CHAPTER 1

Introduction

1.1 Scope of Research Work:

The focus of this research work is the development of simple and cost-effective, aqueous solution based chemical methodologies for synthesis of nanostructured α-Fe$_2$O$_3$ and Ni-Zn ferrites. In particular, this work will describe three different chemical methodologies that have been utilized to synthesize and characterize pure α-Fe$_2$O$_3$ and series of Ni-Zn ferrite nanopowders. The developed chemical methodologies are an attempt in the direction of surmounting the limitations associated with the existing methods of synthesizing these nanopowders.

1.2 Introduction to Iron Oxide (α-Fe$_2$O$_3$) and Ni-Zn Ferrites:

Iron oxide

Hematite or α-Fe$_2$O$_3$ is the most common phase of iron oxide that occurs naturally in rocks and soil. The "red pigment", as it is called, has inconspicuously been in use since time immemorial in the form of cave paintings. In hematite, oxygen ions are in a hexagonal close-packed arrangement, with Fe (III) ions occupying two-thirds of the octahedral sites [1]. It is paramagnetic above its Curie temperature of 956 K. At room temperature, it is weakly ferromagnetic and undergoes a phase transition at 260 K (the Morin temperature, T_M) to an antiferromagnetic state [2, 3].

Hematite is used as a catalyst for a number of industrially important reactions such as desulfurization of natural gas [4], dehydrogenation of ethyl benzene to styrene [5], Fisher Tropsch synthesis of hydrocarbons [6], oxidation of alcohol [7]. It is used as a support material

for gold in catalysts for the oxidation of carbon monoxide at low temperatures [8]. It is also used as a photocatalyst for the degradation of chlorophenol and azo dyes [9] and as an optical coating [10]. The red pigment of hematite finds use as synthetic pigments in paints, porcelains and ceramics. Pigments based on hematite are widely used as water repellant stains for wood as they allow wood to be seen while still providing protection against the damaging effects of sunlight [11]. It has also been used extensively as gas sensor for carbon monoxide [12] and as a humidity sensor [13].

Recent years have witnessed a surge of interest in the synthesis and processing of iron oxide nanopowders due to their myriad new and improved applications in various fields. Nanoparticles of hematite are finding applications such as more efficient sensors and catalysts due to their high surface area [14, 15], removal of toxic heavy ions like arsenic from water [16], polymer modified hematite nanoparticles for electrophoretic display [17] and as non-magnetic substrates in magnetic recording media [18]. In particular, superparamagnetic (SPM) particles of iron oxide are finding use in the medical field as magnetic resonance imaging (MRI) contrast agents for molecular and cell imaging, targetted drug delivery vehicle, magnetic hyperthermia to treat cancerous cells etc [19-21].

Ni - Zn Ferrites

Ferrimagnetic oxides or ferrites, as they are usually known as, are magnetic ceramic materials and they are broadly categorized as soft and hard magnetic material. The word ''soft'' means temporary in the sense that ferromagnetism emerges only when a magnetic field is applied. In contrast, "hard" magnetic materials exhibit ferromagnetism even in the absence of an external field. Magnetite is an example of a naturally occurring ferrite and its magnetism found application in the lodestone of early navigators.

The first systematic study on ferrites was made by Hilpert and it dates back to 1909 [22]. Several researchers contributed significantly towards the development and commercialization of ferrites during the period from 1935 to 1970 [22]. For e.g. Hogan's work on microwave ferrite devices, Albers-Schoenberg's development of Mn-Mg ferrites for magnetic memories, Dillon et al contributions to the development of magnetic memory devices and Camaras's discovery of

gamma-Fe_2O_3 acicular fine particles are the most outstanding achievements. Therefore, this period is referred to as the "golden period" of ferrites [22, 23].The magnetic properties of ferrites were considerably inferior to those of ferromagnetic alloys such as Fe-Si. However, ferrites attracted worldwide attention only after new inventions like radio, television, computers and microwave devices as they had the unique combination of being magnetic and having the ability to operate at high frequencies.

Ni-Zn ferrite is a soft magnetic material and possesses the cubic spinel structure. The general formula is given by XY_2O_4 where X represents divalent cations and Y trivalent cations. They have the general chemical composition $MeO.Fe_2O_3$ where Me is a divalent metal such as iron, manganese, magnesium, nickel, zinc, cadmium, cobalt, copper, or a combination of these. In the unit cell that contains 32 oxygen anions in closed pack cubic array, there are 32 octahedral sites (B sites) and 64 tetrahedral sites (A sites). Out of these, 16 of the octahedral sites (B sites) are filled and 8 of the tetrahedral sites (A sites) are filled. There are two idealized spinel structures (i) in normal spinel structure, all divalent cations occupy the A sites and (ii) in the inverse spinel structure, the 8 A sites are occupied by trivalent ions while the 16 B sites are equally divided between di and trivalent ions [23, 24].

Ni-Zn ferrite is well known for its high saturation magnetization, low coercivity, high resistivity and low dielectric losses. It has a plethora of applications such as inductors, transformers, choke coils, magnetic heads, power transformers, EM (electromagnetic) wave absorber, magnetic toner etc. [22-27]. Ferrite thin films are frequently used in high frequency operating integrated electronic devices [28, 29]. In the last decade especially, the field of biomedicine has witnessed a surge of interest in the use of magnetic nanoparticles for novel applications such as targeted drug delivery, hyperthermia, as contrast agents in MRI and in magnetic separation of cells [30, 31]. They are also currently being investigated for their applications as nanocomposites where tailoring of their properties is possible by changing their weight ratio with respect to the non-magnetic matrix [32-36].

Although there is a spectrum of applications for these materials, it is not easy to produce ferrites with good homogeneity and desirable properties. Ferrites are known to be highly structure-

sensitive materials and their properties greatly depend on the synthesis routes. As an illustrative example, the comparative DC resistivity and magnetic parameters of Ni-Zn ferrites synthesized by various methods in literature are listed in Table 1.1 and Table 1.2 respectively.

Table 1.1. Comparative room temperature DC electrical resistivity of ferrites prepared by some representative methods.

Synthesis Method	Composition	Sintering Condition (^{0}C)	Grain size	Room temperature DC resistivity (Ω cm)	Reference
Solid State	$Ni_{0.65}Zn_{0.35}Fe_2O_4$	1150 to 1300	~2.5 - 5 μm	~10^4 to 10^5	[37]
Citrate Precursor	$Ni_{1-x}Zn_xFe_2O_4$ (0.20≤x≤0.60)	1100 to 1400	~2μm	~10^8 to 10^{11}	[38]
Flash Combustion	$Ni_{0.80}Zn_{0.20}Fe_2O_4$	1150 to 1350	~2-10 μm	10^8 to 10^9	[39]
Oxalate Precipitation	$Ni_{1-x}Zn_xFe_2O_4$ (0.0≤x≤1.0)	1000	~0.4 to 0.6 μm	~ 10^9	[40]
Coprecipitation	$Ni_{1-x}Zn_xFe_2O_4$ (0.0≤x≤1.0)	400 and 900	~78 nm and 0.9 μm	~ 10^6	[41]
Sol—gel	$Ni_{0.65}Zn_{0.35}Fe_2O_4$	1100	~2 μm	~ 10^8	[42]

Table 1.2 Comparative room temperature magnetic parameters of Ni-Zn ferrites prepared by some representative methods.

Synthesis Method	Composition	Calcination/ Sintering Temperature (^{0}C)	Particle size	M_s (emu/g)	H_C (Oe)	Reference
Solid state	$Ni_{1-x}Zn_xFe_2O_4$ $(0.20 \leq x \leq 0.67)$	1100-1450	~1 μm	283-292 G	0.40-6.8	[23]
Citrate precursor	$Ni_{1-x}Zn_xFe_2O_4$ $(0.20 \leq x \leq 0.60)$	1200	~2 μm	63- 73	1.77-6.2	[43]
Coprecipitation	$Ni_{0.50}Zn_{0.50}Fe_2O_4$	300 - 800	9 - 90 nm	13 - 63	SPM	[44]
Glyoxylate Precursor	$Ni_{0.35}Zn_{0.65}Fe_2O_4$	400 - 1000	~15 - 46 nm	30 - 60	10-41	[45]
Reverse Micelle	$Ni_{0.20}Zn_{0.44}Fe_{2.36}O_4$	Room temperature	7 nm	25	SPM	[46]
Reverse Micelle	$Ni_{0.50}Zn_{0.50}Fe_2O_4$	Room temperature	25 - 40 nm	4.5	SPM	[47]
Autocombustion	$Ni_{0.50}Zn_{0.50}Fe_2O_4$	200 - 1000	~8 - 54 nm	25 - 75	~35-100	[48]
Sol-gel autocombustion	$Ni_xZn_{1-x}Fe_2O_4$ $(0.20 \leq x \leq 1)$	700	35 nm	20 - 69	33-158	[49]
Combustion	$Ni_{1-x}Zn_xFe_2O_4$ $(0 \leq x \leq 0.70)$	600 - 800	18 - 27 nm	39 - 47	0-6990	[50]

1.3 Nanostructured Materials and their Processing:

Bulk nanostructured materials are defined as bulk solids with nanoscale or partly nanoscale microstructures. This category of nanostructured materials has historical roots going back many decades but the relatively recent focus is due to new discoveries of unique properties of some nanoscale materials [51, 52].

Early in the 20th century, when ''microstructures'' were revealed primarily with the help of optical microscope, it was recognized that refined microstructures, for example, small grain sizes, often provided attractive properties such as increased strength and toughness in structural materials. Nanostructured materials (grain size < 100nm) are known to exhibit exotic properties as compared to those exhibited by conventional ceramics (grain size > 10µm). A unique feature of these materials is that a large fraction of their atoms resides in their grain boundaries. As the particle size decreases, the interfacial volume increases. As a result, the properties of nanostructured materials are strongly governed by their surface structure and/or interface volume, which represents a significant fraction of their total volume. It is thus plausible that many of the microstructure based properties such as hardness, resistivity, specific surface area, thermal expansion coefficient, magnetic property etc. of nanostructured materials would differ from those of conventional bulk materials, in which the interface volume fraction is negligible. These nanopowders, therefore, give rise to myriad of potential applications that could not have been feasible with the regular bulk microstructure [53 - 57].

Processing of bulk nanostructured materials can in principle be accomplished by either the ''bottom-up'' assembly of atoms or molecules into nanoscale clusters which require subsequent consolidation into bulk material, or the ''top-down'' methods which start with a bulk solid and obtain a nanostructure by structural decomposition. Many of the useful attributes of ceramic materials such as iron oxide and ferrites depend on their preparation methods (Table 1.1 and Table 1.2). The preparation method plays a key role in determining the particle size and shape, size distribution, surface chemistry and therefore the properties and applications of the material. Many synthesis routes have been developed to achieve proper control of particle size, polydispersity, shape, crystallinity, and the magnetic properties of these materials. We have

critically reviewed the different patented methods in order to synthesize a wide variety of ferrites depending on their applications [58]. Herein we will briefly describe some general methodologies that are used to synthesize ultrafine iron oxide and ferrite nanopowders.

1.3.1 Solid State Method [59-68]:

Bulk iron oxide or ferrites have conventionally been prepared by the high temperature solid-state route that involves mechanical mixing of oxides or carbonates followed by calcination at high temperatures ($>1000^0$C). This method, although successful for large-scale production of bulk ceramic powders, has several limitations as far as production of nanostructured ceramics is concerned.

High temperatures and long heating schedules, which are the requisites of this method, lead to coarsening of grains. Moreover, volatilization/melting of the constituent components may occur during the high temperature processing of some of the multicomponent mixed oxides systems [66-68].

1.3.2 Gas Phase Methods:

(a) Chemical Vapor Deposition (CVD)

In the CVD process, a carrier gas stream with precursors, (e.g. metal β-diketonates, carboxylates and alkoxides), is delivered continuously by a gas delivery system to a reaction chamber maintained under vacuum at high temperature ($>900^0$C). The CVD reactions take place in the heated reaction chamber and the products combine to form clusters or nanoparticles. The CVD process has been employed to deposit iron oxide and ferrite films at 800 to 1000^0C [69-71].

(b) Metal Organic Chemical Vapor Deposition (MOCVD):

In the MOCVD process, metallo organics are used as precursors that allow reactions to take place at a somewhat lower temperature (300 to 800^0C) and at pressures varying from 1 Torr to ambient. Iron oxide thin films have been obtained via decomposition of acetylacetonate at 400-500^0 C, and iron trifluoro-acetylacetonate at 300^0C in oxygen [72]. Ferrite films have also been obtained in a similar manner [73, 74].

(c) Laser Ablation Method:

Well-crystallized and uniform iron oxide nanoparticles, including nanoparticles of hematite and maghemite, have been obtained in one step using laser pyrolysis [75]. Iron pentacarbonyl is commonly used as a precursor in this method and ethylene is used as the carrier gas to transport the carbonyl vapor to the reaction zone, as ethylene does not absorb radiation at the laser wavelength [76]. Series of Ni-Zn ferrite and Zn ferrite thin films have been obtained by laser ablation process on Si substrates [77].

1.3.3 Solution Phase Methods:

(a) Co-precipitation Method [78-88]

Co-precipitation method is a very well established technique for preparation of ferrites with wide range of compositions. In this wet chemical process, ferrites with desired chemical compositions are simultaneously precipitated from aqueous solutions of metal ions. Co-precipitation occurs by the reaction of the metal ion solutions with precipitating agent, generally alkaline solution of carbonates, hydroxides, ammonia or ammines. The resulting solid precipitate contains ferrous and other metal carbonates or hydroxides, which decompose to the oxides when calcined at temperatures ranging from 500 - 800^{0}C. Final sintering at 1000 - 1200^{0}C produces the desired ferrites. Rao et al [84] have synthesized Ni-Zn ferrite by a coprecipitation method using metal chlorides as the starting materials and sodium hydroxide as the base. Coprecipitation occurred at 100^{0}C and further heat treatment at 200^{0}C resulted in single phase Ni-Zn ferrite nanopowder.

Precise control over the chemical composition of the product is the main advantage of the technique in comparison with the conventional solid-state technique. The co-precipitation method, however, is associated with the limitation of producing materials that are not exceptionally homogeneous and reproducibility of the process for some cases is poor. Formation of gelatinous precipitate often causes difficulty in separation and retention of impurities in the product might cause poor magnetic properties.

(b) Sol-Gel Method [89-95]

In this method, the organometallic compounds, namely alcoholate, carboxylate or chelate compounds of different metals are generally used as starting materials. Acid or base catalysized

hydrolysis followed by condensation and polycondensation reaction of starting compounds in organic solvent produce gel. The gel, upon calcination at various temperatures in presence of oxygen produces desired ferrites. Lee et al [92] have reported a sol-gel route to prepare Ni-Zn ferrite powder. The starting compounds were nickel acetate and nitrates of Zn and Fe that were dissolved in a mixed solvent of ethanol, distilled water and acetic acid. The mixture was refluxed and then dried in oven at 100^0C for 3 days. Calcination at 300^0C and above resulted in single phase ferrite powder.

Sol-gel technique is generally employed to prepare finely divided powders that are useful particularly in the manufacture of coating compositions, intricately shaped and fine-grained ceramics, and cermets. Use of expensive metal alkoxides or complex metal compounds is the main limitation of this method.

(c) Hydrothermal method [96-105]

In this method, a mixture of aqueous solutions of metal ions, and/or aqueous slurry containing metal hydroxides is mixed with alkali solution and the mixture is autoclaved between 100-400^0C. This is a comparatively low temperature technique, which provides a uniform mixture of the metallic components to form ferrites with required chemical composition. Li et al [104] have synthesized superparamagnetic nanoparticles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ by using iron chloride, nickel sulphate and zinc sulphate as the starting materials. Aqueous solutions of the metal salts were prepared and NaOH was used as the base to adjust the pH to 9.The resulting suspension was stirred vigorously and then placed in an autoclave between 90-120^0C for 1.5 hours. The resulting precipitates were collected and washed several times with distilled water and ethanol and then dried for 6-8 hours. They were then ground to obtain Ni-Zn ferrite nanopowder.

Hydrothermal method is widely used for the preparation of ferrite powders, which find applications where uniform dispersion of ferrite particles is required such as application in high-density recording medium. This process is found to be superior to the conventional high temperature process because it avoids the sintering or agglomeration of ferrite grains. Although hydrothermal technique is very versatile, one of the main drawbacks of the conventional hydrothermal method is the slow reaction kinetics at any given temperature.

(d) Precursor based Method [106-115]

This method involves the preparation of a "precursor" compound which is a complex combination of cations and a polymeric /chelating agent. The pyrolysis of the precursor at various temperatures gives rise to nanoscale particles of the desired single or mixed oxide system. Various organo-metallic complexes, metal hydroxides/oxalates/citrates/hydrazine carboxylates etc. are some of the commonly used precursor compounds. Verma et al [113] have used the citrate based precursor method to synthesize Ni-Zn ferrites where the starting compounds are iron citrate, nickel nitrate, zinc nitrate and citric acid.

The precursor method permits good control of the product stoichiometry, especially for multicomponent systems. However, it is not always easy to choose a suitable precursor to synthesize a particular compound.

(e) Combustion Method [116-122]:

The method utilizes a precursor that ignites at a low temperature and leads to a gas producing exothermic reaction that is self-propagating and yields voluminous fine oxides in a few minutes. Various organo-metallic complexes, metal hydroxides/oxalates/citrates/hydrazine carboxylates etc. are some of the commonly used precursor compounds. Costa et al [118] have used a combustion process wherein they used metal nitrates and urea as starting compounds. Single phase Ni-Zn ferrite was formed due to self-ignition of the mixture at 600^0C.

This method is also known as the "self-sustaining/propagating synthesis process." The process is rapid and may approach direct conversion from the molecular mixture of the precursor solution to the final oxide product. The disadvantage is that sometimes the exothermic reaction might be difficult to control especially when being performed on a large-scale.

(f) Reverse Micelle Method [46, 47]

A reverse micellar system consists of nanometer sized water droplets that are dispersed in an oil medium and stabilized by a surfactant. In this method, tiny droplets of water are encapsulated as a reverse micelle. The structure of a reverse micelle is characterized by a polar core formed by hydrophilic heads of the surfactant and a non-polar shell formed by hydrophobic tails of the surfactant. The droplet size of reverse micelles can be readily modulated in the nanometer range particularly by controlling the water: surfactant ratios. Morrison et al [46] have synthesized Ni-

Zn ferrite at room temperature using reverse micelle technique. Reverse micelle system was prepared using sodium dioctylsulfosuccinate with isooctane oil phase. The reverse micelle system was mixed with aqueous metal chloride solution whose pH was controlled using ammonia. Further processing and drying over-night in a vacuum chamber resulted in Ni-Zn ferrite nanoparticles.

The reverse micelle method leads to the controlled synthesis of ceramic materials and metals having a tailored shape, size and composition. The method can be used to synthesize monodispersed nanoparticles with various morphologies. However, this method requires a large amount of organic solvent and also the yield of production is low.

1.4 Gap in Existing Research:

Based on literature survey, it has been found that the existing methods of preparation for iron oxide and Ni-Zn ferrites are associated with one or more limitation.

Solid state method is incapable of producing nanostructured ceramic powders due to its inherent limitation of long heating schedules at high temperatures ($>1000^0$C) that results in coarsening of grains.

Although gas phase methods are able to deliver high quality products, the yields are usually low and scale-up of the equipment is challenging. Variables such as oxygen concentration, gas phase impurities, and the heating time must be controlled precisely to obtain pure products. Moreover, the equipment used in these methods is also expensive and requires maintenance.

Conventional solution phase methods are capable of producing nano-structured iron oxide and ferrite powders but they are also associated with some inherent limitations such as (i) use of expensive metal alkoxides or complex metal compounds, (ii) use of delicate reagents which are difficult to handle, (iii) frequent use of strong acids/bases and organic solvents, (iv) formation of heterogeneous/undesirable crystalline phases (v) requirement of elaborate experimental setup and time consuming processes. The importance of single phase material should not be undermined as the electrical and magnetic properties of materials are highly sensitive to the purity of phase of the synthesized material.

A synthesis method becomes highly attractive if it is versatile and has the capability to produce single phase, nanopowders at a comparatively low temperature in a cost-effective and time-efficient manner without using any elaborate experimental set up. Therefore, development of a technically simple but cost-effective synthetic methodology for preparation of pure and homogeneous iron oxide and ferrite nanopowders is a major challenge till now.

1.5 Objective:

The objective of the present research work is the development of simple and aqueous solution based chemical methodologies to synthesize nanostructured α-Fe_2O_3 and series of $Ni_{1-x}Zn_xFe_2O_4$ $(0 < x < 1)$ nanopowders.

1. Development of aqueous solution based chemical methodologies for synthesis of α-Fe_2O_3 and $Ni_{1-x}Zn_xFe_2O_4$ $(0 < x < 1)$ nanopowders by the following methods:

    Method 1: PVA precursor based method.

    Method 2: Oxalate precursor based method.

    Method 3: EDTA precursor based method.

2. Structural characterization of the synthesized nanopowders by using X-Ray Diffraction, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

3. Investigations on electrical and magnetic properties of synthesized nanostructured α-Fe_2O_3 and $Ni_{1-x}Zn_xFe_2O_4$ $(0 < x < 1)$ powders.

1.6 Characterization Details:

The as-synthesized nanopowders were characterized by the following techniques:

1. Thermal Analysis:

Thermo gravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) analyses were carried out for the precursors by using Shimadzu DTG–60 and Shimadzu DSC–60 respectively. The thermal analyses were performed in air at a constant heating rate of $20^0C/min$ in the temperature range of 40 to 550^0C.

2. X-Ray Diffraction (XRD) Analysis:

Room temperature XRD spectra of the precursors and the calcined powders for all compositions were recorded by using a Rigaku Powder X-Ray Diffractometer (Mini Flex II) with Cu K_α (λ = 0.15405 nm) radiation. The scan was performed between 10 to 70 degrees.with a sampling speed of 2 degree per minute and sampling width of 0.01 degree. The slow scans were performed with a sampling speed of 1.2 degree per minute and a sampling width of 0.02 degree.

3. Transmission Electron Microscopy (TEM) Analysis:

The particle size of the calcined powders was determined by using a FEI HRTEM (Tecnai G2 30 S-Twin, Netherlands) and a Field Emission Gun TEM (JEOL JEMS FEG-TEM, 2100).

4. Scanning Electron Microscopy (SEM) Analysis:

Microstructures of the calcined and sintered samples were studied by using JEOL Scanning Electron Microscopy (JSM-6360LV). The sintering of the samples was performed in the temperature range of 1100 to 1300^0C for 2 hours. Grain growth, size and shape of the grains and porosity etc. of the samples were assessed by using the SEM micrographs.

5 DC Resistivity by two-probe Method:

DC resistivity was measured from room-temperature to 225^0C by the two-probe method using a Keithley Electrometer (6517 A). For this measurement, powders were pressed into pellets of ~13 mm diameter and ~ 2 mm thickness by applying a pressure of 3 tons. The pellets were coated with silver on both surfaces for resistivity measurements.

6. Magnetization Measurement:

Room temperature magnetization measurement was performed for calcined powders for all compositions by using an ADE Vibrating Sample Magnetometer (VSM) (EV5). The applied field varied between ±2kOe.

1.7 Outlay of the Thesis:

The thesis is divided into eight chapters and each chapter is followed by a summary.

In Chapter 1, the subject of nanostructured iron oxide and ferrites, general methods for their synthesis, identification of research gaps based on literature review and the objective of the present research work have been discussed.

Chapter 2 describes a PVA precursor based method to synthesize and characterize α-Fe_2O_3 nanopowder.

An Oxalate precursor based method has been described in Chapter 3 that has been used to synthesize and characterize α-Fe_2O_3 nanopowder.

Chapter 4 describes an EDTA precursor based method that was used to synthesize and characterize α-Fe_2O_3 nanopowder.

In Chapter 5, a PVA precursor based method has been described that has been used to synthesize and characterize $Ni_{1-x}Zn_xFe_2O_4$ $(0 < x < 1)$ nanopowders.

Chapter 6 describes an Oxalate precursor based method to synthesize and characterize $Ni_{1-x}Zn_xFe_2O_4$ $(0 < x < 1)$ nanopowders.

An EDTA precursor based method has been described in Chapter 7 that was used to synthesize and characterize $Ni_{1-x}Zn_xFe_2O_4$ $(0 < x < 1)$ nanopowders.

In Chapter 8, the conclusions and future scope of research work have been presented along with a comparative summary of results for the three developed chemical methods.