Contents lists available at ScienceDirect

Microchemical Journal

Chemical analysis of size-tailored magnetic colloids using slurry nebulization in ICP-OES

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ARTICLE INFO

ABSTRACT

In this work, inductively coupled plasma emission spectroscopy was utilized to directly determine the chemical composition of magnetic fluids constituted of size-sorted ferrite nanoparticles in aqueous solution. Nickel and cobalt nanoferrites were chemically synthesized following a bottom-up route and dispersed under various pH conditions. Size and structural characteristics of nanograins were investigated by X-ray diffraction using a synchrotron source. Chemical analysis was then carried out by directly introducing diluted magnetic fluid samples (slurries) into the spectrometer. To achieve reliable measurements, sample conditions and apparatus parameters were carefully investigated. Slurry stability must be optimized in order to obtain reproducible and accurate analysis. The instrument must also be calibrated to minimize the difference between the signal produced by slurries and that of aqueous ordinary solutions. Furthermore, slurry sample introduction offers many advantages over conventional sample digestion, including reduced sample pretreatment time, less possibility of contamination and the use of direct calibration with aqueous solutions.

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1. Introduction

Surface engineering of nanoparticles has opened new frontiers in science through the design of new functional materials with novel properties; these are widely appreciated in applications ranging from electronics to medicine[1].

In such a context, special attention has been paid to magnetic nanostructures, particularly spinel ferrites with general formula MFe_2O_4, where M is usually a divalent transition metal. The surface of these oxides is extremely reactive to the chemical attachment of functional molecules or to generating a superficial density of charge which, for example, permits the nanograins to disperse into several non-polar or polar matrixes of different viscosities[2]. Furthermore, other applications are possible, depending on surface modification, which can vary from a simple molecule to a more complex biostructure. Given the correct surface modification, nanoparticles can be applied in the field of medicine, in drug delivery, cell separation or advanced clinical uses in cancer diagnosis and treatment[3].

In order to evaluate the composition and the concentration of nanoparticles in administrated magnetic fluid (MF) samples, tissues, blood and other fluids, the quantification of nanograins has traditionally been achieved by chemical analysis. The techniques used for this vary from classic titrations[4] to instrumental methods such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)[5]. These methods normally require metal ions in aqueous solution and, before chemical analysis, sample digestion by acidic dissolution of nanograins in concentrated acidic medium. However, it is important to emphasize that the digestion procedure increases the time of analysis and, as a consequence, it is not uncommon to experience losses or sample contamination, dilution of analytes, or even incomplete dissolution of solids[6]. In spite of the problems encountered with sample digestion, the direct analysis of slurries in plasmas is an alternative to minimize these effects and significantly reduce sample preparation time by combining matrix destruction and analyte atomization/excitation in a single step[7].

It is well known that slurries containing particle sizes smaller than 5 μm are easily analyzed using an ICP-OES with proper introduction system and operational conditions. Thus, for the samples studied in this work, the digestion process seems not to be crucial to perform chemical analysis. However, slurry introduction it is not a usual application and it is worth to evaluate its analytical behavior with this kind of sample.

In fact, this is a versatile technique which also permits the introduction of finely divided powders into the plasma, thus significantly increasing potential for the analysis of a wider range of materials, from inorganic to biological samples[8]. When slurries are used, the main advantages lie in sample preparation: it is simple, no aggressive reagents are needed (so contamination can be minimized), it is relatively quick and calibration can be done using aqueous standards as in conventional

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methods[9]. However, it is important to keep in mind that if accurate analyses are to be obtained some ideal conditions must be met: the particles should be as small as possible, the slurry must present high colloidal stability and the maximum amount of solid sample in the slurry must be kept low to ensure its stability and low viscosity[10].

In this work one proposes slurry sample injection, with ICP-OES as the instrumental method, to directly determine the chemical composition of MF samples. Thus, to investigate the validity of the proposed method, MF's were analyzed by direct injection of the samples as slurries in the ICP device, and compared to those of conventional acidic digestion. The MF samples utilized here are based on size-tailored cobalt ($CoFe_2O_4$) and nickel ($NiFe_2O_4$) ferrite nanograins dispersed in aqueous solution at different pH conditions. Furthermore, the experimental settings such as aerosol gas flow rate and colloidal stability were optimized in order to use M^{2+} and Fe^{3+} aqueous solutions as calibration curves in the proposed slurry nebulization technique. The results of direct sampling and aqueous introduction analysis were statistically compared, to confirm the reliability of our proposed method.

2. Materials and Methods

2.1. Samples

The MF samples investigated in this work correspond to colloidal suspensions of ferrite nanoparticles dispersed in aqueous solution. Cobalt ferrite nanoparticles were electrostatically peptized into acidic solution while $NiFe_2O_4$ nanostructures were stabilized in neutral medium after surface functionalization with citrate molecules. The process of elaboration involves the chemical synthesis of nanostructures, nanoparticle peptization and a size-sorting procedure performed in colloidal samples.

2.1.1. Nanoparticle synthesis

Cobalt[11] and nickel[12] nanoferrites were synthesized by forced hydrolysis of Fe^{3+} and M^{2+} ($M = Co^{2+}$ or Ni^{2+}) in aqueous alkaline solution. In this process, 500 mL of a stoichiometric Fe^{3+}/M^{2+} solution, containing 250 mmol of Fe^{3+}, reacted with 2000 mL of concentrated NaOH solution at boiling temperature under vigorous stirring, for 60 minutes. Then the obtained solid was magnetically separated from supernatant and washed three times with distilled water. After that, the precipitate was acidified overnight with a 2 mol/L HNO_3 solution and the supernatant was discarded. The nanograins were hydrothermally treated by boiling 1 mol/L $Fe(NO_3)_3$ for 30 minutes and the excess of ferric nitrate was removed from the solution by magnetic decantation.

2.1.2. Nanoparticle peptization

The precipitates were dispersed in aqueous solution as follows: cobalt ferrite was directly peptized in aqueous acidic medium according to the procedure reported in ref. 12. In this case, the nanograins were washed with acetone three times, then the desired amount of water was added and the excess of acetone was evaporated in order to form a magnetic fluid with pH of about 2. In the case of nickel ferrite, the nanoparticles were functionalized with citrate molecules using the experimental conditions described elsewhere[13]. After that, by removing the excess of citrate and adjusting the acidity of the solution, a magnetic sol could be obtained at pH of around 7.

2.1.3. Size-sorting

A sample based on $CoFe_2O_4$ nanoparticles was size-sorted by centrifugation[14], at 4000 RPM for 15 minutes, yielding a supernatant (sample C1) and a bottom part (C2) which were separated and re-dispersed in aqueous solution.

In the case of $NiFe_2O_4$ sol, the size separation was done by using NaCl to increase the ionic strength of the sol, which induces a phase transition in the colloid[13]. This procedure was repeated twice, yielding four samples that were re-dispersed in water (N1 to N4).

2.2. ICP-OES analyses

The chemical determination of metals was carried out using a Varian-Liberty Sequential ICP atomic emission spectrometer (optical emission mode), equipped with a Sturman-Masters nebulizer chamber coupled with a V-groove nebulizer and radial torch, operated under the guidelines presented in the Table 1. Iron, nickel and cobalt were analyzed at 259.837, 221.647 and 228.616 nm respectively. Calibration curves were obtained using 1000 ppm standard Fe^{3+}, Co^{2+} and Ni^{2+} solutions and diluted to the concentration ranges presented in the results of this work. For ICP-OES analysis, two methods of sample introduction were compared: *i*) the traditional procedure, in which the nanoparticles are dissolved by acidic digestion with concentrated HCl, here named Aqueous Solution Introduction (ASI) and *ii*) our suggested Slurry Sample Introduction (SSI), where samples are directly injected into the ICP torch as slurries obtained from direct dilution of ferrofluids with water. Furthermore, it is important to emphasize that in both methods aqueous samples or slurries must be diluted to the calibration curve range before introduction. To refine this study, instrumental parameters and chemical conditions (such as pH and slurry concentration) were investigated with a view to determining best conditions for analysis.

2.3. Structure characterization

The crystalline structure of the solids and their mean crystalline sizes were determined by synchrotron X-ray diffraction (XRD)[15]. The diffraction patterns were measured at the Brazilian Synchrotron Light Laboratory (LNLS) using the D12A-XRD1 beam line. Powders of ferrites were obtained by evaporating the MF samples at room temperature. Diffractograms were obtained typically within $15° \leq 2\theta \leq 100°$ range, using a 1.771 Å X-ray beam and a rotating sample holder to improve the randomization of the crystallites. The average crystal size (d_{XR}) was deduced by means of the Scherrer formula from the width at half maximum of the diffraction line (311).

3. Results and Discussion

3.1. Samples

As shown in Fig. 1a, examples of diffractograms for $CoFe_2O_4$ and $NiFe_2O_4$ nanograins, a typical system of lines characteristic of the spinel structure was identified for all the obtained precipitates.

Table 2 lists the cubic lattice parameters (deduced from XRD results) in good agreement with Inorganic Crystal Structure Database values of 8.40 Å and 8.34 Å for cobalt and nickel ferrites respectively. Additionally, the broadening of the 311 main peak, which can be observed in detail in Fig. 1b and c, respectively, for $CoFe_2O_4$ and $NiFe_2O_4$ powders, allowed calculation of the mean crystalline sizes d_{XR} of the grains through the Scherrer formula (see Table 2).

These results confirm the reliability of the chemical procedure to synthesize nanoparticles with spinel structure and the efficiency of the size-sorting methods to produce sol samples with nanoparticles of

Table 1
ICP-OES operational parameters.

Parameter	Operating Conditions
Power	1.2 Kw
Plasma flow	15.0 L/min
Auxiliary flow	1.5 L/min
Nebulizer pressure	200 KPa
Viewing height	10 mm
PMT	650 V
Pump rate	15 rpm