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Talanta 68 (2005) 25–30

Talanta
www.elsevier.com/locate/talanta

Nanometer titanium dioxide immobilized on silica gel as sorbent for preconcentration of metal ions prior to their determination by inductively coupled plasma atomic emission spectrometry

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Received 27 December 2004; received in revised form 23 April 2005; accepted 23 April 2005
Available online 23 May 2005

Abstract

Nanometer titanium dioxide immobilized on silica gel (immobilized nanometer TiO_2) was prepared by sol–gel method and characterized by using X-ray diffraction (XRD) and scanning electron microscope (SEM). The adsorptive potential of immobilized nanometer TiO_2 for the preconcentration of trace Cd, Cr, Cu and Mn was assessed in this work. The metal ions studied can be quantitative retained at a pH range of 8–9, and $0.5\,\mathrm{mol\,L^{-1}}$ HNO_3 was sufficient for complete elution. The adsorption capacity of immobilized nanometer TiO_2 for Cd, Cr, Cu and Mn was found to be 2.93, 2.11, 6.69 and $2.47\,\mathrm{mg\,g^{-1}}$, respectively. A new method using a microcolumn packed with immobilized nanometer TiO_2 as sorbent has been developed for the preconcentration of trace amounts of Cd, Cr, Cu and Mn prior to their determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). The method has been successfully applied for the determination of trace elements in some environmental samples with satisfactory results.

Keywords: Immobilized nanometer titanium dioxide; Preconcentration; Metal ions; ICP-AES

1. Introduction

Sensitive, fast, reproducible, simple and accurate analytical methods are required for the determination of trace elements in geological, biological and environmental samples. The direct determination of extremely low concentrations of the required trace elements by modern atomic spectroscopic methods, such as atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) is often difficult. The limitations are not only associated with the insufficient sensitivity of these techniques but also with matrix interference. For this reason, the preliminary separation and preconcentration of trace elements from matrix is often required [1].

The most widely used techniques for the separation and preconcentration of trace elements include liquid–liquid extraction [2], solid-phase extraction [3–5], coprecipitation [6] and floatation [7], etc. Recently, solid-phase extraction (SPE) technique has become increasingly popular in compared with the classical liquid–liquid extraction method because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [8]. The main requirements with respect to substances to be used as solid-phase extraction sorbents are as follows [9]: possibility of extracting a large number of elements over a wide pH range, fast and quantitative sorption and elution, high capacity, regenerability and accessibility. Numerous substances have been proposed and applied as solid-phase extraction sorbents, such as chelating resin [10,11], modified silica [12,13], PTFE beads and turnings [14–16], active carbon [17], polyurethane foam [18], cellulose [19] and biological substances [20].

The field of nanocomposite materials has had the attention, imagination, and close scrutiny of scientists and engineers in recent years [21,22]. Nanomaterials are made of

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doi:10.1016/j.talanta.2005.04.035

nanoparticles; the regime of nanoparticle is from 1 nm to almost 100 nm, falls between the classic fields of chemistry and solid-state physics. The sizes, surface structures and interparticle interactions of nanomaterials determine their unique properties and the improved performances, and make their potential application in many areas such as electronics, optics, catalysis, ceramics and magnetic data storage.

One of the specific properties of nanomaterials is that a high percent of the atoms of the nanoparticle is on the surface. The surface atoms are unsaturated and can therefore bind with other atoms, possess highly chemical activity. Nanoparticulate metal oxides exhibit intrinsic surface reactivity and high surface areas, and can strongly chemisorb many substances, such as acidic gases and polar organics [23]. Vassileva and Hadjiivanov investigated the surface chemistry of high surface area oxides, e.g. TiO_2, ZrO_2, CeO_2 and ZnO and found that these materials have a very high adsorption capacity towards metal ions and give promising results when used for trace elements analyses of different samples [24–26]. Liang et al. studied the adsorption behavior of nanometer TiO_2 towards metal ions and used it for the separation and preconcentration of metal ions in biological and environmental samples [27–30]. The adsorption behavior of metal ions on nanometer Al_2O_3 has also been studied by Chang et al. [31]. All the results show that the nanomaterial is a promising solid-phase extraction adsorbent for metal ions.

However, due to the fine grain size of nanometer TiO_2, when the suspension nanometer TiO_2 is used for adsorption of metal ions, it is easy to coacervate and loss of activity, and difficult to be recovered. These problems can be avoided by immobilizing nanometer TiO_2 on different substrates. The immobilized nanometer TiO_2 can be prepared by coating the support substrates with a TiO_2 sol by different techniques such as chemical vapor deposition [32], chemical spray pyrolysis [33], and sol–gel method [34]. Among the different techniques the sol–gel coating is the simplest, economical and has advantages such as TiO_2 is easily anchored on the substrates bearing the complicated shapes and large area substrates [35]. The immobilized nanometer TiO_2 has been widely applied as chemical sensors [36], electrochemical solar cells [37] and photocatalyst [38], and so far there is not the report of application of immobilized nanometer TiO_2 for the adsorption of metal ions.

In this work, nanometer TiO_2 immobilized on silica gel was prepared by sol–gel method and characterized by using X-ray diffraction (XRD) and scanning electron microscope (SEM). The adsorptive potential of immobilized nanometer TiO_2 for the preconcentration of trace Cd, Cr, Cu and Mn was assessed using column method. A new method using a microcolumn packed with immobilized nanometer TiO_2 as sorbent has been developed for the preconcentration of trace Cd, Cr, Cu and Mn prior to their determination by ICP-AES.

2. Experimental

2.1. Apparatus

An Optima 2000DV inductively coupled plasma optical emission spectrometer (Perkin Elmer Instruments, Shelton, CT, USA) was used. The operation conditions and the wavelength of the emission lines are summarized in Table 1. XRD pattern was obtained using Y-2000 diffractometer (Dandong Liaodong Radial Instrument Co. Ltd., Liaoning, China) with Cu Kα radiation. SEM images were obtained on a SX-650 field emission scanning electron microscope (Hitachi, Japan). The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) was used in separation/preconcentration process. A self-made PTFE microcolumn (20 mm × 3.0 mm i.d.), packed with immobilized nanometer TiO_2, was used in the manifold for separation/preconcentration. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connection.

2.2. Standard solution and reagents

Stock standard solutions ($1000\,\mu g\,mL^{-1}$) of Cd, Cr, Cu and Mn were obtained from the National Institute of Standards (Beijing, PR China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Silica gel (40–60 mesh, Qingdao Ocean Chemical Factory, Qingdao, China) was boiled with (1 + 1) nitric acid for 3 h, then immersed in (1 + 1) hydrochloric acid for 24 h, finally washed with doubly distilled water until no chloride appeared in the washings. The cleaned silica gel was dried at 120 °C for 24 h. All reagents used were of the highest available purity and of at least analytical reagent grade. Doubly distilled water was used throughout. Titanium tetrabutoxide (Aldrich chemicals) was used without further purification. The following buffers were used to control the pH of the solutions: hydrochloric acid–glycine (pH 1–3), sodium acetate–acetic acid (pH 3–6), ammonium acetate–ammonia (pH 6–8), and ammonium chloride–ammonia (pH 8–9).

Table 1
ICP-AES operating conditions and wavelengths of analytical lines

Parameters	
Incident power (W)	1100
Plasma gas (Ar) flow rate ($L\,min^{-1}$)	15
Auxiliary gas (Ar) flow rate ($L\,min^{-1}$)	0.5
Nebulizer gas (Ar) flow rate ($L\,min^{-1}$)	0.8
Observation height (mm)	15
Integration time (s)	3
Solution pump rate ($mL\,min^{-1}$)	1.5
Wavelength (nm)	Cd 228.6, Cr 283.5, Cu 324.7, Mn 257.6

2.3. *Preparation of immobilized nanometer TiO_2*

An 10 mL of titanium tetrabutoxide ($Ti(OC_4H_9)_4$) was added to 12.5 mL of ethanol. Then a mixture of doubly distilled water (0.5 mL), ethanol (12.5 mL) and HCl (0.25 mL) was added slowly dropwise into the solution under stirring. The solution was kept stirring at ambient temperature for hydrolysis and form sol–gel. The resulting TiO_2 sol can be used after aging for 12 h. Silica gel was immersed into the viscous Ti-precursor sol for 10 min, then taken out and dried. This process was repeated three times. The coated silica gel was washed with doubly distilled water to remove the unimmobilized TiO_2, then dried at 100 °C for 1 h and subsequently calcined in 450 °C for 2 h to obtain the immobilized nanometer TiO_2.

2.4. *Column preparation*

An 50 mg of immobilized nanometer TiO_2 was introduced into a PTFE microcolumn (20 mm × 3.0 mm i.d) plugged with a small portion of glass wool at both ends. Before use, 1.0 mol L^{-1} HNO_3 solution and doubly distilled water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH with buffer solution.

2.5. *General procedure*

A portion of aqueous sample solution containing Cd, Cr, Cu and Mn were prepared, and the pH value was adjusted to the desired value with corresponding buffer solution. The solution was passed through the column by using a peristaltic pump adjusted to the desired flow rate. Afterwards, the retained metal ions were eluted with 1.0 mL of 0.5 mol L^{-1} HNO_3 solution. The analytes in the effluents were determined by ICP-AES. The column could be used repeatedly after regeneration with 1.0 mol L^{-1} HNO_3 solution and distilled water, respectively.

3. Results and discussion

3.1. *Characterization of immobilized nanometer TiO_2*

The SEM image of immobilized nanometer TiO_2 is shown in Fig. 1. The SEM image shows dense microstructure and granular grain. The average grain size of immobilized nanometer TiO_2 is about 60 nm.

The crystal structure of immobilized nanometer TiO_2 was characterized using XRD. The diffraction pattern of XRD for 2θ diffraction angles from 10° to 90° was shown in Fig. 2. The sharp peaks at 25.27, 37.84 and 48.07 can be attributed to anatase TiO_2 according to the standard pattern of anatase TiO_2 [39]. It can be concluded that immobilized nanometer TiO_2 existed as anatase structure.

The amount of TiO_2 coated was determined by treating the modified silica gel with the hot mixture of conc. H_2SO_4 and H_2O_2 (1 + 1). The solid was filtered and the Ti in the solution was determined by ICP-AES. The amount of TiO_2 coated was found to be 220 mg g^{-1}.

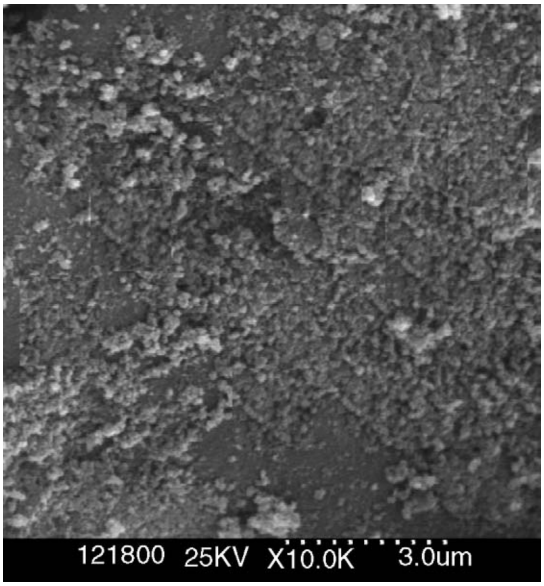

Fig. 1. SEM micrographs of immobilized nanometer TiO_2.

The surface area of the immobilized nanometer TiO_2, determined by the Brunauer–Emmett–Teller (BET) method of nitrogen adsorption at low temperature, was 364 m^2 g^{-1}.

The TiO_2 coated onto the surface of silica gel was shown to be very stable to treatment with acid. No leaching of Ti(IV) from the surface was detected using 2.0 mol L^{-1} HNO_3 and HCl.

3.2. *Effect of pH on adsorption*

The pH value plays an important role with respect to the adsorption of different ions on oxide surfaces. According to Morterra [40], the pH of solution influences the distribution of active sites on the surface of TiO_2. At high pH, the OH^- on the surface provides the ability of binding cations. The decrease of pH leads to the neutralization of surface charge,

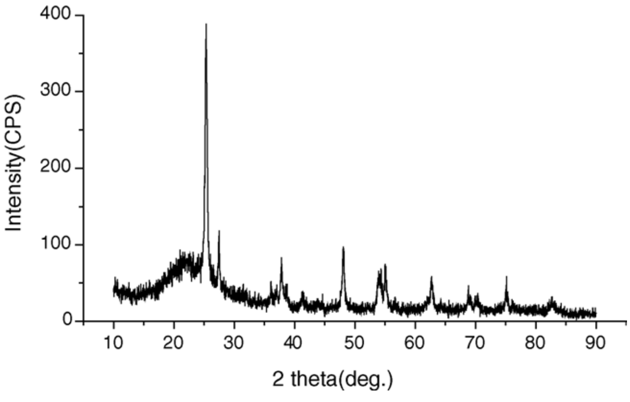

Fig. 2. XRD pattern of immobilized nanometer TiO_2.

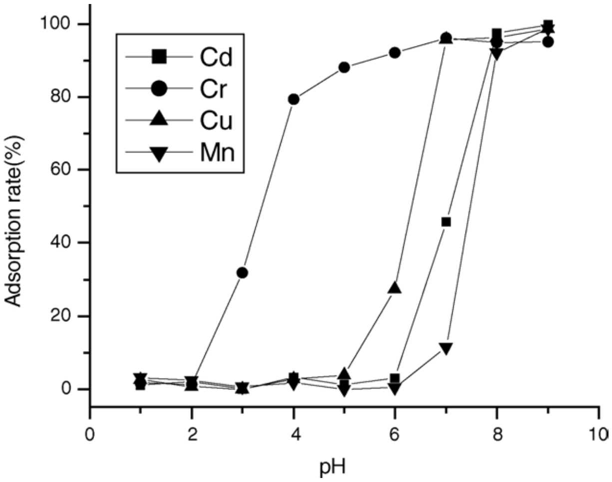

Fig. 3. Effect of pH on the adsorption of the studied metal ions on immobilized nanometer TiO_2 Cd, Cr, Cu and Mn: 1.0 μg mL^{-1}.

and OH^- is displaced from the surface, so the adsorption of cations onto TiO_2 decreases quickly.

In order to evaluate the effect of pH, the pH values of sample solutions were adjusted to a range of 1–9. The results of the effect of pH on the recoveries of studied ions are shown in Fig. 3. A quantitative recovery (>90%) was found for Cr at the pH range of 6–9 and Cu at the pH range of 7–9. For Cd and Mn, the highest recovery was obtained in the pH range of 8–9. In order to preconcentration all studied ions simultaneously, a pH of 8.0 was selected as the compromise condition.

3.3. *Effect of flow rate of sample solutions*

The flow rate of the sample solution affects the retention of cations on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions (pH, eluent, etc.). The flow rate was adjusted in a range of 0.5–2.5 mL min^{-1}. It was found that the retention of the studied ions was practically not changed up to 2.0 mL min^{-1} flow rate. The recoveries of the analytes decrease slightly when the flow rate is over 2.0 mL min^{-1}. Thus, a flow rate of 2.0 mL min^{-1} is employed in this work.

3.4. *Elution of the adsorbed metal ions*

It is found from Fig. 3 that the adsorption of cations at pH < 2 could be negligible. For this reason, various concentrations HNO_3 were studied for the elution of retained cations from the microcolumn at the flow rate of 0.5 mL min^{-1}. The results obtained are given in Table 2. As can be seen, 0.5 mol L^{-1} HNO_3 was sufficient for complete elution. The effect of eluent volume on the recovery of analytes was also studied by keeping the HNO_3 concentration of 0.5 mol L^{-1}, it was found that with 1.0 mL of 0.5 mol L^{-1} HNO_3 quantitative recoveries (>90%) could be obtained. Therefore, the volume of 1.0 mL eluent was used in the following experiments.

Table 2
Eluent data (%) for metal ions adsorbed on immobilized nanometer TiO_2

Eluent (HNO_3, mol L^{-1})	Cd	Cr	Cu	Mn
0.05	57.2	78.1	47.1	81.9
0.1	53.9	82.5	83.7	97.8
0.5	98.5	93.3	96.3	98.2
1.0	98.4	94.2	95.3	95.6
2.0	97.6	92.7	94.2	96.4

Eluent volume 1.0 mL.

3.5. *Effect of the sample volume*

In order to explore the possibility of enriching low concentrations of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 25, 50, 100, 150 and 200 mL of sample solutions containing 1.0 μg of Cd, Cr, Cu and Mn, respectively were passed through the microcolumn with optimum flow rate. As shown in Fig. 4, quantitative recoveries (>90%) were obtained for sample volumes up to 50 mL for Cd and Cr, 100 mL for Mn and 150 mL for Cu, the adsorbed metal ions can be eluted with 1.0 mL 0.5 mol L^{-1} HNO_3, so the enrichment factor achieved by this method is 50 for Cd and Cr, 100 for Mn and 150 for Cu. In this experiment, 50 mL of sample solution was adopted for the preconcentration of analytes from water sample.

3.6. *Adsorption capacity*

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. To determine the adsorption capacity, 25 mL of each metal ions solution at 10 μg mL^{-1} was adjusted to the appropriate pH, then precon-

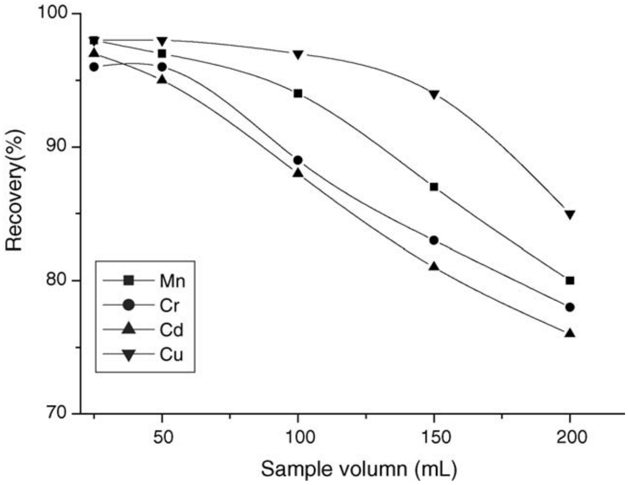

Fig. 4. Effect of sample volume on the recovery of the studied metal ions on immobilized nanometer TiO_2 Cd, Cr, Cu and Mn: 1.0 μg; pH: 8.0.

centrated and eluted according to the recommended procedure. The amount of metal ions adsorbed was determined by ICP-AES. The adsorption capacity of immobilized nanometer TiO_2 for Cd, Cr, Cu and Mn was found to be 2.93, 2.11, 6.69 and 2.47 mg g^{-1}, respectively, and it is similar to the adsorption capacity of nanometer TiO_2 reported in Ref. [28].

3.7. *Column reuse*

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 10 mL 1.0 mol L^{-1} HNO_3 and 20 mL distilled water respectively, and stable up to at least 20 adsorption-elution cycles without obviously decrease in the recoveries for the studied ions.

3.8. *Effects of coexisting ions*

The effects of common coexisting ions on the adsorption of the studied ions on immobilized nanometer TiO_2 were investigated. In these experiments, solutions of 1.0 μg mL^{-1} of Cd, Cr, Cu and Mn containing the added interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of the studied elements less than 90%, were found to be 5000 mg L^{-1} for Na^+, K^+, 2000 mg L^{-1} for Ca^{2+}, Mg^{2+}, 1000 mg L^{-1} for Al^{3+}, 200 mg L^{-1} for Co^{2+}, Ni^{2+}, Pb^{2+} and 100 mg L^{-1} for Zn^{2+}, Fe^{3+}. Due to the adsorption competition between the transition metals and the analytes, these metals have the lower tolerance limits. The contents of these metals in the CRM or water sample applied in this study are within the tolerated concentration range, and will not cause interferences on the preconcentration of the analytes.

3.9. *Detection limits and precision*

The detection limits (evaluated as the concentration corresponding to three times the standard deviation of 11 runs of the blank solution) of this method for Cd, Cr, Cu and Mn are 48, 36, 21 and 24 ng L^{-1}, respectively; and relative standard deviations (RSDs) are 3.5, 4.4, 2.6 and 2.2%, respectively ($n = 11$, $c = 10$ ng mL^{-1}).

3.10. *Analytical application*

In order to establish the validity of the proposed procedure, the method has been applied to the determination of the content of the studied elements in standard reference material (GBW07604, poplar leaves). Portions (0.5000 g) of GBW07604 poplar leaves were transferred into PTFE beakers, 10 mL of concentrated HNO_3 and 3 mL of H_2O_2 were added, heated until the solution become transparent, continuously heated to near dryness and the residue dissolved in 0.1 mol L^{-1} HCl. After adjustment of pH to 8.0, the solution was made up with distilled water to 50 mL. The content of the studied elements was determined according to the recommended procedure. The results are presented in Table 3. As can be seen, the results obtained are in good agreement with reference values.

Table 3
The analytical results of standard reference material (GBW07604) (μg g^{-1})

Element	Found[a]	Certified value
Cd	0.30 ± 0.08	0.32 ± 0.05
Cr	0.52 ± 0.03	0.55 ± 0.05
Cu	9.4 ± 0.3	9.3 ± 0.5
Mn	44 ± 3	45 ± 2

[a] The value following "±" was the standard deviations ($n = 3$).

Table 4
Determination of metal ions in lake water (ng mL^{-1})[a]

Element	Added	Found	Recovery (%)
Cd	0	0.8	
	5.0	5.9	102
Cr	0	1.6	
	5.0	6.4	96
Cu	0	3.0	
	5.0	8.0	100
Mn	0	5.6	
	5.0	10.5	98

[a] Sample volume: 50 mL.

The proposed method was applied to the determination of Cd, Cr, Cu and Mn in nature lake water sample (East Lake, Wuhan, China), and the recoveries of spikes of the studied ions were also studied. The lake water sample was filtered through a 0.45 μm membrane filter and analyzed as soon as possible after sampling. The analytical results and the recovery were given in Table 4. The results indicated that the recoveries were reasonable for trace analysis, in a range of 96–102%.

4. Conclusions

Nanometer TiO_2 was successfully immobilized on silica gel through sol–gel method and used in a microcolumn for trace metal enrichment. For nanometer TiO_2 coated on the silica surface, the exchange property was preserved. The material showed relatively high chemical stability towards the action of acidic solutions. The packed microcolumn used in proposed procedure did not show any over pressure or swelling and can be used up to at least 20 adsorption–elution cycles without decrease in the performance. The proposed method presented good sensitivity, precision and accuracy for all analytes analyzed.

References

[1] Y.A. Zolotov, N.M. Kuzmin, Preconcentration of Trace Elements, Elsevier, Amsterdam, 1992.

[2] R.E. Sturgeon, S.S. Berman, J.A.H. Desaulniers, A.P. Mykytluk, J.W. McLaren, D.S. Russell, Anal. Chem. 52 (1980) 1585.

[3] Z.L. Fang, L.P. Dong, J. Anal. At. Spectrom. 7 (1992) 439.
[4] J.H. Wang, E.H. Hansen, Anal. Chim. Acta 435 (2001) 331.
[5] J.H. Wang, E.H. Hansen, J. Anal. At. Spectrom. 16 (2001) 1349.
[6] T. Akagi, H. Haraguchi, Anal. Chem. 62 (1990) 81.
[7] K. Cundeva, T. Stafilov, G. Pavlovska, Spectrochim. Acta Part B 55 (2000) 1081.
[8] K. Pyrzynska, Crit. Rev. Anal. Chem. 29 (1999) 313.
[9] J.S. Fritz, Analytical Solid-phase Extraction, Wiley–VCH Verlag, New York, 1999.
[10] B.S. Garg, R.K. Sharma, N. Bhojak, S. Mittal, Microchem. J. 61 (1999) 94.
[11] P.C. Rudner, A.G. de Torres, J.M.C. Pavon, F.S. Rojas, Talanta 46 (1998) 1095.
[12] E. Matoso, L.T. Kubota, S. Cadore, Talanta 60 (2003) 1105.
[13] A. Goswami, A.K. Singh, B. Venkataramani, Talanta 60 (2003) 1141.
[14] G.A. Zachariadis, A.N. Anthemidis, P.G. Bettas, J.A. Stratis, Talanta 57 (2002) 919.
[15] J.H. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 248.
[16] J.H. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 1278.
[17] I. Narin, M. Soylak, L. Elci, M. Dogan, Talanta 52 (2000) 1041.
[18] R.J. Cassella, D.T. Bitencourt, A.G. Branco, S.L.C. Ferreira, D.S. Jesus, M.S. Carvalho, R.E. Santelli, J. Anal. At. Spectrom. 14 (1999) 1749.
[19] K. Pyrzynska, Crit. Rev. Anal. Chem. 29 (1999) 313.
[20] H. Bag, A.R. Turker, M. Lale, A. Tunceli, Talanta 51 (2000) 895.
[21] P.M. Ajayan, L.S. Schadler, P.V. Braun, Nanocomposite Science and Technology, Wiley–VCH Verlag, Weinheim, 2003.
[22] K.J. Klabunde, Nanoscale Materials in Chemistry, Wiley, New York, 2001.
[23] Z.L. Wang, Characterization of Nanophase Materials, Wiley–VCH Verlag, Weinheim, 2000.
[24] K. Hadjiivanov, D. Klissurski, M. Kantcheva, J. Chem. Soc., Faraday Trans. 87 (1991) 907.
[25] E. Vassileva, B. Varimezova, K. Hadjiivanov, Anal. Chim. Acta 336 (1996) 141.
[26] E. Vassileva, N. Furuta, Fresenius J. Anal. Chem. 370 (2001) 52.
[27] P. Liang, Y.C. Qin, B. Hu, C.X. Li, T.Y. Peng, Z.C. Jiang, Fresenius J. Anal. Chem. 368 (2000) 638.
[28] P. Liang, Y.C. Qin, B. Hu, T.Y. Peng, Z.C. Jiang, Anal. Chim. Acta 440 (2001) 207.
[29] P. Liang, T.Q. Shi, H.B. Lu, Z.C. Jiang, B. Hu, Spectrochim. Acta Part B 58 (2003) 1709.
[30] P. Liang, T.Q. Shi, J. Li, Int. J. Environ. Anal. Chem. 84 (2004) 315.
[31] G. Chang, Z.C. Jiang, T.Y. Peng, B. Hu, Acta Chim. Sinica 61 (2003) 100.
[32] B.H. Kim, J.Y. Lee, Y.H. Choa, M. Higuchi, N. Mizutani, Mater. Sci. Eng. B 107 (2004) 289.
[33] H. Yanagi, Y. Ohoka, T. Hishiki, K. Ajito, A. Fujishima, Appl. Surf. Sci. 113–114 (1997) 426.
[34] A. Mills, S.K. Lee, A.J. Lepre, Photochem. Photobiol. A: Chem. 155 (2003) 199.
[35] R.S. Sonawane, B.B. Kale, M.K. Dongare, Mater. Chem. Phys. 85 (2004) 52.
[36] M. Li, Y. Chen, Sens. Actuators B 32 (1996) 83.
[37] A. Kay, M. Gratzel, J. Phys. Chem. 97 (1993) 6272.
[38] A. Haarstrick, O.M. Kut, E. Heinzle, Environ. Sci. Tech. 30 (1996) 817.
[39] JCPDS No. 21-1272, The International Center for Diffraction Data, Philadelphia, PA, 1988.
[40] C.J. Merterra, Chem. Soc., Farad. Trans. 84 (1988) 1617.