

A comparison of TEM and DLS methods to characterize size distribution of ceramic nanoparticles

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 J. Phys.: Conf. Ser. 733 012039

(<http://iopscience.iop.org/1742-6596/733/1/012039>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 80.82.77.83

This content was downloaded on 19/03/2017 at 03:57

Please note that [terms and conditions apply](#).

You may also be interested in:

[Size Distribution of Magnetic Marker Estimated from AC Susceptibility in Solution for Biosensor Application](#)

Keiji Enpuku, Tsuyoshi Tanaka, Yuya Tamai et al.

[Using neural networks for dynamic light scattering time series processing](#)

Dan Chicea

[Lead \(II\) ion detection in surface water with pM sensitivity using aza-crown-ether-modified silver nanoparticles via dynamic light scattering](#)

Liang Zhang, Yao Yao, Jin Shan et al.

[Green synthesis of silver nanoparticles with antibacterial activities using aqueous Eriobotrya japonica leaf extract](#)

Bo Rao and Ren-Cheng Tang

[Enhanced cellular uptake and cytotoxicity of folate decorated doxorubicin loaded PLA-TPGS nanoparticles](#)

Hoai Nam Nguyen, Thi My Nhung Hoang, Thi Thu Trang Mai et al.

[Optimization of the double-Gauss objective with the various evolution strategies and the damped least squares](#)

S Bakic and D Vasiljevic

[Sugar-mediated 'green' synthesis of copper nanoparticles with high antifungal activity](#)

Debajyoti Ray, Satadru Pramanik, Ranju Prasad Mandal et al.

[Determination of liquid viscosity at high pressure by DLS](#)

K Fukui, Y Asakuma and K Maeda

A comparison of TEM and DLS methods to characterize size distribution of ceramic nanoparticles

T. G. F. Souza¹, V. S. T. Ciminelli², N. D. S. Mohallem^{3*}

¹Graduate program on Metallurgical, Materials and Mining Engineering, UFMG

²Department of Metallurgical and Materials Engineering, UFMG

³Chemistry Department,

Universidade Federal de Minas Gerais, Belo Horizonte, CEP 31270-901, Brazil

E-mail: nelcy@ufmg.br

Abstract. The accuracy of dynamic light scattering (DLS) measurements are compared with transmission electron microscopy (TEM) studies for characterization of size distributions of ceramic nanoparticles. It was found that measurements by DLS using number distribution presented accurate results when compared to TEM. The presence of dispersants and the enlargement of size distributions induce errors to DLS particle sizing measurements and shifts its results to higher values.

1. Introduction

Nanoparticles (NP) present unique properties related to their size. Therefore it is important to be able to accurately characterize NP size distributions. Different techniques may provide different results [1, 2]. TEM is an excellent tool for characterizing NP [3], since its resolution reaches about 0.07 nm depending on sample thickness and accelerating voltage [4], but have a high cost and is operationally complex. For nanoparticles dispersed in solvents, DLS is a suitable technique that may allow access not just to particle size but also to the presence of agglomerates and aggregates [5]. It is a non-invasive, non-destructive, and low cost technique, and its operation is relatively simple and rapid. The main disadvantage is the data interpretation for polydisperse samples [4].

The present work compares size distributions of two ceramic NP with different sizes and assesses the effect of mixing (polydisperse system) in the final results.

2. Material and methods

2.1. Materials

Titanium oxide (TiO₂) was obtained from Minérios Ouro Branco. The cobalt ferrite (CoFe₂O₄) powders were prepared with stoichiometric amounts of cobalt and iron nitrates, precipitated by sodium hydroxide as described in previous works [5]. Both powders were dispersed (0.1% w/v) into deionized water with citric acid from Cargil. The two materials were analysed separately and together by mixing equal volumes of dispersions (TiO₂- CoFe₂O₄).



2.2. Transmission Electron Microscopy (TEM)

The diluted solution was dropped onto carbon-coated copper grids and then dried at environmental conditions. Images were acquired using a transmission electron microscope Tecnai G2-12 – Spirit Biotwin - 120 kV, from FEI. At least 10 locations on the TEM grid were examined. The quantity of NPs necessary to obtain reliable measurements was evaluated similarly as described in NIST protocol [3]. Image J software, freely available on the internet, was used for image analysis. Area sizes enclosed by the oval selection tool previously calibrated to the scale bar imprinted on the TEM images were determined. The diameter was calculated considering perfectly spherical shape.

2.3. Dynamical Light Scattering (DLS)

The DLS methodology followed recommendations outlined in the NIST-protocol [9]. The DLS measurements were performed using a Microtrac Instruments-Zetatrac 173 and its software. Measurements were performed at 25°C. The results were presented at intensity and number-based distributions.

2.4. Statistical Analysis

The NPs were prepared and analyzed in triplicate from the same batch and for each technique, under condition of repeatability. The normality of each sample data was tested using the Shapiro-Wilk Test. A p-value of ≤ 0.05 was considered statistically significant for all analyses, and ran using the R free Software [6], with an interface Excel via Action Software [7].

3. Results

TEM images show a good sample preparation and dispersion of the titanium oxide nanoparticles (figure 1). After each particle size was manually measured, the set of data was submitted to a normality test, since a normal distribution is mandatory for several hypothesis tests. Besides, the curve distribution determines the standard deviation and confidence interval calculation [10].

The Shapiro-Wilk test showed that the particle sizes distribution from the material analyzed do not follow a normal distribution, as depicted in figure 2 for TiO₂ NP. Particle size distributions are usually fitted by log-normal, Weibull or log-hyperbolic probability distributions [11].

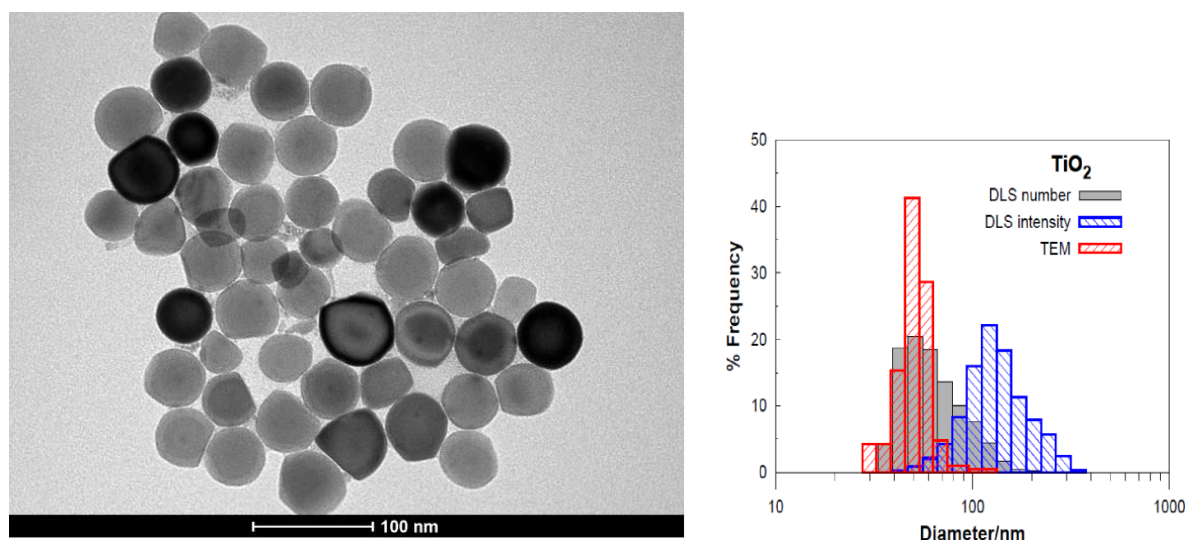


Figure 1. TEM images of TiO₂ NPs and the correspondent TEM and DLS particle size distribution.

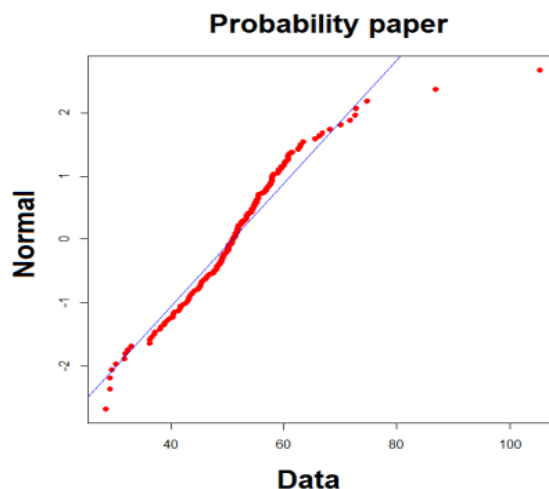


Figure 2. Probability paper of normality tests of TiO₂ nanoparticles sizes analyzed by TEM.

Table 1 summarizes the size measurements results of TiO₂ nanoparticles. It was expected that mean and median values from DLS would be a slightly higher than TEM due to the interference of the dispersant into the hydrodynamic diameter. However, DLS-numbers are close to the TEM results whereas DLS-intensity presents a large difference with TEM. Since the particle size distribution is not narrow, the presence of bigger particles may contribute to an increase light scattering, shifting the measured particles size towards larger values. The DLS measurements show a higher quantity of bigger particles (D95).

Table 1. Particle size measurements of TiO₂ in nm.

	TEM 190 NPs	DLS- Number	DLS- Intensity
D10	39.3	38.6	77.2
D95	66.2	108.3	224.8
Median	51.0	54.2	117.9
Mean	50.9	61.5	127.8

The results obtained from CoFe₂O₄ are summarized in figure 3 and table 2. The DLS technique was not able to identify the particles with sizes below 15nm. These results may be related to the agglomeration of smallest particles as evidenced by the red circle in figure 3. For CoFe₂O₄ the DLS-number results were also near to TEM values and the difference may be explained by the increased size in the latter by the presence of dispersant.

The mixture of TiO₂ and CoFe₂O₄ (TiO₂- CoFe₂O₄) dispersion was also analysed and the results are presented in figure 4 and table 3. The size distribution obtained by TEM is not bimodal as one would expect by the difference in the mean sizes. Besides, the dispersion used had the same concentration, and therefore, the number of CoFe₂O₄ NPs in a given mass was bigger than the number of TiO₂ NP, since the size of CoFe₂O₃ NP is smaller. Thus, the particle size distribution is centred at 20nm and TiO₂ has a minor contribution to the curve due to a smaller number of particles. The values from DSL are much higher than those from TEM since DLS-intensity shows values about five times larger than TEM. These results may be related to the broad distribution formed by mixing the two particles. These results corroborates the previous affirmation were the distribution is not narrow and the presence of

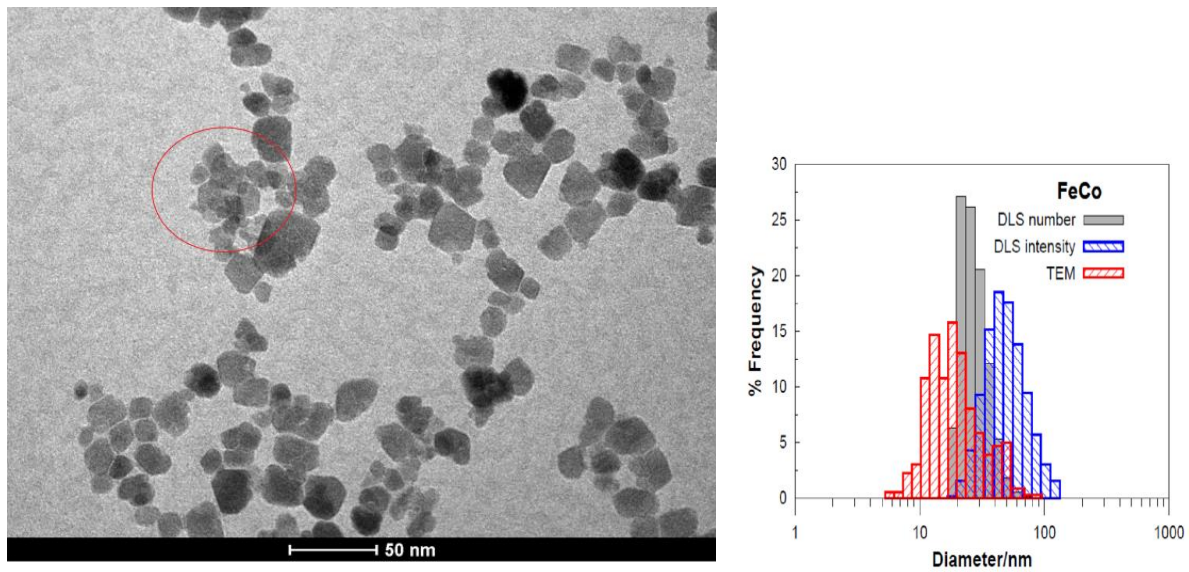


Figure 3. TEM images and DLS particle size distribution of CoFe_2O_4 NPs.

Table 2. Particle size measurements of CoFe_2O_4 in nm.

	TEM 360 NPs	DLS- Number	DLS- Intensity
D10	10.8	18.6	27.9
D95	45.8	38.8	84.5
Median	18.1	23.9	43.5
Mean	21.2	25.7	47.4

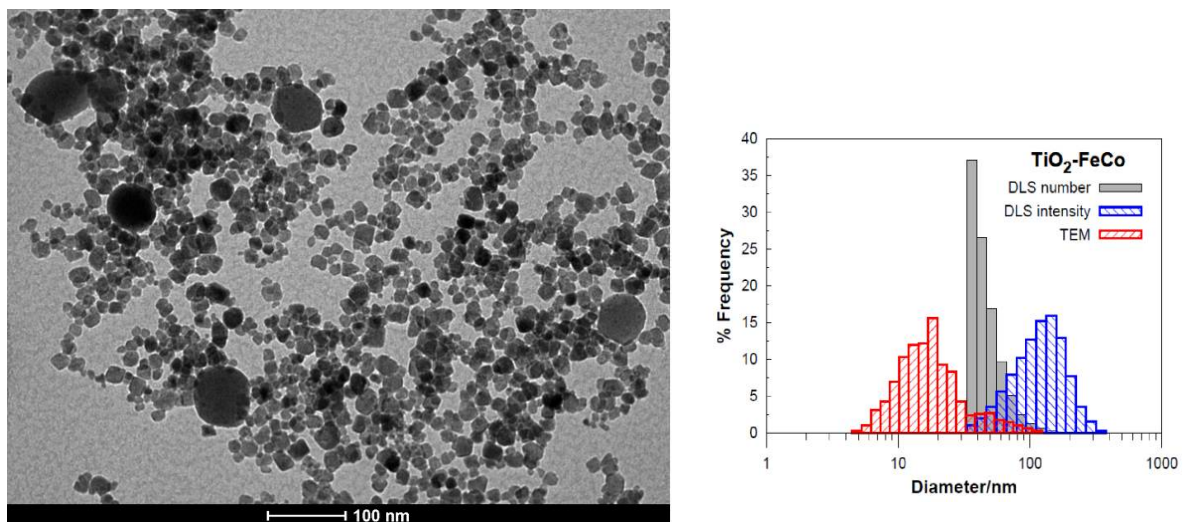


Figure 4. TEM Images of $\text{TiO}_2\text{-CoFe}_2\text{O}_4$ NPs and the correspondent TEM and DLS particle size distribution.

Table 3. Particle size measurements of TiO₂-CoFe₂O₄ in nm.

	TEM 800 NPs	DLS- Number	DLS- Intensity
D10	9	32.2	57.4
D95	50.5	71.4	207
Median	16.7	38.9	111
Mean	20.9	43.8	116.6

bigger particles shift the measured particle sizes towards larger values. Even the DLS - number shows large errors compared to TEM.

4. Conclusions

The DLS – number for a monomodal sample shows a good approximation to the size parameters obtained by TEM while DSL – intensity does not. The DLS mean is app. 20% higher than TEM mean size; the errors for the other parameters are larger. The difference is ascribed to the presence of dispersant. The enlargement of size distributions induces errors to DLS particle sizing measurements when compared to TEM analyses. These errors are more evident on the results of mixed samples with different sizes, where the DLS-intensity present values five times larger than TEM.

5. Acknowledgements

The authors acknowledge CNPq, CAPES and FAPEMIG for financial support, the Nanum Nanotecnologia Ltda and Microscopy Centre-UFMG for technical support and INCT-Acqua.

References

- [1] Hoo C M; Starostin N; West P and Mecartney M L 2008 *Journal of Nanop. Research* **10** 89
- [2] Anderson W *et al.* 2013 *Journal of Colloid and Interface Science* **405** 322
- [3] Bonevich J E and Haller W K 2010 Measuring size of nanoparticles using TEM Gaithersburg:NIST 20p
- [4] Kim H A; Seo J K; Kim T and Lee B T 2014 *Environmental Health and Toxicology* **29** 1
- [5] Linkov P; Artemyev M; Efimov A E and Nabiev I 2013 *Nanoscale* **5** 8781
- [6] Contadini J F, Souza T G F, Mohallem T D S 2014 US Patent n° 8815393 B2, p. 07
- [7] <http://www.R-project.org/>
- [8] <http://www.portalaction.com.br/>
- [9] Hackley V A and Clogston D J 2007 Measuring the Size of Nanoparticles in Aqueous Media Using DLS Gaithersburg:NIST, 22p.
- [10] Merkus, H G 2009 *Particle Size Measurements* e-book:Springer, 533p.
- [11] Purkait, B 2002 *India Journal of Sedimentary Research* **72** 367.