Characterization of iron oxide nanoparticles by magnetometry: temperature deviation from Langevin law

D. Henrard[1] [daniel.henrard@umons.ac.be], Q. L. Vuong[1], S. Delangre[1], X. Valentini[2], D. Nonclercq[2], Y. Gossuin[1]

[1]*Biomedical Physics Department, University of Mons, Belgium*
[2]*Department of Histology, University of Mons, Belgium*

Introduction

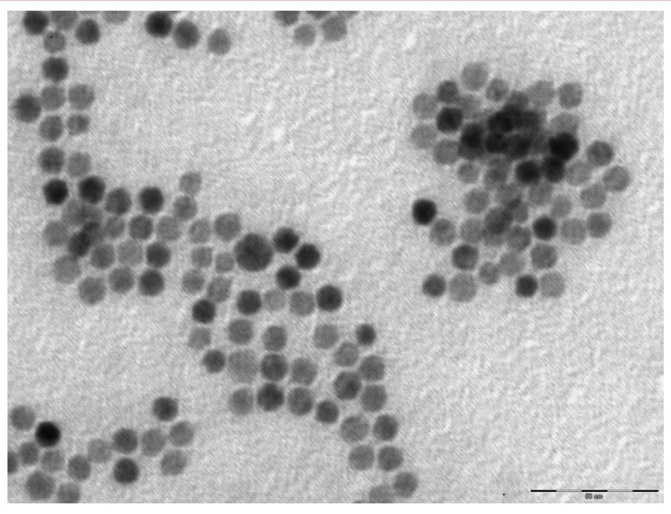


Figure 1. TEM image of iron oxide nanoparticles (Magnification = 60000)

Iron oxide nanoparticles (NP) →

- Hyperthermia
- Tumor targeting
- Drug delivery therapy.
- Magnetic Resonance Imaging (MRI) as negative contrast agent.
- etc…

Key role : **size and magnetization**.
We need optimal characterization.

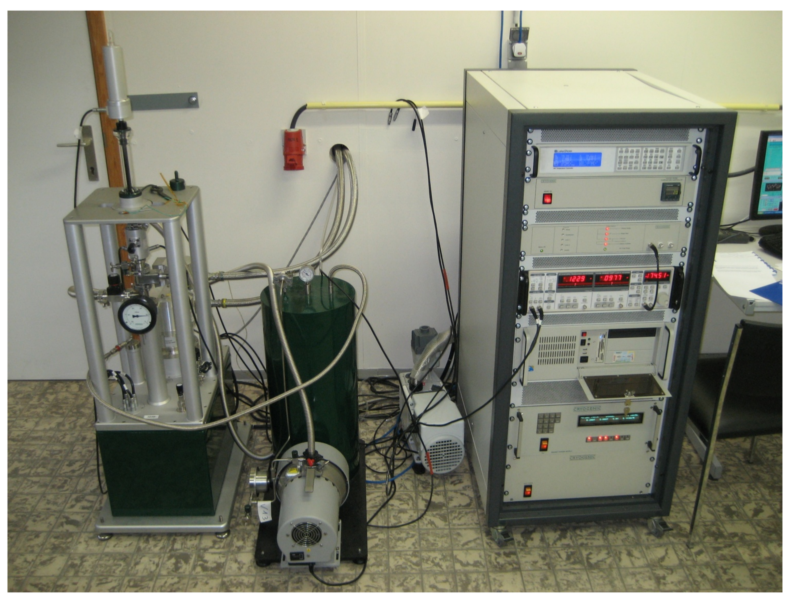


Photo of the Vibrating Sample Magnetometer (VSM)

In this work, we explored the characterization by magnetometry with a Vibrating Sample Magnetometer (VSM), in particular the effects of temperature, size distribution and anisotropy on magnetization of different-sized magnetite NP (Fe_3O_4). We carried out magnetization as function of the magnetic field (MH curves) at 100, 200, 275 and 300K.
Transmission electron microscopy (TEM) were also performed for comparison.

Superparamagnetism

- **Single Weiss domain. Giant magnetization. No interaction between NP.**
- **Easy axes but weak anisotropy K_A** allows magnetic moment **thermal fluctuations** at low magnetic fields.
- **Neel relaxation time τ_N : characteristic time between two fluctuations**. If **τ_{xp} is the characteristic time for measurement**, each NP can be in **two states** :
  - **Superparamagnetic** if $\tau_{Neel} << \tau_{xp}$ (**for small NP : $r_{NP} < r_B$**). Thermal fluctuations; average magnetic moment is measured.
  - **Blocked** if $\tau_{Neel} >> \tau_{xp}$ (**for large NP : $r_{NP} > r_B$**). No thermal fluctuations. Blocked magnetic moment is measured.

$$r_B = \sqrt[3]{\frac{75 k_B T}{4\pi K_A}} \quad (1)$$ **is the blocking radius.**

Global magnetization[1] : $$M = N\int_0^{\infty} \mu L\left(\frac{\mu B}{k_B T}\right) f_{\log}(r, r_0, \sigma)\, dr \quad (2)$$

N = 1/<V> : number of NP per unit volume.
$\mu = M_{sat} V$: magnetic moment of the NP
L(x) : langevin function.
f_{log} : log-normal size distribution ; r_0 is the median radius ; σ is the logarithm standard deviation.

$$f_{\log}(r, r_0, \sigma) = \frac{\exp\left(-\left(\ln r/r_0\right)^2 / 2\sigma^2\right)}{r\sigma\sqrt{2\pi}}$$

Methodology

VSOP were purchased from Ferropharm gmbh. **To prevent from clustering**, the solutions were **stabilized with citrate**.

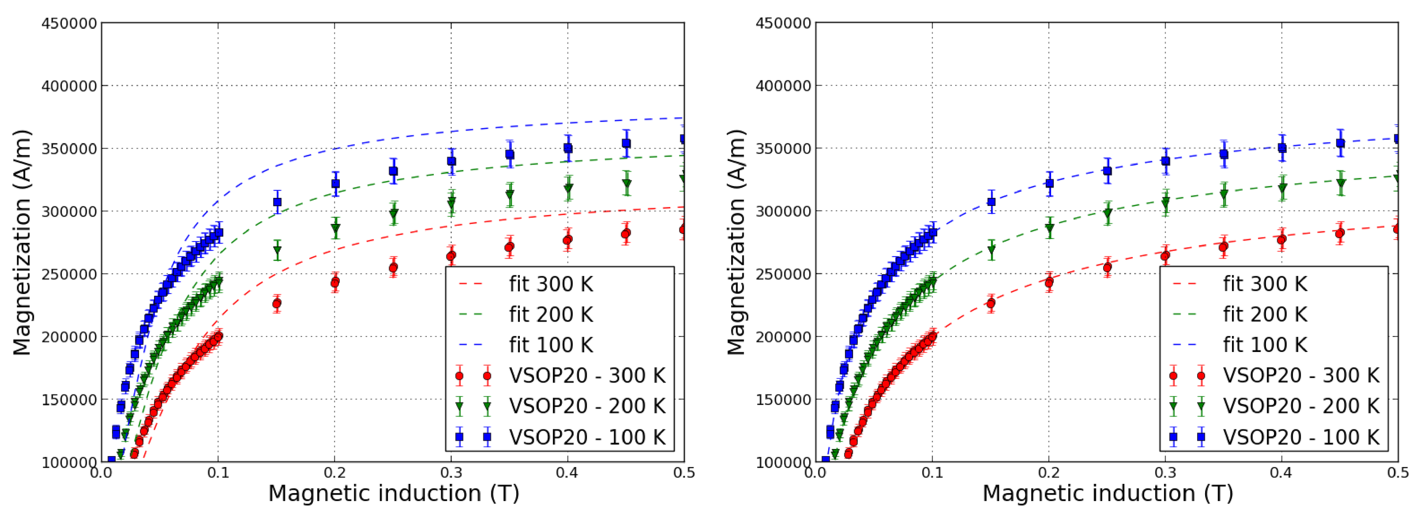
- **Iron concentration** were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy **(ICP-AES)** after microwave digestion.
- **Transmission electron microscopy (TEM)** images were used to count NP with ImageJ. Lognormal size distribution worked slightly better than gaussian distribution.
- **MH curves** were fitted with equation (2) with three free parameters : r_0, σ and M_{sat}.
  - All our fits were analyzed with R^2_{adj} . This estimator tends to decrease if too many parameters are used.
  - **Diamagnetic contribution is subtracted** : $S_{corr} = S_{meas} - pB$ where p comes from fit pB M_{sat} to points whose |B| ≥ 2.5 T. This method worked well (all R^2_{adj} for diamagnetic fits > 0.99995) because saturation is reached quickly : magnetization is at least 99% of saturation when |B| ≥ 2 T (see example on figure 3).
  - To evaluate the appropriateness of each parameter, we tested 4 different fits : r_0 as the only parameter (fit r_0) ; r_0 and σ as parameters (fit r_0 + σ) ; r_0 and M_{sat} as parameters (fit r_0 + M_{sat}) ; r_0, σ and M_{sat} as parameters (fit r_0 + σ + M_{sat}). When M_{sat} is not a free parameter, it is fixed at S_{corr} maximum value.
  - Errors on magnetization, magnetic field and temperature are estimated (really mainly evaluated) at 3%. Errors on fitted parameters is evaluated by summing fitted error (< covariance matrix) and maximum difference between fitted parameters and parameters obtained by fitting with same data 3% errors.

Results and discussion

- **Fit r_0 + σ is better** than other fits (see table 1 and figures 2).
- Best consistency between TEM results and MH fit at 300K (see tables 2).
- r_0 parameter decreases when temperature decreases. }*
- σ parameter increases when temperature decreases. }*

	fit r_0	fit r_0+σ	fit r_0+M_s	fit r_0+σ+M_s
$\langle R^2_{adj} \rangle$	0.9982	0.9999	0.9984	0.9998

Table 1. $\langle R^2_{adj} \rangle$ for all fits.



Figures 2. Fit r_0 (left) and fit r_0 + σ (right) of MH curves for VSOP20. Graphically, fit r_0 + M_{sat} is similar to fit r_0 (left) ; fit r_0 + σ + M_{sat} similar to fit r_0 + σ (right).

fit r_0+σ	300K		275K		200K		TEM	
	r_0 (nm)	σ	r_0 (nm)	σ	r_0 (nm)	σ	r_0 (nm)	σ
VSOP3	3.53 +/- 0.10	0.1965 +/- 0.0037	3.41 +/- 0.09	0.2084 +/- 0.0030	2.95 +/- 0.08	0.2910 +/- 0.0031	3.131 +/- 0.033	0.167 +/- 0.009
VSOP5	3.54 +/- 0.09	0.1558 +/- 0.0041	3.46 +/- 0.09	0.1684 +/- 0.0036	3.22 +/- 0.09	0.2132 +/- 0.0025	3.171 +/- 0.025	0.214 +/- 0.007
VSOP10	3.98 +/- 0.11	0.2953 +/- 0.0026	3.89 +/- 0.11	0.3049 +/- 0.0027	2.95 +/- 0.08	0.3859 +/- 0.0030	3.58 +/- 0.07	0.274 +/- 0.015
VSOP20	2.99 +/- 0.09	0.3611 +/- 0.0036	2.92 +/- 0.09	0.3683 +/- 0.0034	2.45 +/- 0.07	0.4184 +/- 0.0029	3.47 +/- 0.06	0.247 +/- 0.013

Table 2. Median radius r_0 (nm) and sigma fitted to MH curves (left) and TEM results (right).

* This is not logical : no reason that NP shrink when temperature decreases. Thermal dilatation is not so strong ! ☺

Diff params	fit 300K – fit 275K		fit 300K – fit 200K		Néel blocked NP contribution to signal (‰)	
	r_0 (%)	σ (%)	r_0 (%)	σ (%)	300K	200K
VSOP3	+3.5	-6	+16	-48	< 0.001	< 0.001
VSOP5	+2	-8	+9	-37	0.055	0.6
VSOP10	+2.5	-3	+26	-30.5	37	95
VSOP20	+2.5	-2	+18	-16	8.5	32

Table 3. Temperature variation of the fitted parameters r_0 and sigma (left) and blocked NP contribution to signal (right) calculated using TEM distribution size (see right of table 2) and r_b from equation (1). Constant anisotropy K_A comes from Zero-Field-Cooling (ZFC) magnetometre experiment.

<u>Hypothesis to explain this phenomenon :</u>

- Langevin law could be not sufficient to fit the data (e.g. anisotropy is not taken into account). On figure 3, 300K and 200K MH curves superimpose well so Langevin law works well in this range of temperature. Deviation is observed at and below 100K (figure 3), so, it could explain part of difference at and below 100K but not between 300K and 200K curves.
- Néel relaxation decreases when temperature decreases. Because of this, large NP (blocked) could not align as fast as "normally" possible with magnetic field. It could change the curves' slope at low magnetic fields and so influence fitted parameters. However, blocking effect is suppress above 273K by Brown relaxation that allows magnetic moments to align (by NP rotation) with magnetic field (in fact, there is no blocked NP at 300K). So, this hypothesis could explain part of difference below 273K but not between 300K and 275K curves.
- The difference could also come from an artifact in the fitting equation (2). Theoretical calculations show that, at same temperature, these two curves superimposes well : r_0 = 3.5 nm, σ = 0.2 compared to r_0 = 3 nm, σ = 0.3 The fitting program could decrease r_0 artificially increasing σ artificially. It could explain difference between 300K and 275K MH curves and part of difference below 273K, combined with the effects of other hypothesis (see table 3).

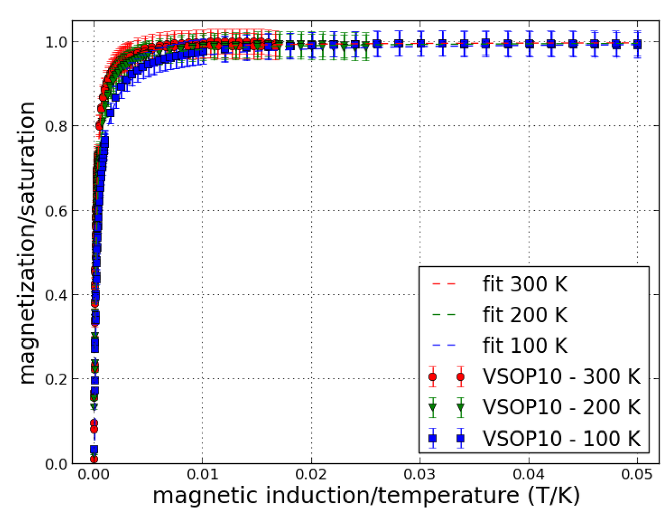


Figure 3. Fit r_0 + σ of MH curves for VSOP10. Magnetization is normalized by saturation magnetization ; magnetic field by temperature. When Langevin law works well, MH curves superimpose[1].

Outlook

- Zero-Field-Cooling and Field-Cooling : ZFC fitting done (provides anisotropy constant and size distribution too) but we have to understand deeper the physical mechanisms.
- Test deeper hypothesis and/or new ones : agglomeration effect ? Anisotropy influence ?

[1] M. Respaud and al., **Surface effects on the magnetic properties of ultrafine cobalt particles**, Physical Review B, 57, 5: 2925-2935 (1998)
[2] M. Respaud, **Magnetization process of noninteracting ferromagnetic cobalt nanoparticles in the superparamagnetic regime: deviation from Langevin law,** J. Appl. Phys, 86, 1, 556-561 (1999).