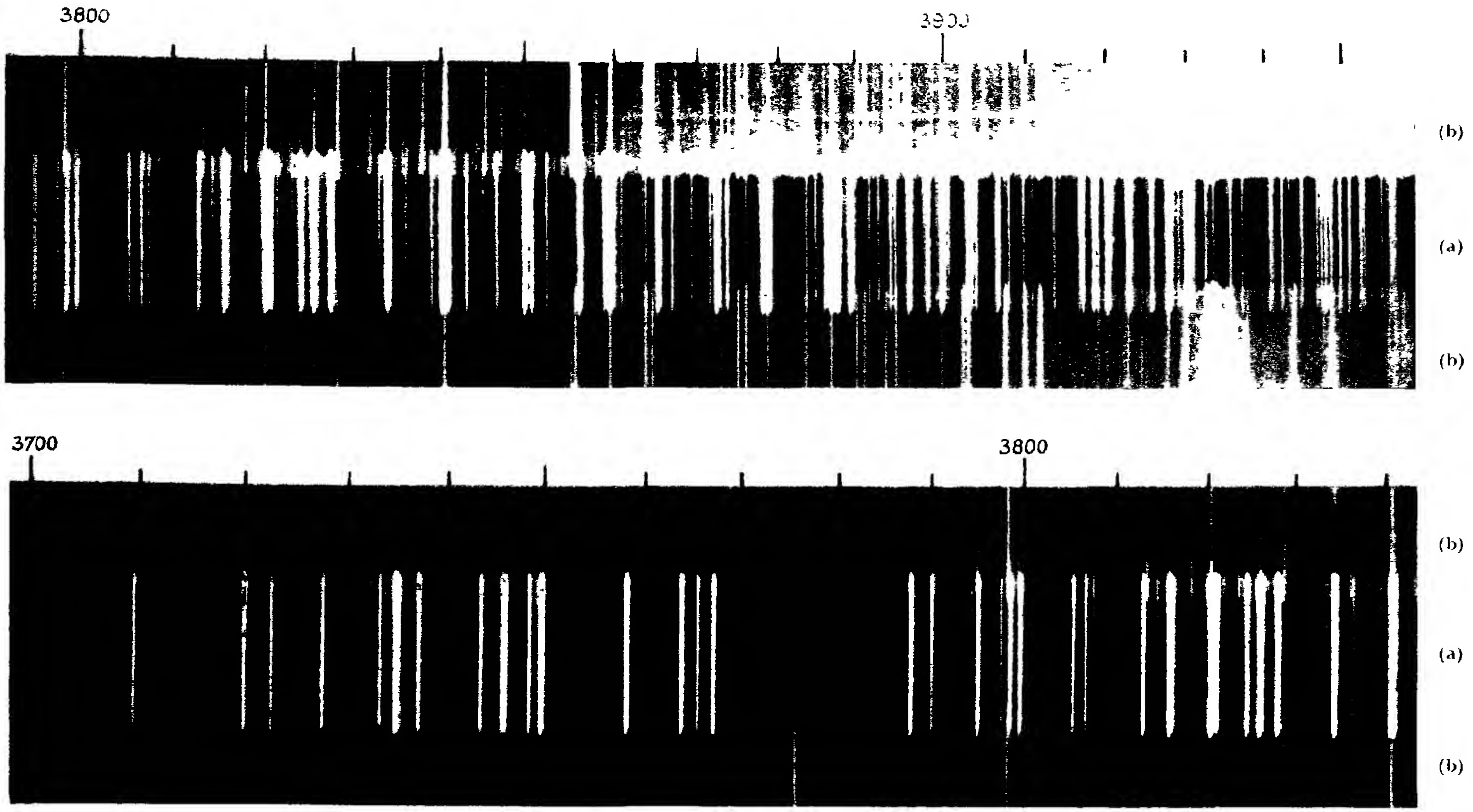


PLATE V
(a) Iron (b) Mixture

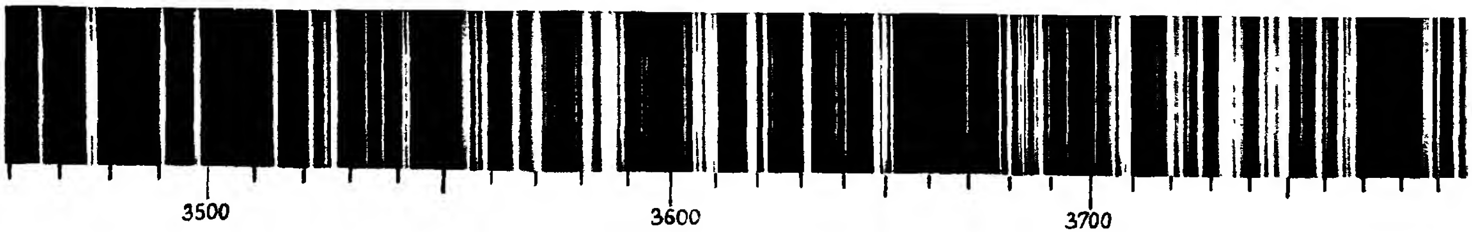


PLATE VI
Iron Arc Spectrum

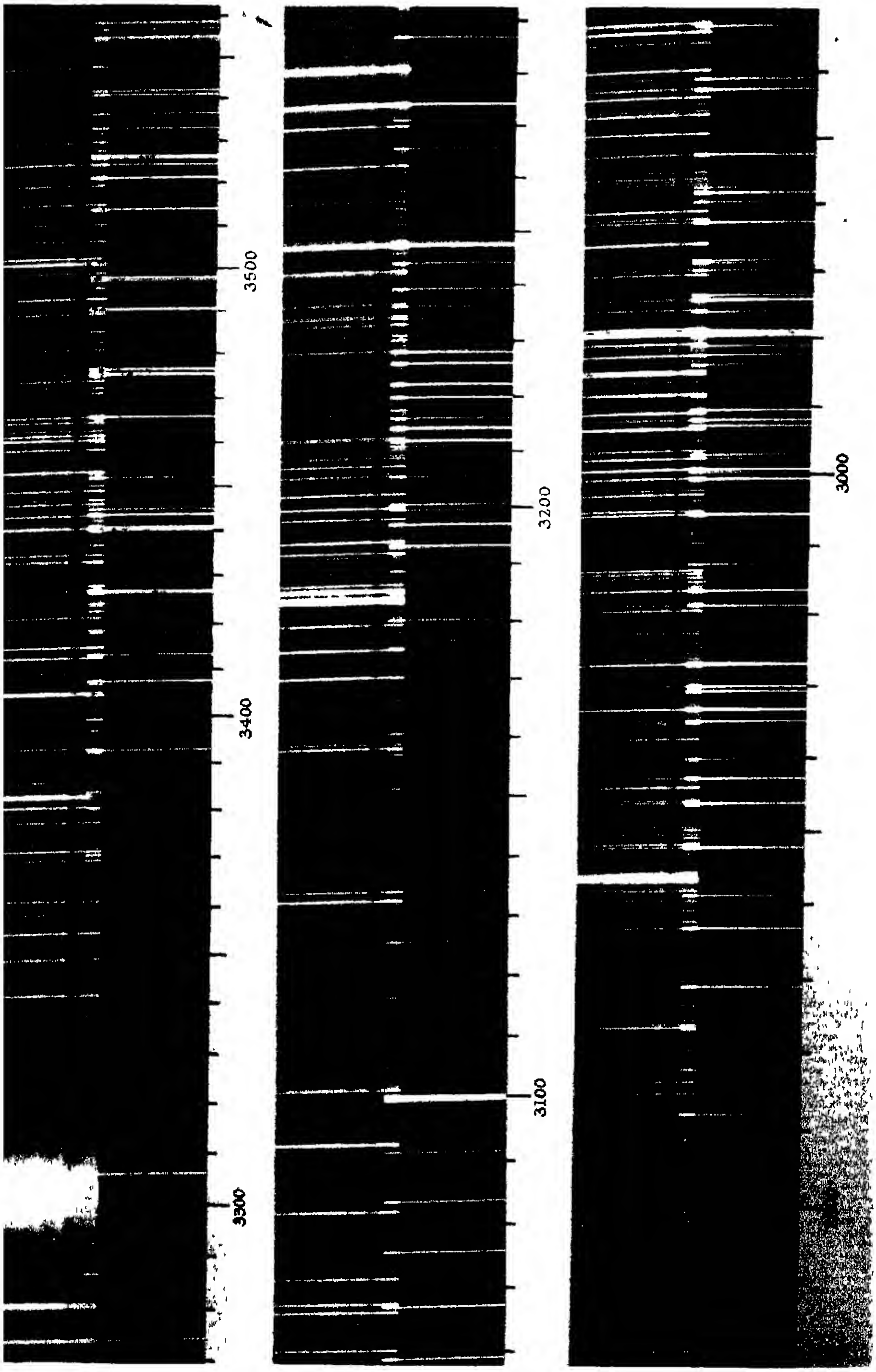


PLATE VII
(a) Iron, (b) Mixture

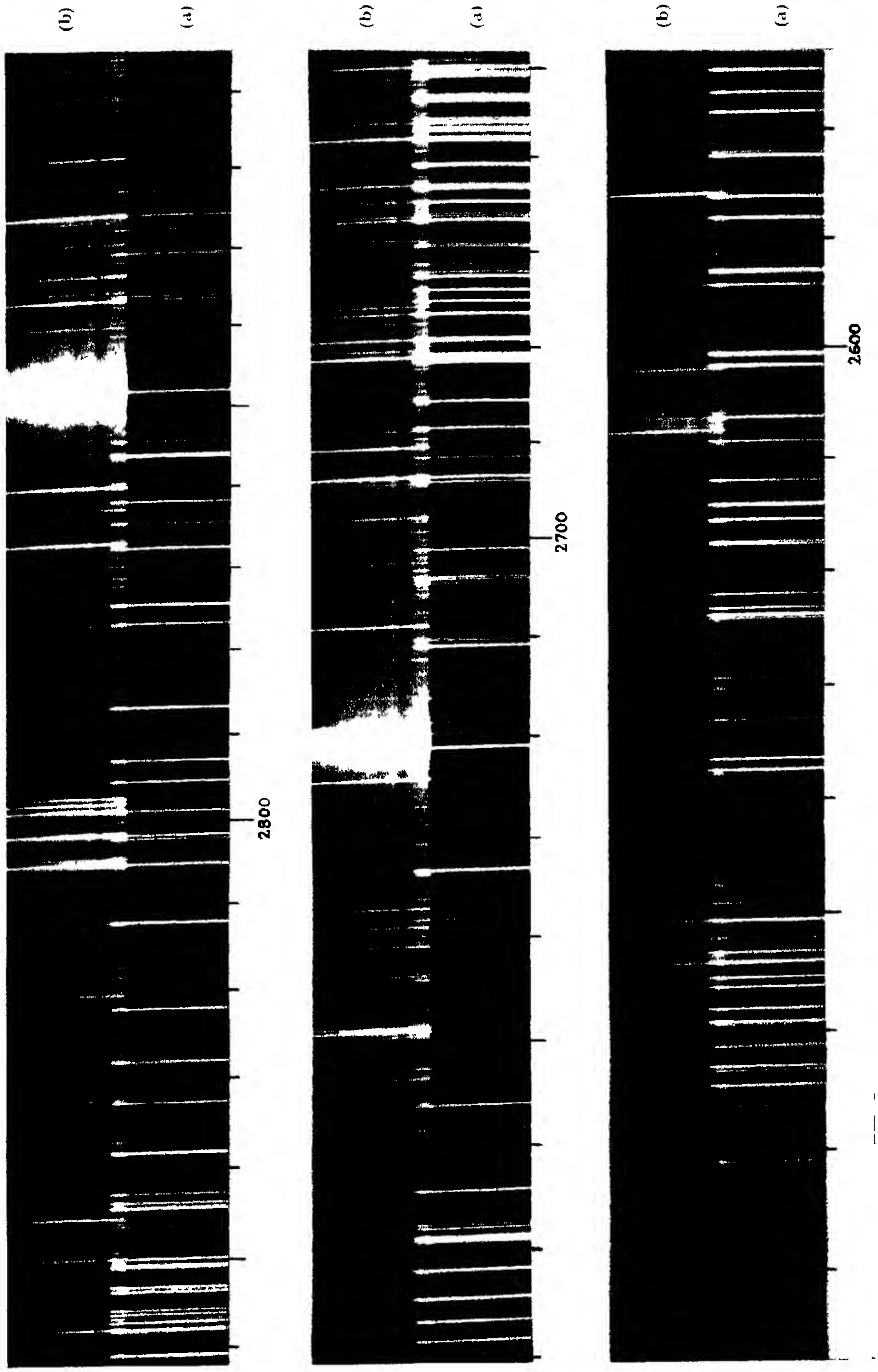


PLATE VIII
(a) Iron, (b) Mixture

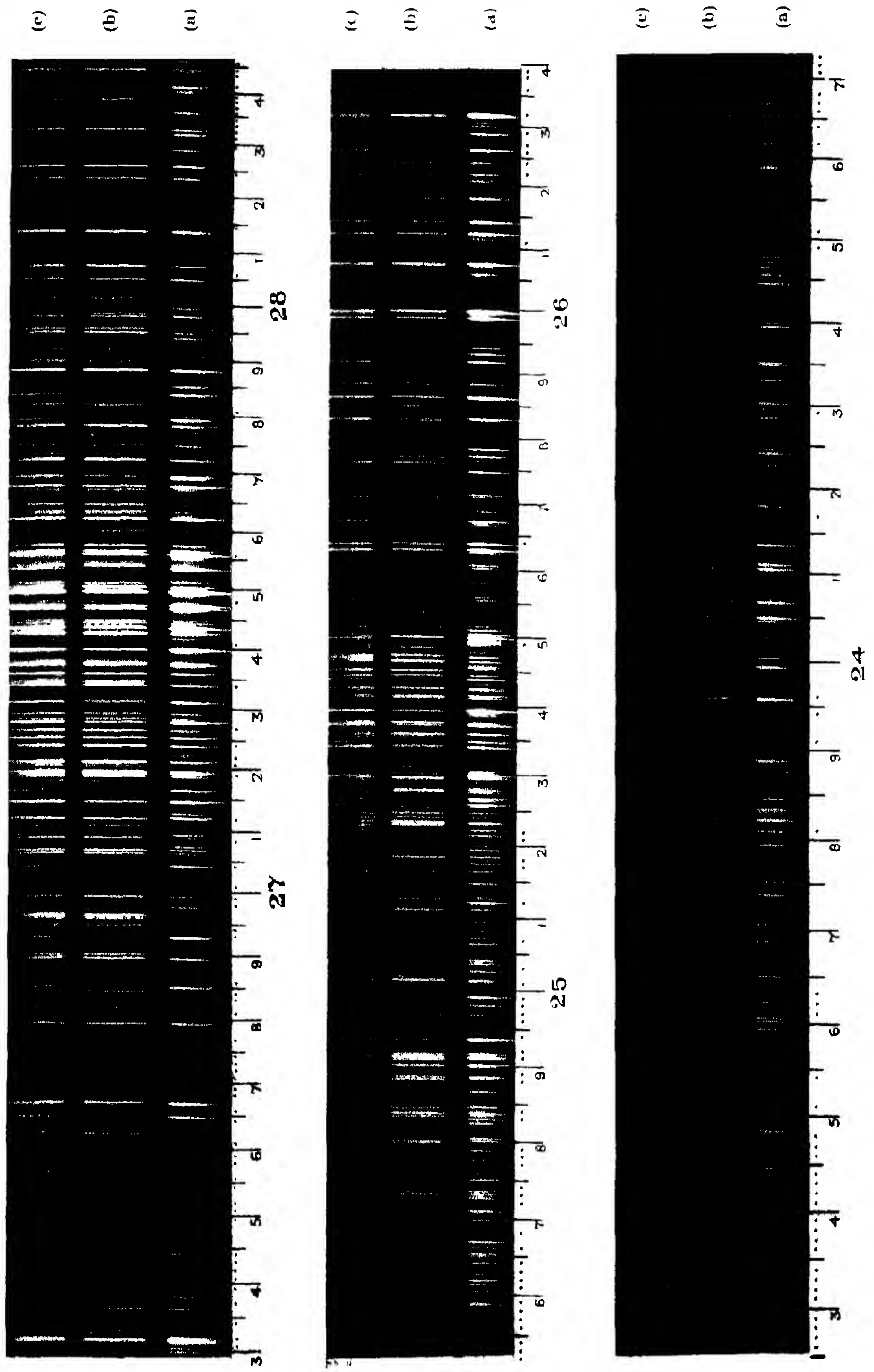


PLATE IX—IRON ARC
(a) Positive Pole, (b) Centre of Arc; (c) Negative Pole

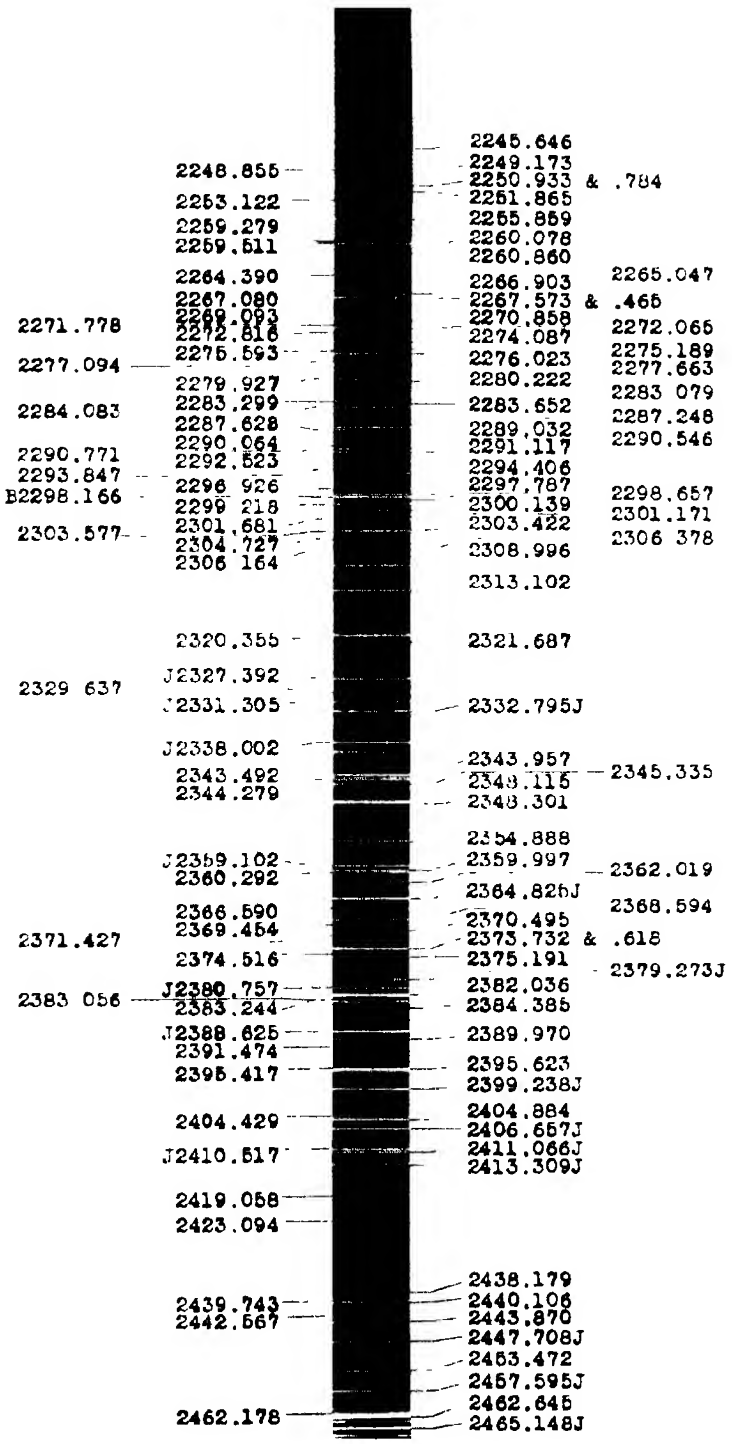


Plate X

Iron Arc Spectrum

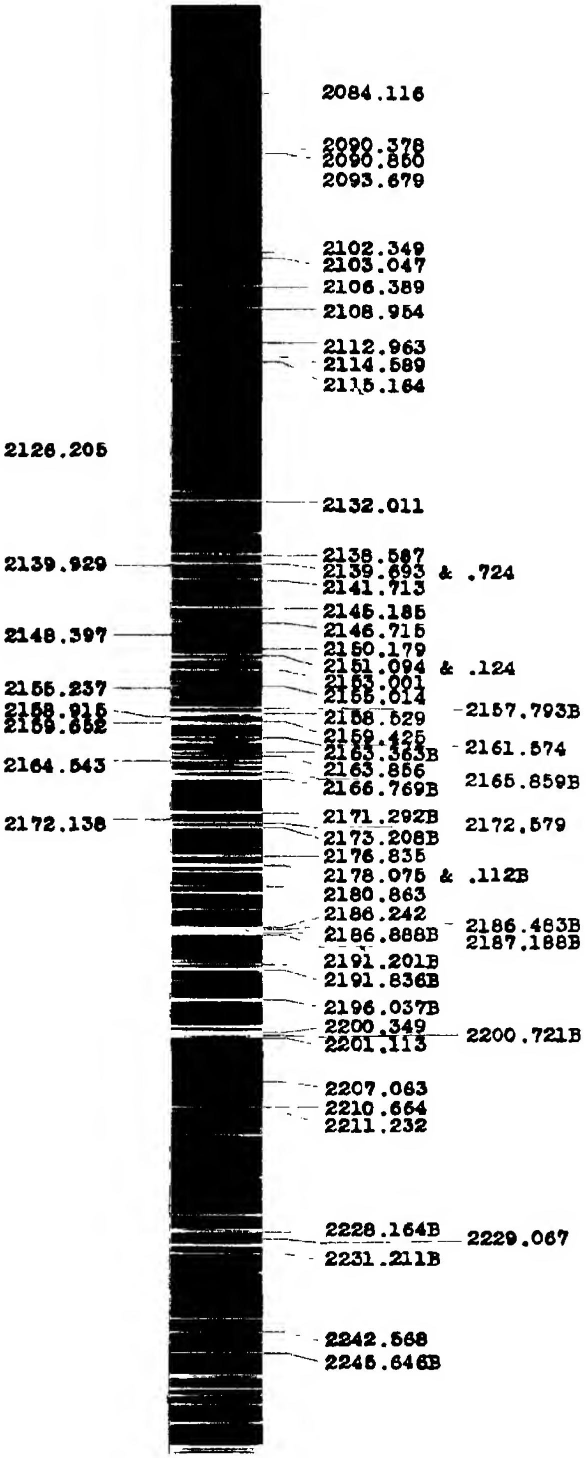


PLATE XI
Iron Arc Spectrum

PLATE XII

(a) Iron arc through Nitroso-dimethyl-aniline ; (b) Iron arc through air (shorter exposure)

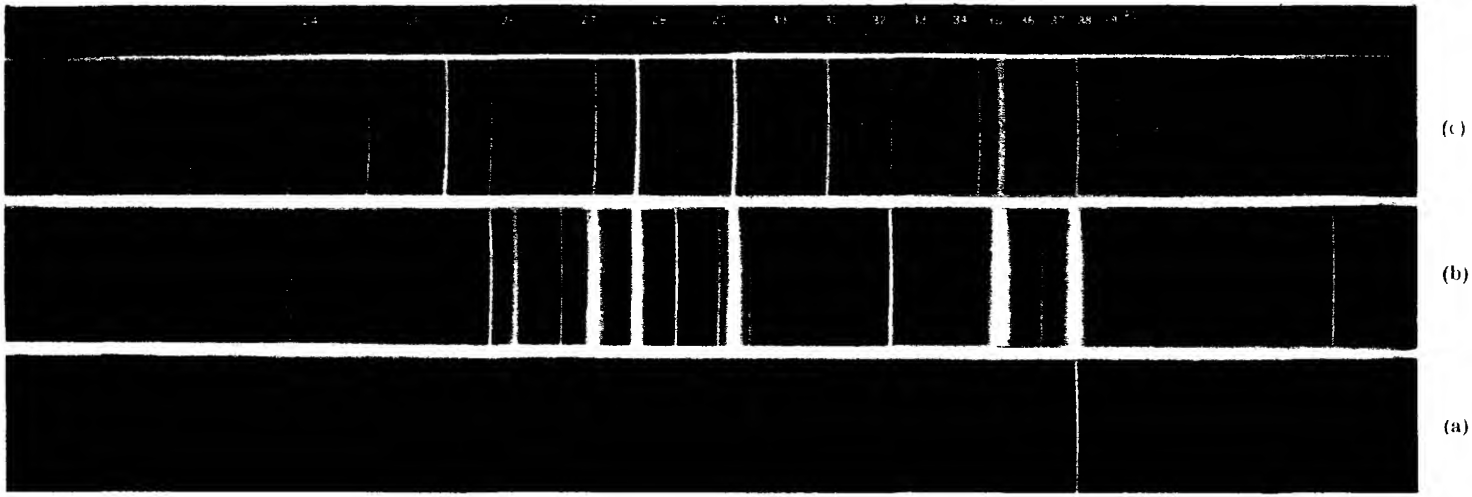
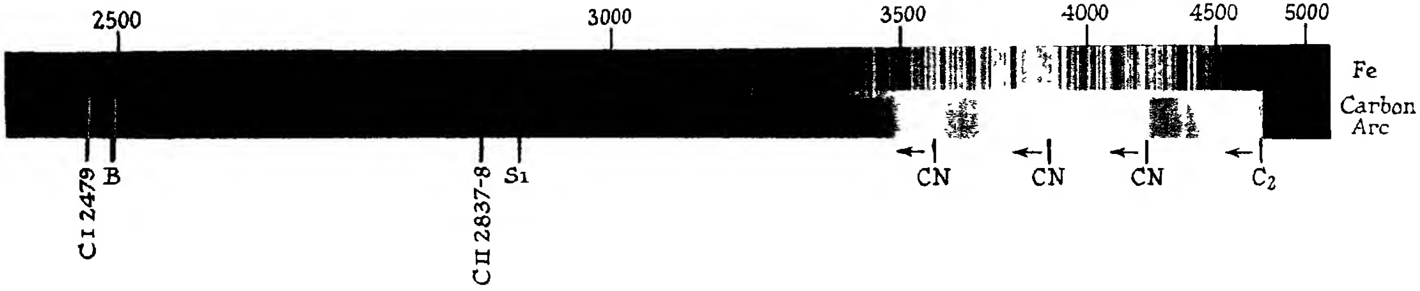


Plate XIII

Spectrum of Thallium under various conditions

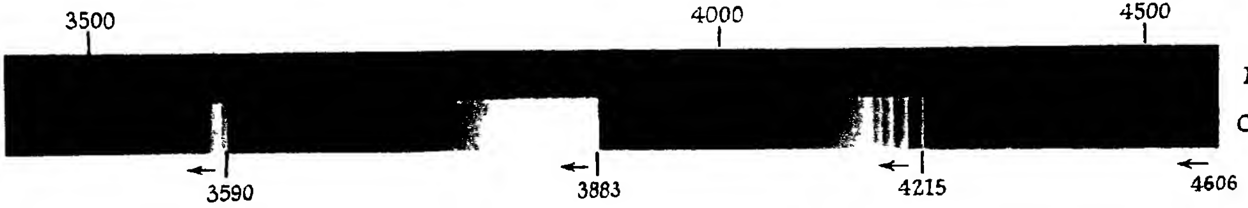
(a) Flame of Meker burner, (b) Arc between metallic electrodes, (c) Spark between metallic electrodes

(A)



Arc Spectrum of Graphite

(B)



A few sequences in the CN spectrum

PLATE XIV

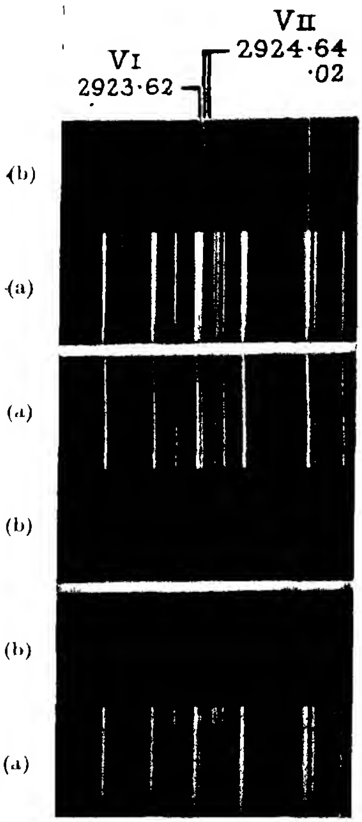
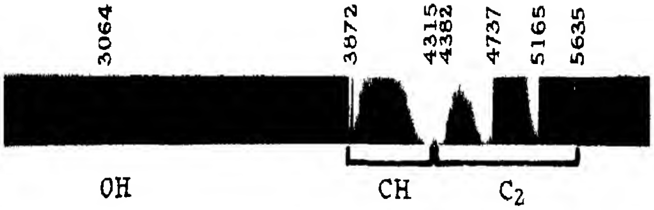


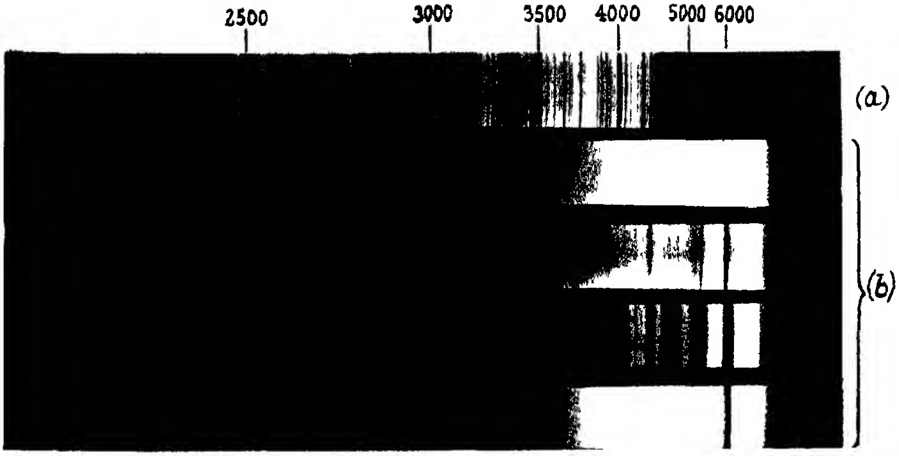
PLATE XV
(a) Iron
(b) Graphite with various impurities

(A)



Spectrum of Coal-Gas Flame

(B)



(a) Iron arc; *(b)* Nernst lamp through neodymium chloride solutions of different strengths

Plate XVI

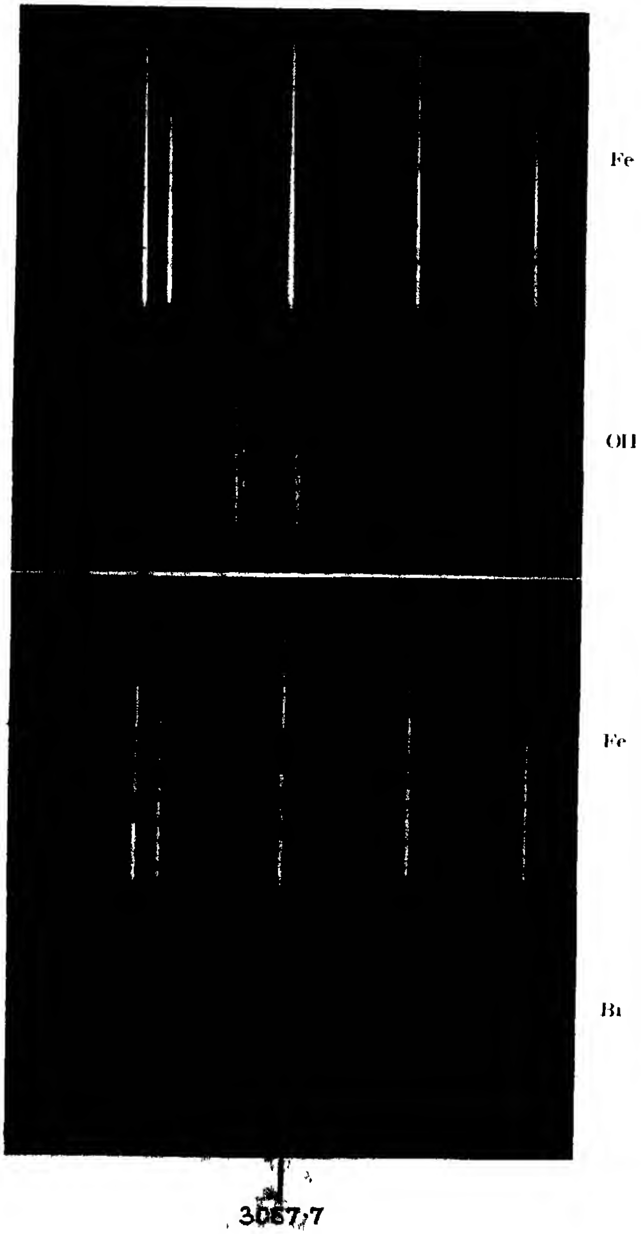
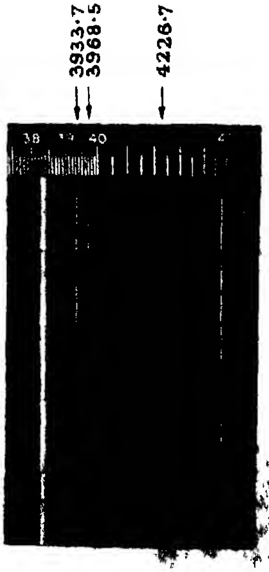
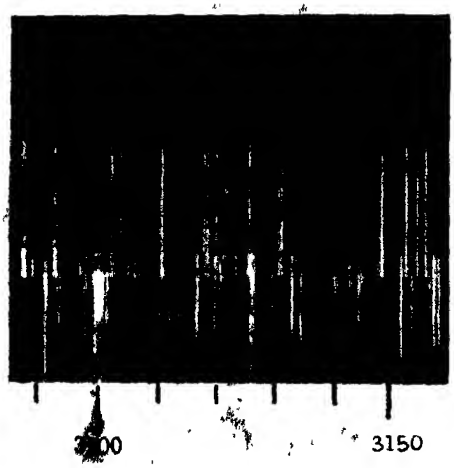


Plate XVII

(A)



Standard spectra for quantitative analysis



(B)

(C)

Ghosts in Grating Spectrum

PLATE XVIII

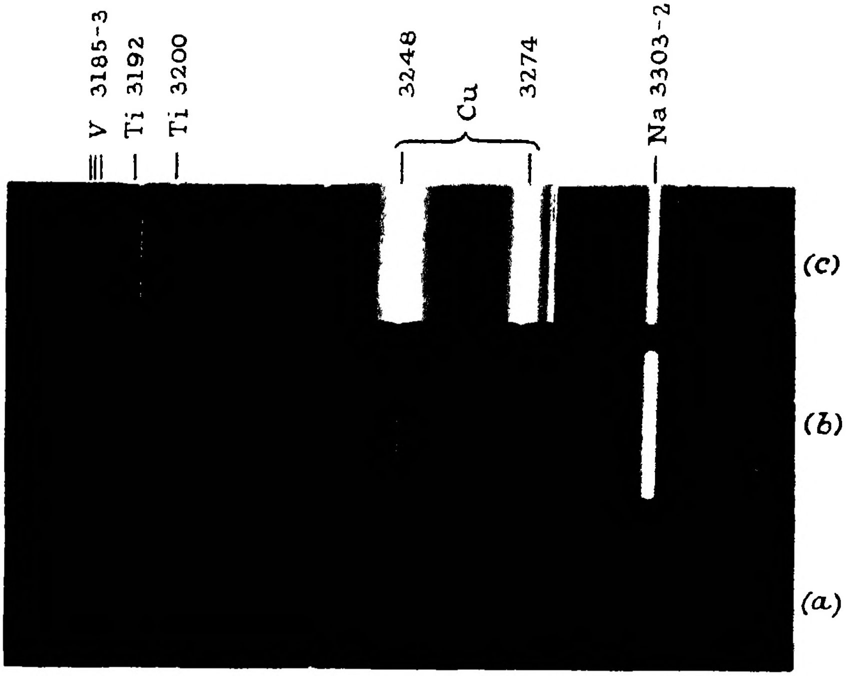


PLATE XIX

(a) Graphite, (b) Graphite + NaCl, (c) Copper + NaCl