# PREPARATION OF SOFT MAGNETIC MATERIALS AND CHARACTERIZATION WITH INVESTIGATION METHODS FOR FLUID SAMPLES

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*The present study was focused on the comparison of magnetite nanoparticles prepared by two variants of chemical coprecipitation method and stabilized with sodium oleate in aqueous suspension. Coated ferrophase was showed to have crystalline structure with typical spinel features and superparamagnetic properties in both sample types. Colloidal suspension analysis evidenced higher zeta-potential and lower polydispersity index in the samples treated with acidic washing agent. Multifractal study of imagers provided by Nanoparticle Tracking Analysis displaying particle movement in real time showed significantly smaller($p<0.00001$) fractal dimension for the sample prepared with intermediate acidification step – in concordance also with previous analyses results.*

**Keywords**: nanosized magnetite, steric stabilization, X-ray diffractometry, Vibrating Sample Magnetometry, Dynamic light Scattering

## 1. Introduction

Widely spread applications of magnetite nanoparticles in biomedicine is due to iron nontoxicity and biocompatibility [1] –being known that human body contains various biomolecules containing iron, like cytochromes from mitocondrial membranes that catalyze redox reactions underlying cell energetics or haemoglobins ensuring tissue respiration. Nanoparticle supply in the organism can be done only in the form of aqueous fluid products resulted by magnetite coating with suitable molecules also nontoxic and biocompatible that could impede magnetic attraction forces to generate agglomerates in the complex fluid.

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Further, upon the protective coating shell other molecules could be grafted as drugs against cancer – their targeted delivery being magnetically assisted.

Among various other organic acids able to develop physical forces with iron ions from magnetite nanoparticles, oleic acid is recognized as longest chain and strongest interaction provider; however it is not soluble into water so that polymers like polyethylene glycol [2] polysaccharide polymer dextran or protein bovine serum albumin were applied to modify particle surface for yielding water dispersive products. More recently oleate ions from sodium oleate were considered for magnetite stabilization in aqueous suspensions [3-7] due to their good biological compatibility [8].

## 2. Experimental

**2.1 Materials.** Ferrous chloride tetrahydrate ($FeCl_2 \times 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \times 6H_2O$), sodium hydroxide (NaOH) and sodium oleate ($C_{18}H_{33}O_2Na$) used in this experimental protocol (analytical high purity reagents) were purchased from Sigma-Aldrich, while deionised water (18.2 MΩ/cm) used throughout the whole experiment to prepare the solutions was obtained using Barnstead EasyPureII water purification system.

**2.2. Synthesis method**. Magnetite particles were synthesized by chemical co-precipitation at high temperature (Massart's method [9]). 150 ml of 2.0 M NaOH solution was added dropwise into the mixture of the iron salts aqueous solutions (3.996 g $FeCl_2 \times 4H_2O$ and 10.866 g $FeCl_3 \times 6H_2O$ in the stoichiometric ratio of 1:2) under intense magnetic stirring at 80 °C. The ferrophase particles were separated from the reaction medium in magnetic field gradient and purification by repeated washing with warm deionized water - for P1 sample, but for P2 sample with an intermediate acidification step was applied before the last washing. Ferrophase was sterically stabilized with 1.5 % sodium oleate at 75 °C - with homogenization and deionized water dropwise addition up to 100 ml total volume under constant mechanical stirring for 1 h.

**2.3 Sample characterization.**

2.3.1. Crystalline structure of ferrophase was evidenced by X-ray Diffractometry (XRD) with Shimadzu 6000 device using Cu-$K_\alpha$ radiation at $\lambda$ = 1.5406 Å. Average size of the crystalline domains $D_{ijk}$ was calculated from Scherrer's equation [10]:

$$D_{ijk} \qquad D_{ijk} = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where $k$ is a dimensionless factor which varies with the shape of the crystallite (in this case $k=0.9$), $\beta$ is line broadening at half the maximum intensity and $\theta$ is the Bragg angle.

2.3.2. Ferrophase magnetic properties were investigated using Vibrating Sample Magnetometer (VSM) System (MicroMag model 2900/3900).

Magnetic core diameter was assessed from magnetization curve based on Langevin's theory [11]:

$$d_M^3 = \frac{18k_BT}{\pi\mu_0 M_S m_S}\left(\frac{dM}{dH}\right)_{H\to 0} \tag{2}$$

where $d_M$ is the magnetic diameter of particle (the diameter of its magnetic core), $k_B$ is Boltzmann's constant, $T$ is the absolute temperature, $Ms$ is the saturation magnetization value of the prepared sample and $\mu_0$ is the magnetic permeability of vacuum, while the value of bulk magnetite saturation magnetization was $m_s$=0.48·10$^6$ A/m [12].

2.3.3. Dynamic Light Scattering (DLS) analysis (with DelsaNano C analyzer coupled with an Autotitrator DelsaNanoAT module), was used for assessing colloidal stability of magnetite particle suspension. Nanoparticle Tracking Analysis (NTA) (with NanoSight module) allowed real-time visualization and measurement of ferrophase particles in diluted ($10^{-4}$) aqueous solution, relating the rate of Brownian motion to particle hydrodynamic diameter.

2.3.4. Fractal dimension of NTA images was calculated using FracLac (a plugin for ImageJ1 software) as an average for about 50 calculations carried out for images taken at 1 second interval from the real time display provided by NTA in the case of each fluid suspension sample.

## 3. Results and discussion

### 3.1 Coated ferrophase investigation.

Investigation of coated ferrophase microstructural features has revealed good crystalline properties with mono-phase typical spinel structure of magnetite (Fig. 1). All characteristic diffraction peaks were identified with no other impurity presence. Average size of magnetite crystallite was estimated applying Scherrer's formula for all measurable XRD peaks that resulted in about 7.5 nm for P1 and 10.2 nm for P2. VSM data allowed observing similar superparamagnetic properties (no hysterezis in the magnetization curves – Fig. 2) with about the same saturation magnetization density (20 Am$^2$/kg) and approximately the same magnetic diameter of 7.5 nm.

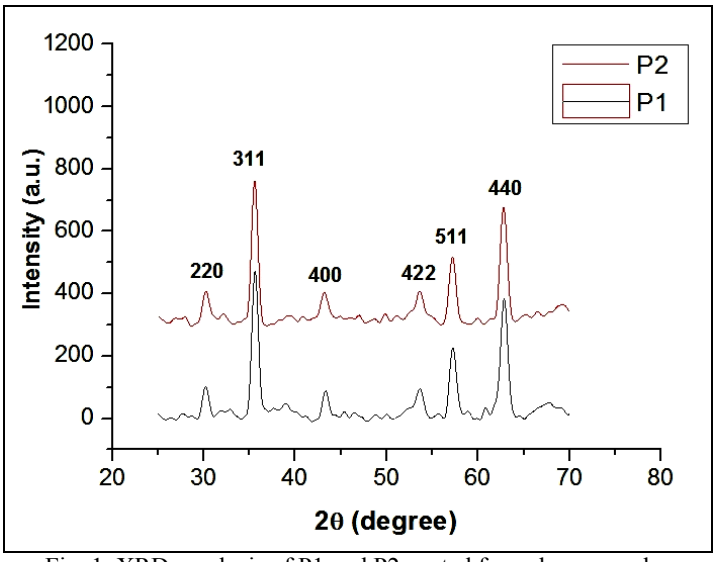


Fig. 1. XRD- analysis of P1 and P2 coated ferrophase samples

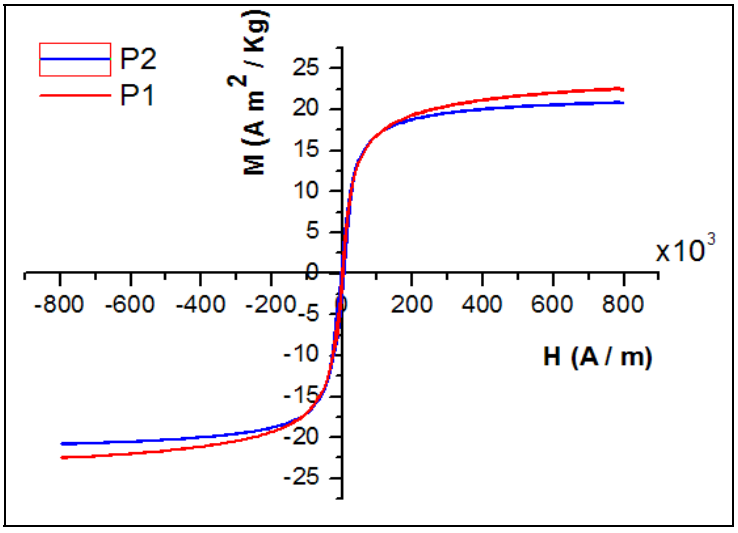


Fig. 2. Magnetization curves for P1 and P2 coated ferrophase samples

Similar level of sample magnetizability corresponding to about 20 $Am^2/kg$ was reported in [13] for magnetite core/oleate shell nanosized systems.

It can be concluded that from the viewpoint of structural and magnetic properties both samples are good crystalline materials with similar soft magnetic properties.

### 3.2. Fluid colloidal sample investigation.

DLS data allowed the evidence of very good stability of colloidal particles in suspensions as long as both values of zeta-potential were over the theoretical threshold of – 40 mV. Indeed, both zeta-potentials were higher in absolute values with more than 50% compared to the threshold; slight but suggestive difference was noticed in the favor of P2 sample, with – 65 mV compared to -61 mV for P1. Zeta potential is critical parameter in estimating electrical charge characteristics of nanoparticulate sample in fluid which determines the overall behavior of colloidal suspension. It seems that magnetite particles have been actually well coated with oleate ions provided through sodium oleate dissociation in water. Ion oleate was frequently proved to be the best stabilizer of magnetic nanoparticles in fluid phase, beginning with the first oily ferrofluids prepared by magnetite suspension in hydrocarbons – that presents good miscibility with oleic acid - known as hydrophobic long chain fatty acid able to develop the strongest interaction with iron cations. Those oily ferrofluids were addressed to technical applications but later biomedical purposes required aqueous soft magnetizable materials.

Thus, magnetite particles could be coated with oleate ions from the hydrophilic and biocompatible [8] sodium oleate (in low concentration and warmed at temperatures considerably over environmental one). In the present case sodium oleate was the stabilizing ingredient for both types of magnetite particles – resulting however in some differences in the favor of the sample prepared with intermediate acidic washing step.

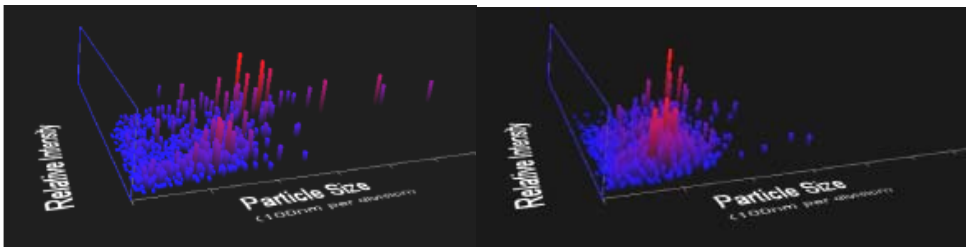


Fig. 3. Left side – P1; right side – P2; 3-D graph of particle dimensional distribution (1800 display frames of 78 particles each)

Thus, polydispersity – as consequence of particle dimensionality, was better for P2, characterized by polydispersity index of 0.65 -remarkably lower than 0.95 in the case of P1. It is undoubtedly that acidic washing step during P2 ferrophase extraction from the reaction medium was able to ensure better cleaning of particle surface, favoring better adsorption of coating oleate ions compared to P1 sample– washed only with hot deionized water. It is presumable that in the case of P1 sample, as consequence of slighter coating with oleate ions some particle association occurred and thus wider size distribution resulted as suggested by higher polydispersity index. NTA investigation method allowed counting

particle concentration and dimensional distribution by analyzing 1800 frames (30 frames/s) and 78 particles/frame (Fig. 3).

It was evidenced smaller hydrodynamic diameter for P2 compared to P1 (106 nm and respectively 162 nm, Fig. 4) while particle concentration was similar ($8.87\times10^8$/ml and respectively $11.66\times10^8$ /ml); also smaller standard deviation of hydrodynamic diameter distribution was found for P2**.**

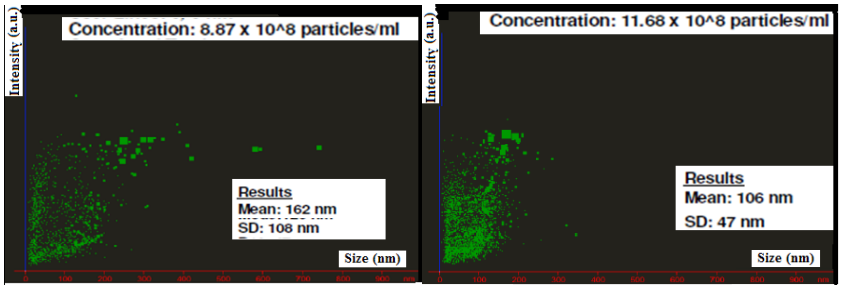


Fig. 4. NTA analysis result - relative intensity versus particle size; left side – P1; right side – P2

Hydrodynamic diameter values suggested that particles have occasionally agglomerated before or after oleate ions addition although the accuracy of light scattering technique seems to be not completely controlled because of unevaluated effects related to particle concentration in suspension, scattering angle, and shape anisotropy of nanoparticles [14].

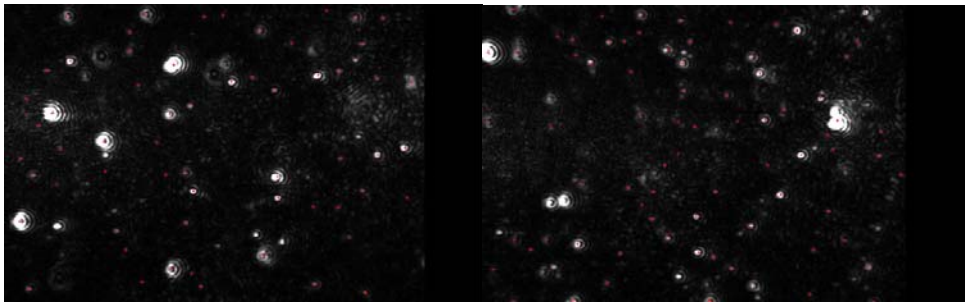

Fig. 4. Original images taken for particle tracking recordings used for fractal analysis; left side – P1; right side – P2

Fractal analysis was applied to consecutive images taken from NTA display at every 5 seconds (Fig. 4) to compare the complexity of particle spatial distribution in the fluid samples. Images were pre-processed to eliminate artifacts generated by particle image shadows.

Significant differences were evidenced in the average fractal dimensions estimated for P1 and P2 samples, respectively 1.19 compared with 1.22 – with

remarkable statistic significance ($p<0.000001$). We think that more complex image, with higher fractal dimension is concordant with lower dimensions of suspended particles that generated more details in the analyzed pictures.

## 4. Conclusions

Coating magnetic nanoparticle following surface washing with acidic medium seems to contribute significantly to colloidal suspension stabilizing efficacy.

For approximately identical magnetic properties of magnetic cores, better granularity and lower polydispersity for the coated particles were evidenced in colloidal systems resulted from ferrophase treated by acidic intermediate washing.

In the next research study on magnetite core/oleate shell products, further improving of particle coating efficiency is planned together with increasing accuracy of granularity control in colloidal samples.

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