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

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Abstract: This paper compares the accuracy of dynamic light scattering (DLS) and transmission electron microscopy (TEM) for characterizing size distributions of ceramic nanoparticles. It was found that measurements by DLS using number distribution presented more accurate results when compared to TEM. The presence of dispersants and the enlargement of size distributions induce errors to DLS particle sizing measurements and shift the results to higher values.

Keywords: nanoparticle size measurement, DLS, TEM

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 noninvasive, nondestructive, 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. MATERIALS AND METHODS

2.1. Material

Titanium oxide (TiO_2) was obtained from *Minérios Ouro Branco*. The cobalt ferrite ($CoFe_2O_4$) 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 together by mixing equal volumes of dispersions (TiO_2- $CoFe_2O_4$).

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 an 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. Dynamic Light Scattering (DLS)

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

2.3. 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].
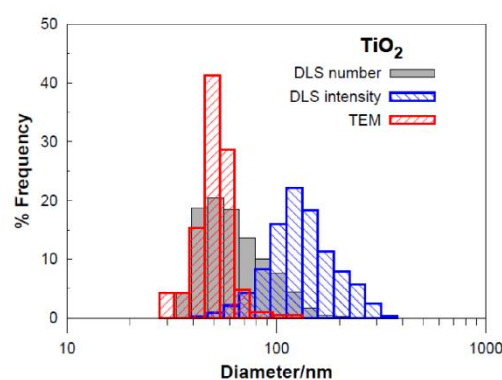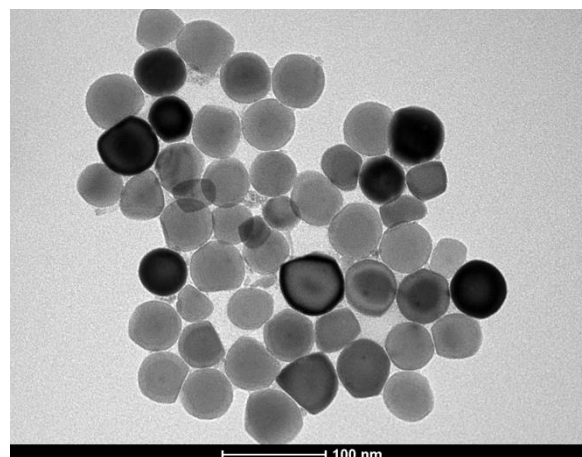

Figure 1: TEM images of TiO_2 NPs and the correspondent TEM and DLS particle size distribution.

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 TiO_2 NP. Particle size distributions are usually fitted by log-normal, Weibull or log-hyperbolic probability distributions [11].

Table 1 summarizes the size measurements results of TiO_2 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

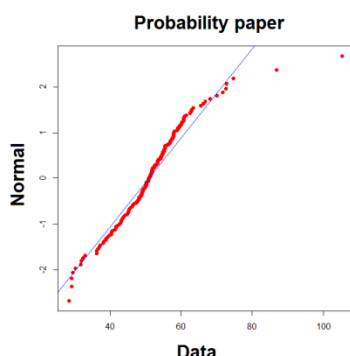towards larger values. The DLS measurements show a higher quantity of bigger particles (D95).

Figure 2: Probability paper of normality tests of TiO_2 nanoparticles sizes analyzed by TEM

Table 1: Particle size measurements of TiO_2 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 $CoFe_2O_4$ 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 $CoFe_2O_4$ 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 TiO_2 and $CoFe_2O_4$ (TiO_2-$CoFe_2O_4$) 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 $CoFe_2O_4$ NPs in a given mass was bigger than the number of TiO_2 NP, since the size of $CoFe_2O_3$ NP
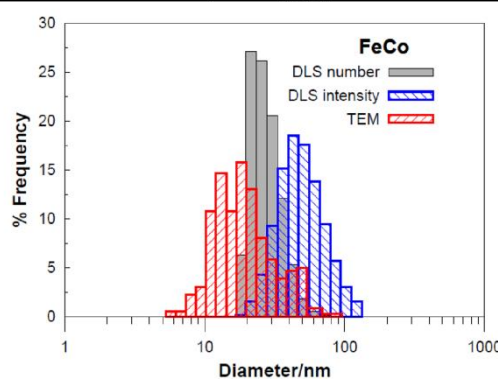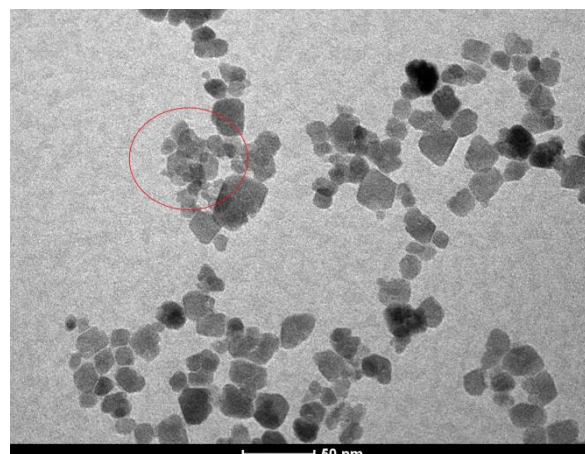

Figure 3: TEM images and DLS particle size distribution of $CoFe_2O_4$ NPs.

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

is smaller. Thus, the particle size distribution is centred at 20nm and TiO_2 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 bigger particles shift the measured particle sizes towards larger values. Even the DLS - number shows large errors compared to TEM.
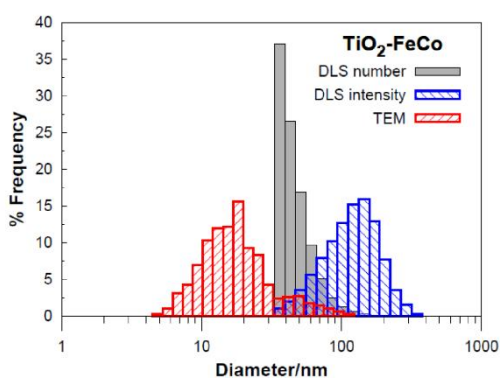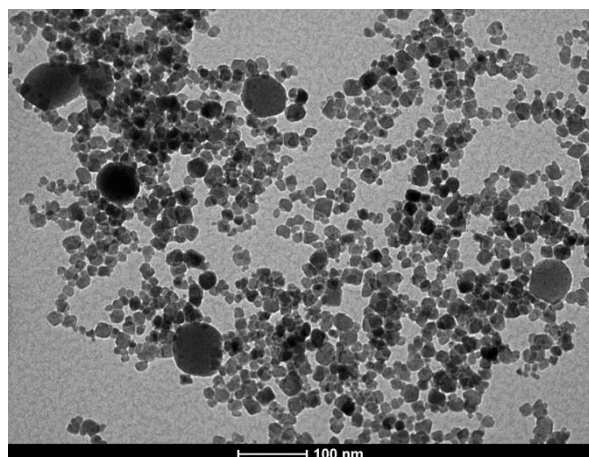

Figure 4: TEM Images of TiO_2-$CoFe_2O_4$ NPs and the correspondent TEM and DLS particle size distribution.

Table 3: Particle size measurements of TiO_2-$CoFe_2O_4$ 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

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. REFERENCES

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