Simultaneous spectrophotometric determination of titanium oxide and iron oxide nanoparticles in water by using PLS algorithm

Iu. Bakhteeva¹ · I. Byzov¹ · M. Filinkova¹ · I. Medvedeva^{1,2} · S. Zhakov¹ · M. Uimin¹

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Abstract

The method for determination of the component partial concentrations in mixed two-component water suspension from the UV spectrophotometry by applying the PLS algorithm is suggested. This quantitative method does not require special probe preparations, it is convenient and inexpensive and it can be realized for water quality monitoring by using portable devices. As an example, the water suspensions of TiO_2 and Fe_3O_4 —coated by SiO_2 nanoparticles were analyzed. The concentration range for the simultaneous determination of nanoparticles is 0.5–10 mg/l. The relative standard errors for single components determination are 1.8% for TiO_2 and 3.9% for Fe_3O_4 -coated by SiO_2 . The processes of nanoparticles aggregation in the studied mixed suspensions are reversible and do not distort significantly the results of the partial concentrations determination. The method suggested can be used for detection of the residual partial concentrations of titanium oxides and iron-containing nanoparticles in water treatment technologies.

Keywords Multicomponent systems · Nanoparticles · UV quantitative spectrophotometry · Water suspension

1 Introduction

The growing volume of production and consumption of nanoparticles, in particular, those engineered for special functions (ENP) leads to their increasing arrival into natural water bodies and soils [1, 2]. Presence of surfactants and NOM in stock waters might bring about a formation of stable suspensions [3–5], which prevents their natural outlet and leads to accumulation in an environment and in food chains [6, 7]. Therefore quantitative detection of nanoparticles in water becomes very important [8]. Besides, the development of water cleaning technologies requires fast and inexpensive methods of detection of residual particle concentrations at any stage of water treatment.

Nanoparticle suspensions are characterized by the particle composition and shape, the particle surface charge, concentration in water, distributions by size, etc. [9].

Correspondingly, the determination of the NP concentrations should be done by consideration of these parameters [10]. Some detection methods available today are based on the registration of the physical properties of the nanoparticle suspensions (e.g., light absorption), in other methods the particles concentration is detected directly from the particle number counting [11]. Although these methods use different approaches, they have limitations on nanoparticle sizes and compositions.

Different methods are used for quantitative detection of nanoparticles in water which are mainly based on a combination of size separation techniques (e.g., size-exclusion chromatography [12], field flow fractionation [13, 14], capillary electrophoresis [15]) with various detectors (e.g., UV, mass- and inductively coupled plasma mass spectrometry [16, 17]. For the majority of these methods, a granulometric composition of the starting particles mixture is

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✉ Iu. Bakhteeva, bakhteeva@inbox.ru | ¹M.N. Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, S. Kovalevskaya 18, Ekaterinburg, Russia 620990. ²Ural State Mining University, Kuibyshev 30, Ekaterinburg, Russia 620144.

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important, and the deviation from the true size distribution might give wrong results [11, 18, 19].

In analytical methods, the most attention is devoted to detection of small concentrations of chemical and dispersed impurities [20]. These methods require special probe preparations which are complex and expensive. In many real situations, in particular, during a water cleaning processing, it is sufficient to determine the dispersed particle concentrations at the level of environmental and sanitary norms.

Ultraviolet spectrophotometry can be applied as a convenient and inexpensive quantitative method of nanoparticles detection. Usually, the UV spectrophotometry method is used for detection of compounds in a dissolved state. The concentration detection of dispersed impurities in water is not widely spread for that the dispersed impurity should be preliminary dissolved. However recently the UV spectrophotometry was used for detection of carbon nanotube concentrations [21], gold nanoparticle concentrations [22], and titanium oxide nanoparticle concentrations detection [3, 23] free of preliminary solid phase dissolving. In these cases, the method was applied for one component detection only.

If a water solution contains several types of nanoparticles of different compositions and sizes, the simultaneous detection of their partial concentrations by UV spectrophotometry is not that simple, as their characteristic absorption ranges might be overlapping. To reduce the error bars for the particle concentrations detection in a majority of cases a preliminary sample preparation is required. In particular, it is desirable to make size separation that will make the process of nanoparticles concentration detection more complex.

Simultaneous determination of the partial concentration of nanoparticles in the mixed suspension is possible on the basis of quantitative spectrophotometry by using multivariate statistical methods, such as PCR (Principal Component Regression) and PLSR (Partial Least Squares Regression or Projection on Latent Structures) and its modifications, such as PLS1 and PLS2 methods. Multivariate calibrations are effective in the spectrophotometric analysis as they provide high precision in the component detection and the possibility of their separation. While the PCR and PLS1 methods let construct separate models for each particles type in the mixture suspension, the PLS2 method [24] enables to construct the joint regression model for all the components of the mixture.

Method PLS has shown its efficiency for the UV-spectra separation for analysis of different ions mixtures, such as Fe(III), Co(II), Cu(II) [25], Sb (III) and Sb (V) [26], phosphate and silicate in water and soil samples [27], mixtures of drugs [28, 29], mixtures of organic matter and nitrates in wastewater [30] and many others. The application of this

method for the dispersed particles detection is not known, so far.

Today TiO₂ nanoparticles are widely used in dyes, hygiene products, nutritional supplements [31], as catalysts of chemical reactions in an industry [32], etc. Natural systems usually have rather low concentrations of ENM particles [33], so the sensitivity of many analytical techniques is insufficient. A preconcentration of these particles by adding magnetic nanoparticles can be helpful [34, 35]. So, the problem of separate detection of the single component concentration will be important.

In this research, the UV-Vis spectrophotometry together with PLS2 method was applied for the determination of partial concentrations in the two-component mixture suspension. As an example, the TiO₂ and Fe₃O₄—coated by SiO₂ nanoparticles dispersed in water were used.

2 Materials and methods

2.1 Suspension characterization

SiO₂ coated manganite nanoparticles—Fe₃O₄—SiO₂ (MNPs) were synthesized as described in [36]. The titanium oxide nanoparticles (TNPs) were supplied by Degussa (grade P25) [37]. Analytical reagent grade chemicals and distilled water were used. Firstly, the water suspensions of MNPs and TNPs at the concentration of 100 mg/l were prepared, and then they were mixed at different proportions.

Water suspensions of nanopowders were characterized by a dynamic light scattering (DLS) method using a NanoZS apparatus (Malvern, UK). Laser beam $\lambda = 633$ nm was generated by He-Ne laser, operating in back-scattering mode under the angle of 173°. Hydrodynamic aggregates size in starting suspensions was 180–190 nm for MNPs and 160–170 nm for TNPs.

As a buffer solution, the ammonia water solution (pH = 11) was used to provide the colloidal stability of the suspensions during the measurement. Partial concentrations of the MNP and TNP powders in the mixture suspensions were changed in the interval 0.5–10 mg/l in different proportions. The solid state concentration was chosen randomly to obtain maximum information for calibration procedure for each oxide samples.

UV-Visible absorbance digitized spectra were collected at the wave length range of 190–1100 nm using SF-102 spectrophotometer for a water suspension sample placed in a quartz cell (12.5 × 12.5 × 45 mm³). The spectral intervals 190–290 and 1050–1100 nm were cut off by the model construction, as they are poor informative because of the buffer solution influence.

2.2 PLS calibration procedure

For calibration, the standard suspensions of 100 mg/l MNPs and TNPs were mixed at different given proportions (1–50) with subsequent ultrasonic activation for 10 s. Both given and detected suspensions were prepared by the same route.

For the calibration model construction, the absorption spectra of the mixed suspensions were measured and the PLS methodology was applied. This method uses multidimensional data which are projected in a new lower-dimensional coordinate system with new (other) variables (principal components, PC). The X (predictors) and Y (responses) matrices are simultaneously decomposed:

$$T = XW \quad (1)$$

$$X = TP^T + E \quad (2)$$

$$Y = UQ^T + F \quad (3)$$

where W weight matrix, T , U matrices of scores, P , Q matrices of loadings.

Projection is constructed in the direction of maximum correlation between the corresponding vectors of matrices T and U . Then the regression coefficients B are calculated using the formula:

$$B = W(PTW)^{-1}QT \quad (4)$$

Score plot shows how the samples are placed in project space relative to each other in correspondence to their parameters (absorption spectra). Each point corresponds to the spectrum for one sample. Loading plot shows what variables (wavelengths) contribute to the sample position in the coordinate system of the PC. In this work was applied PLS2. The calculations were performed by using R-language (version 3.4.0) [38] and the pls- package (version 2.6-0) [39].

To test the use of the calibration model under the conditions when the initial system was unstable the following experiment was performed. The titanium and iron oxide suspensions with solid phase concentrations of 10 mg/l and 1 mg/l were mixed in the mass proportions 1/1, then the mixtures have been kept for some time (10–60 min), after that the aliquots were transferred into a buffer solution at pH = 11, and then the ultrasonic activation for 15 s was applied. The average aggregates size and zeta potential were detected for these suspensions, which indicated the stability of the systems. The absorption spectra were measured in a buffer solution and then the calibration model was applied to the experimental data.

3 Results and discussion

3.1 UV absorption spectra and aggregation effect

Figure 1 shows the absorption spectra of the water suspensions of separate MNPs and TNPs and the spectrum of their mixture. TiO_2 and $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles strongly absorb light with wavelengths smaller than 500 nm [40, 41], therefore their spectra overlap and it is impossible to extract the data for one component concentration directly. However, the application of the mathematical PLS methodology gives a possibility for such a resolution.

It is important to take into account that all the methods based on particle detection without their dissolving can be dependent on the particle size. The aggregation of small particles into larger structures can distort the results of the detection. By spectrophotometric measurements, the aggregation process is easy to be followed by an independent method (in our case by DLS method). Also, the time changes of the measured spectrum give evidence of the aggregation process in the disperse system. For a heterogeneous system like the mixture of TNPs and MNPs water suspensions, the aggregation phenomena should be considered, so the effect of the particle size on the absorption spectra was investigated.

Figure 2a shows the hydrodynamic size (d_h) and the zeta potential for the mixed (10 mg/l) MNPs/TNPs water suspension for their mass ratio 1/1. Hydrodynamic size d_h increases up to 1 μm while the zeta potential value decreases, which is an indication of aggregation process caused by interparticle repulsions decrease due to surface charge decrease for the observed time period (20–60 min).

The aggregate sizes make a noticeable effect on the absorption spectrum peaks, which might be reflected in

Fig. 1 Absorption spectra of water suspensions of MNPs and TNPs (10 mg/l) and of their (1/1) mixture

Fig. 2 **a** Time dependences of the average hydrodynamic size (solid triangle) and the zeta potential (solid square), **b** absorption spectra for the (10 mg/l) mixed MNPs/TNPs suspensions at the mass concentration ratio 1/1 for different nanoparticles size: 1—200 nm, 2—400 nm, 3—1000 nm

the concentration detection reproducibility. Figure 2b shows that the absorption intensity in the short wavelength range is reduced with the aggregate size increase, and it is increased in the long wavelength range, which can be accounted for a reduction of the particle number due to the aggregation process. In this work, we submit that the calibration will be valid for the suspensions with the aggregate sizes of (200 ± 30) nm.

Figure 3 shows the absorption spectra for two mixtures with different particle concentrations in a buffer solution. The curves 1, 2 show the 1/1 mixture spectra for solid phase concentration $c = 10$ mg/l and the curves 3, 4 refer to $c = 1$ mg/l. Spectra 2 and 4 were recorded after 60 min exposure of the mixed suspensions in a buffer solution. It can be seen as well that exposure of the mixture suspension in the buffer for 60 min does not result in a noticeable shift of the spectral lines (Supporting Information, Fig. 1). The time independence of the average hydrodynamic size and of the zeta potential (inset) evidences the absence of irreversible aggregation effects. Therefore the usage of the buffer solution allows to obtain a reproducible

Fig. 3 Absorption spectra for the mixed MNPs/TNPs suspensions at the mass concentration ratio 1/1 exposed in the buffer solution for 0 (black curves) and 60 min (red curves) for different particle concentrations (1, 2— $c = 10$ mg/l; 3, 4— $c = 1$ mg/l). Inset—Time dependences of the average hydrodynamic size and the zeta potential in the mixed MNPs/TNPs suspensions for particle concentration—10 mg/l (solid square), and 1 mg/l (solid triangle) exposed in the buffer solution

dependence of absorption on the particle concentrations in the suspensions.

3.2 Calibration in model suspensions

The first step in the simultaneous determination of the partial component concentrations by PLS methodology involves a construction of the calibration matrix for the binary mixture, in our case, of MNPs/TNPs. To build a regression model, the spectra were used as predictors (X), and the concentrations of TNPs and MNPs were used as responses (Y). For that, we prepared two separate suspension sample sets. For the calibration set the suspension samples of different compositions (39 samples) were prepared and the concentration values were used as the matrix elements (Fig. 4). The test set was presented by concentration ratio values taken from the same intervals as the calibration set values. The 15 samples of the test set were prepared additionally. The samples for the test set were not used for the calibration matrix construction.

The concentrations of the TNPs and MNPs were determined from the spectra of the test samples by using the calibration PLS model. Taking the actual (c_{act}), mean of actual (c_{mean}) and predicted (c_{pr}) concentration values the values of RMSEP (Root-Mean Square Error of Prediction), R_t^2 (Determination coefficient) and RSE (Relative Standard Error) were calculated:

$$RMSEP = \sqrt{\frac{1}{n} \sum (c_{act} - c_{pr})^2} \quad (5)$$

Fig. 4 Sets of MNPs and TNPs concentrations used for calibration and testing in the PLS model for the mixed MNPs/TNPs water suspension (solid circle—calibration set, open circle—test set)

$$R_t^2 = 1 - \frac{\sum (c_{act} - c_{pr})^2}{\sum (c_{act} - c_{mean})^2} \quad (6)$$

$$RSE = \sqrt{\frac{\sum (c_{act} - c_{pr})^2}{\sum c_{act}^2}} \times 100\% \quad (7)$$

From the dependences of the *RMSEP* value on the PC numbers (Fig. 5a) one can conclude that for the mixed MNPs/TNPs suspension the optimal PC number should be higher than 2, so we can take three principal components (at this PC number the *RMSEP* value is minimal) [42]. The values of R_t^2 for TNPs and MNPs are respectively: 0.9993 and 0.9995. The tangent of the linear regression «actual–predicted» function is close to 1, the *RSE* values for single components are 1.827% for TNPs and 3.94% for MNPs, which confirms a correct concentration values determination (Fig. 5b). Analysis of the values of X-scores suggests that the PC1 is associated with the total concentration of MNPs and TNPs, and the PC2 is associated with the MNPs and TNPs concentrations ratio (Supporting Information, Fig. 2, Table SI1). The third principal component, presumably, indicates the MNPs concentration contributions. Dependencies of P-loadings on the wavelength (Fig. 6) evidence that the main contributions to PC1 and PC2 come from the part of the spectrum at the wavelength interval of 290–590 nm, while the spectrum at the wavelengths higher than 590 nm contributes to PC3.

Fig. 5 **a** Dependence of the *RMSEP* and R_t^2 values on the principal components for MNPs and TNPs; **b** correlation between actual and predicted concentration values $y = A \times x + B$: (b) for TNPs ($A = 1.00499$, $B = 0.00005$, $R^2 = 0.9993$); (c) for MNPs ($A = 0.99991$, $B = 0.00004$, $R^2 = 0.9995$)

Fig. 6 Plots of P-loadings versus wavelengths for principal components for the mixed MNPs/TNPs water suspension

3.3 The particle aggregation and the concentration ratio effects on the recovery results

In order to obtain the reproducible calibration model, the buffer solution should be used to prevent particle aggregation. However, when MNPs and TNPs having the opposite zeta potentials are staying in water simultaneously for some time period an irreversible aggregation can take place. In this case, the absorption curve might be shifted, thus distorting the results of the partial concentration detection. To exclude this effect the exposure of heterogeneous mixtures before their placement into the buffer solution was performed. Figure 7 shows the absorption spectra for two mixtures with different solid

Fig. 7 Absorption spectra for the mixed MNPs/TNPs suspensions at the mass concentration ratio 1/1 in the buffer solution after an exposure during 20 (black curves) and 60 min (red curves) for different particle concentrations (1, 2— $c = 10$ mg/l; 3, 4— $c = 1$ mg/l). Inset: Time dependences of the zeta potential and of the average hydrodynamic size (solid square 10 mg/l, solid triangle—1 mg/l)

phase concentrations after the exposure. The curves 1, 2 show MNPs/TNPs mixture spectra for $c = 10$ mg/l and the curves 3, 4 for $c = 1$ mg/l with the equal mass concentration ratios MNPs/TNPs. The spectra 1 and 3 were measured after the exposure for 20 min, the spectra 2 and 4 were measured after the exposure for 60 min. Figure 7 shows that the absorption spectra practically coincide in 20 and 60 min of the exposure. The inset of Fig. 7 shows that both zeta potential values and hydrodynamic size values do not change noticeably during the time period of 60 min, which indicates the stability of the suspensions placed into the buffer.

The actual and predicted values of the partial concentrations of the two components in the mixed MNPs/TNPs suspension (10 mg/l) after exposure for aggregation and by placement into a buffer solution are presented in Table 1. The comparison between c_{act} and c_{pr} shows that the exposure during 60 min does not lead to irreversible aggregation of TNPs and MNPs, therefore the applied calibration model allows to obtain the individual component concentrations in the mixed suspensions with sufficiently high precision (Table 1).

One should mention that initially the calibration model was designed for different component ratios. However, when the ratio is going too high, that is, the concentration of one component is much higher than the concentration of another component, the separation of the spectrum corresponding to small concentration component from the total spectrum leads to bigger uncertainty (Table 2). This is, probably, the reason for a high error in MNPs concentration detection for $c(\text{MNPs})/c(\text{TNPs}) = 20$ and 50. At the same time, the TNPs—rich component partial concentration for the same ratios is detected with satisfactory precision. This might be accounted by different features of separate TNPs and MNPs spectra, however, this question stays open and requires special investigation.

Table 1 Actual and predicted values of the partial concentrations of nanoparticles in the mixture suspensions after exposure for aggregation during 60 min

Time (min)	TNPs			MNPs		
	c_{act} (mg/l)	c_{pr} (mg/l)	Recovery (%)	c_{act} (mg/l)	c_{pr} (mg/l)	Recovery (%)
10	10.00	9.79	97.9	10.00	10.05	100.5
20	10.00	9.64	96.4	10.00	10.53	105.3
30	10.00	9.67	96.7	10.00	10.40	104.0
40	10.00	9.35	93.5	10.00	10.21	102.1
50	10.00	10.41	104.1	10.00	10.47	104.7
60	10.00	9.04	90.4	10.00	10.55	105.5

Table 2 Actual and predicted values of the partial concentrations of nanoparticles in the mixture suspensions for different component ratios

	TNPs			MNPs		
	c_{act} (mg/l)	c_{pr} (mg/l)	Recovery (%)	c_{act} (mg/l)	c_{pr} (mg/l)	Recovery (%)
<i>c</i> (TNPs)/ <i>c</i> (MNPs)						
1	10.00	9.95	99.5	10.00	10.03	100.3
2	10.00	9.96	99.6	5.00	4.88	97.5
5	10.00	10.00	100.0	2.00	2.17	108.5
10	10.00	9.93	99.3	1.00	1.06	106.3
20	10.00	9.97	99.7	0.50	0.53	106.3
50	10.00	9.99	99.9	0.20	0.26	132.2
<i>c</i> (MNPs)/ <i>c</i> (TNPs)						
1	10.00	10.03	100.3	10.00	9.86	98.6
2	5.00	4.85	97.0	10.00	9.95	99.5
5	2.00	2.07	103.5	10.00	10.39	103.9
10	1.00	0.96	96.0	10.00	10.87	108.7
20	0.50	0.71	142.0	10.00	10.32	103.2
50	0.20	0.50	250.0	10.00	10.36	103.6

4 Conclusion

The method for determination of partial concentrations of the components in the mixed two-component water nanosuspensions from the UV spectrophotometry by applying the PLS algorithm is suggested.

The heterogeneous suspension of TiO_2 and $\text{Fe}_3\text{O}_4\text{-SiO}_2$ nanoparticles can be considered as a model system, so the method can be useful for other mixed systems as well.

In particular, the method suggested can be used for detection of the residual partial concentrations of TiO_2 and $\text{Fe}_3\text{O}_4\text{-SiO}_2$ nanoparticles in water treatment technologies by the TiO_2 nanosorbent usage with magnetic seeding and subsequent magnetic separation. The UV-spectrophotometric measurements together with PLS algorithm will provide simple express monitoring of the water purification efficiency.

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Compliance with ethical standards

Conflicts of interest There are no conflict to declare.

References

- Maurer-Jones MA, Gunsolus IL, Murphy CJ, Haynes CL (2013) Toxicity of engineered nanoparticles in the environment. *Anal Chem* 85(6):3036–3049. <https://doi.org/10.1021/ac303636s>
- Wiesner MR, Lowry GV, Alvarez P, Dionysiou D, Biswas P (2006) Assessing the risks of manufactured nanomaterials. *Environ Sci Technol* 40:4336. <https://doi.org/10.1021/es062726m>
- Keller AA, Wang H, Zhou D, Lenihan HS, Cherr G, Cardinale BJ, Miller R, Ji Zh (2010) Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environ Sci Technol* 44(6):1962–1967. <https://doi.org/10.1021/es902987d>
- Li X, Yoneda M, Shimada Y, Matsui Y (2017) Effect of surfactants on the aggregation and stability of TiO_2 nanomaterial in environmental aqueous matrices. *Sci Total Environ* 574:176–182. <https://doi.org/10.1016/j.scitotenv.2016.09.065>
- Raza G, Amjad M, Kaur I, Wen D (2016) Stability and aggregation kinetics of titania nanomaterials under environmentally realistic conditions. *Environ Sci Technol* 50:8462–8472. <https://doi.org/10.1021/acs.est.5b05746>
- Cox A, Venkatachalam P, Sahi Sh, Sharma N (2016) Reprint of: Silver and titanium dioxide nanoparticle toxicity in plants: a review of current research. *Plant Physiol Biochem* 107:147–163. <https://doi.org/10.1016/j.plaphy.2016.08.007>
- Tripathi DK, Shweta Singh S, Singh S, Pandey R, Singh VP, Sharma NC, Prasad SM, Dubey NK, Chauhan DK (2017) An overview on manufactured nanoparticles in plants: uptake, translocation, accumulation and phytotoxicity. *Plant Physiol Biochem* 110:2–12. <https://doi.org/10.1016/j.plaphy.2016.07.030>
- Da Silva BF, Pérez S, Gardinalli P, Singhal RK, Mozeto AA, Barcelo D (2011) Analytical chemistry of metallic nanoparticles in natural environments. *Trends Anal Chem* 30(3):528–540. <https://doi.org/10.1016/j.trac.2011.01.008>
- Hassellöv M, Readman JW, Ranville JF, Tiede K (2008) Nanoparticle analysis and characterization methodologies in environmental risk assessment of engineered nanoparticles. *Ecotoxicology* 17:344–361. <https://doi.org/10.1007/s10646-008-0225-x>
- Laborda F, Bolea E, Cepria G, Gomez MT, Jimenez MS, Perez-Arantequi J, Castillo JR (2016) Detection, characterization and quantification of inorganic engineered nanomaterials: a review of techniques and methodological approaches for the analysis of complex samples. *Anal Chim Acta* 904:10–32. <https://doi.org/10.1016/j.aca.2015.11.008>
- Shang J, Gao X (2014) Nanoparticle counting: towards accurate determination of the molar concentration. *Chem Soc Rev* 43(21):7267–7278. <https://doi.org/10.1039/c4cs00128a>

12. Pitkänen L, Striegel AM (2016) Size-exclusion chromatography of metal nanoparticles and quantum dots. *Trends Anal Chem* 80:311–320. <https://doi.org/10.1016/j.trac.2015.06.013>
13. Baalousha M, Stolpe B, Lead JR (2011) Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: a critical review. *J Chromatogr A* 1218:4078–4103. <https://doi.org/10.1016/j.chroma.2011.04.063>
14. Meermann B (2015) Field-flow fractionation coupled to ICP-MS: separation at the nanoscale, previous and recent application trends. *Anal Bioanal Chem* 407:2665–2674. <https://doi.org/10.1007/s00216-014-8416-1>
15. Surugau N, Urban PL (2009) Electrophoretic methods for separation of nanoparticles. *J Sep Sci* 32:1889–1906. <https://doi.org/10.1002/jssc.200900071>
16. Fabricius A-L, Duester L, Meermann B, Ternes ThA (2014) ICP-MS-based characterization of inorganic nanoparticles—sample preparation and off-line fractionation strategies. *Anal Bioanal Chem* 406:467–479. <https://doi.org/10.1007/s00216-013-7480-2>
17. Lapresta-Fernández A, Salinas-Castillo A, Anderson de la Llana S, Costa-Fernández JM, Domínguez-Meister S, Cecchini R, Capitán-Vallvey LF, Moreno-Bondi MC, Marco M-P, Sánchez-López JC, Anderson IS (2014) A General perspective of the characterization and quantification of nanoparticles: Imaging, spectroscopic, and separation techniques. *Crit Rev Solid State Mater Sci* 39:423–458. <https://doi.org/10.1080/10408436.2014.899890>
18. Bandar AJ, Poda AR, Mitrano DM, Kennedy AJ, Gray EP, Ranville JF, Hayes CA, CrockerFH Steevens JA (2013) Comparison of on-line detectors for field flow fractionation analysis of nanomaterials. *Talanta* 104(30):140–148. <https://doi.org/10.1016/j.talanta.2012.11.008>
19. Majedi S-M, Lee HK (2016) Recent advances in the separation and quantification of metallic nanoparticles and ions in the environment. *Trends Anal Chem* 75:183–196. <https://doi.org/10.1016/j.trac.2015.08.009>
20. Heithmara EM, Pergantis SA (2010) Characterizing concentrations and size distributions of metal-containing nanoparticles in waste water. APM 272. U.S. Environmental Protection Agency 600/R-10/117. www.epa.gov
21. Attal S, Thiruvengadathan R, Regev O (2006) Determination of the concentration of single-walled carbon nanotubes in aqueous dispersions using UV-Visible absorption spectroscopy. *Anal Chem* 78:8098–8104. <https://doi.org/10.1021/ac060990s>
22. Haiss W, Thanh NTK, Aveyard J, Fernig DG (2007) Determination of size and concentration of gold nanoparticles from UV-Vis spectra. *Anal Chem* 79:4215–4221. <https://doi.org/10.1021/ac0702084>
23. Dalai S, Pakrashi S, Kumar RS, Chandrasekaran N, Mukherjee A (2012) A comparative cytotoxicity study of TiO₂ nanoparticles under light and dark conditions at low exposure concentrations. *Toxicol Res* 1:116–130. <https://doi.org/10.1039/c2tx00012a>
24. Wold S, Sjöström M, Eriksson L (2001) PLS-regression: a basic tool of chemometrics. *Chemom Intell Lab* 58:109–130
25. Abdollahi H, ShariatPanahi M, Reza Khoshayand M (2003) Simultaneous spectrophotometric determination of iron, cobalt and copper by partial least-squares calibration method in micellar medium. *Iran J Pharm Res* 2:207–212
26. González MJG, Domínguez Renedo O, MartínezMJ Arcos (2005) Simultaneous determination of antimony(III) and antimony(V) by UV-Vis spectroscopy and partial least squares method (PLS). *Talanta* 68(1):67–71. <https://doi.org/10.1016/j.talanta.2005.04.059>
27. Tarighat MA (2016) Simultaneous spectrophotometric determination of phosphate and silicate in different water and soil samples using chemometrics approach. *Int J Environ Sci Technol* 13:11–20. <https://doi.org/10.1007/s13762-015-0833-y>
28. Rontogianni MA, Markopoulou CK, Koundourellis JE (2006) HPLC and chemometrically-assisted spectrophotometric estimation of two binary mixtures for combined hypertension therapy. *J Liq Chrom Relat Tech* 29:2701–2719. <https://doi.org/10.1080/10826070600923241>
29. Asuncion Alonso Lomillo M, Domínguez Renedo O, Arcos Martínez MJ (2004) Resolution of binary mixtures of rifamycin SV and rifampicin by UV/VIS spectroscopy and partial least-squares method (PLS). *Chem Biodivers* 1(9):1336–1343. <https://doi.org/10.1002/cbdv.200490096>
30. Langergraber G, Fleischmann N, Hofstädter F (2003) A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater. *Water Sci Technol* 47(2):63–71
31. Weir A, Westerhoff P, Fabricius L, Hristovski K, von Goetz N (2012) Titanium dioxide nanoparticles in food and personal care products. *Environ Sci Technol* 46(4):2242–2250. <https://doi.org/10.1021/es204168d>
32. Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P (2012) A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl Catal B* 125:331–349. <https://doi.org/10.1016/j.apcatb.2012.05.036>
33. Zhang Y, Chen Y, Westerhoff P, Hristovski K, Crittenden JC (2008) Stability of commercial metal oxide nanoparticles in water. *Water Res* 42:2204–2212. <https://doi.org/10.1016/j.watres.2007.11.036>
34. Afkhami A, Moosavi R, Madrakian T (2010) Preconcentration and spectrophotometric determination of low concentrations of malachite green and leuco-malachite green in water samples by high performance solid phase extraction using maghemite nanoparticles. *Talanta* 82:785–789. <https://doi.org/10.1016/j.talanta.2010.05.054>
35. Giakissikli G, Anthemidis AN (2013) Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation. A review. *Anal Chim Acta* 789:1–16. <https://doi.org/10.1016/j.aca.2013.04.021>
36. Bakhteeva luA, Medvedeva IV, Uimin MA, Byzov IV, Zhakov SV, Yermakov AE, Shchegoleva NN (2016) Magnetic sedimentation and aggregation of Fe₃O₄@SiO₂ nanoparticles in water medium. *Sep Purif Technol* 159:35–42. <https://doi.org/10.1016/j.seppur.2015.12.043>
37. Ohno T, Sarukawa K, Tokieda K, Matsumura M (2001) Morphology of a TiO₂ photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline. *J Catal* 203(1):82–86. <https://doi.org/10.1006/jcat.2001.3316>
38. R Development core team (2011) R: a Language and environment for statistical computing. Vienna, Austria : The R Foundation for Statistical Computing. <http://www.R-project.org/>
39. Mevik B-H, Wehrens R, HovdeLiland K (2015) pls: partial least squares and principal component regression. R Package Version 2.5-0. <http://CRAN.R-project.org/package=pls>
40. Linsebigler AL, Lu G, Yates JT (1995) Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results. *Chem Rev* 95:735–758. <https://doi.org/10.1021/cr00035a013>
41. Vikram S, Vasanthakumari R, Tsuzuki T, Rangarajan M (2016) Investigations of suspension stability of iron oxide nanoparticles using time-resolved UV-visible spectroscopy. *J Nanopart Res* 18:272. <https://doi.org/10.1007/s11051-016-3570-3>
42. Esbensen KH (2000) Multivariate data analysis: in practice, 4th edn. CAMO, Oslo

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