Talanta 81 (2010) 625–629

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of iodate in waters by cuvetteless UV–vis micro-spectrophotometry after liquid-phase microextraction

Francisco Pena-Pereira, Sonia Senra-Ferreiro, Isela Lavilla, Carlos Bendicho*

Departamento de Química Analítica y Alimentaria, Area de Química Analítica, Facultad de Química, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

ARTICLE INFO

Article history:
Received 10 October 2009
Received in revised form
21 December 2009
Accepted 24 December 2009
Available online 11 January 2010

Keywords:
Miniaturization
Liquid-phase microextraction
Microvolume UV–vis spectrophotometry
Iodate determination
Water analysis

ABSTRACT

The combination of liquid-phase microextraction and microvolume UV–vis spectrophotometry has been applied to the determination of iodate in natural water samples. The method is based on the reduction of iodate into vapor iodine and extraction of this volatile onto a single drop of N,N′-dimethylformamide.

The following derivatization reaction was employed:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Optimum conditions employed for iodate determination were as follows: 2.5 μL N,N′-dimethylformamide exposed to the headspace of a 10 mL acidic (HCl 0.2 mol L^{-1}) aqueous solution stirred at 1400 rpm for 7 min after addition of 1 mL of KI 10^{-3} mol L^{-1} for *in situ* iodine generation. The limit of detection was determined as 1.1 μg L^{-1}. The repeatability, expressed as relative standard deviation, was 4.2% (n = 6). A large preconcentration factor (i.e. 396) was obtained in only 7 min.

1. Introduction

In the last years, liquid-phase microextraction techniques have received an increased attention [1]. Among them, single-drop microextraction (SDME) [2], has grown to currently become one of the most successful sample preparation techniques, mainly due to the prospective high enrichment factors achieved as a result of the great reduction of the acceptor-to-donor phase ratio. Headspace single-drop microextraction (HS-SDME) [3] is considered the most appropriate SDME mode for the extraction of volatile and/or semi-volatile analytes as well as volatile forms after derivatization. HS-SDME provides an efficient sample clean-up, since non-volatile compounds would not be extracted in the drop. Moreover, matrix is not an issue when HS-SDME is used, given that the drop is exposed to the headspace above the sample, unlike direct-SDME, where the drop is immersed into the stirred aqueous sample.

UV–vis spectrophotometry is a mature analytical technique applied to many thousands of determinations owing to its simplicity, flexibility, low cost and convenience [4]. Due to the widespread use of UV–vis spectrophotometers for routine analysis and as a result of the great demand to decrease the sample volume needed to perform a measurement, microvolume spectrophotometers have been commercialized. Despite these systems have been developed especially for molecular biology, biochemistry, and microbiology, they are useful in other science areas, among them, in combination with miniaturized sample preparation techniques used in analytical chemistry, as has been demonstrated in recent publications [5–9].

Iodine is one of the most important micronutrients, showing biological and environmental importance. Iodine deficiency remains a major public health problem in Europe, giving rise to brain damage, irreversible mental retardation, and an endemic goitre as major consequences [10]. Several analytical techniques have been proposed for the determination of iodine species, such as spectrophotometry [11–16], spectrofluorimetry [13], chemiluminiscence [17], high-performance liquid chromatography (HPLC) with UV detection [18], ion chromatography (IC) with inductively coupled plasma mass spectrometry (ICP-MS) [19] or with postcolumn reaction and UV–vis detection [20], transient isotachophoresis (tICP) capillary electrophoresis (CE) with UV detection [21,22] or CE-ICP-MS [23]. However, most of the methodologies described in the literature concerning iodine speciation are focused on the iodide determination, then resulting in a lack of methods permitting simple, rapid and low-cost determination of iodate.

The aim of this work is to extend the combination between HS-SDME and microvolume UV–vis spectrophotometry for iodate determination in environmental samples. The method is based on the *in situ* generation of vapor iodine by iodometric reaction and its extraction and preconcentration onto a microdrop of N,N′-dimethylformamide exposed to the headspace.

* Corresponding author. Tel.: +34 986 812281; fax: +34 986 812556.
E-mail address: bendicho@uvigo.es (C. Bendicho).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2009.12.053

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent grade. Deionized water obtained from a Milli-Q water purifier (Millipore, Molsheim, France) was used throughout. A stock standard solution of iodate (1000 mg L^{-1}) was prepared from potassium iodate (Merck, Darmstadt, Germany). Potassium iodide (Merck) and potassium thiocyanate (Panreac, Barcelona, Spain) were used as reductants of iodate. N,N′-dimethylformamide (Merck), was used as extractant phase. Hydrochloric (Prolabo, Paris, France), sulphuric (Panreac) and acetic acids (Merck) were used as sample medium in the iodine generation study. Iodine (Probus, Badalona, Spain) was used to calculate the enrichment factor for iodate. The following reagents were also employed: As_2O_3, As_2O_5, $Ce(SO_4)_2{\cdot}H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $CuCl_2{\cdot}2H_2O$, H_2O_2, NaClO and NaCl from Merck; Na_2SO_4 and $SnCl_2{\cdot}2H_2O$ from Carlo Erba (Milan, Italy); KNO_3, $NaNO_2$ and $(SO_4)_2Fe(NH_4)_2{\cdot}6H_2O$ from Probus; $KSb(OH)_6$ from Sigma (St. Louis, MO, USA); $SbCl_3$, $KBrO_3$ and $Na_2S_2O_3{\cdot}5H_2O$ from Panreac, $K_2Cr_2O_7$ from Prolabo and humic acid from Fluka (Buchs, Switzerland).

2.2. Apparatus

A Nanodrop® (Wilmington, USA) Model ND-1000 Spectrophotometer was used. The spectrophotometer is equipped with a xenon flash lamp and a 2048-element linear silicon CCD array detector. The optical path length is 1 mm. The sample droplet is held in place by surface tension when it is slightly compressed between the drop-supporting surface (pedestal) and the sample arm. Sample pedestals are made of stainless steel and quartz fiber. The spectrum measurement is performed with two optical fibers installed in the pedestal (emitting light of a Xenon lamp) and the sample arm (spectrometer with linear CCD array). A schematic diagram of the deposition of the enriched microdrop on the pedestal of the microvolume UV–vis spectrophotometer for measurement after HS-SDME is depicted elsewhere [5]. Absorption peak measurements were carried out at 295 nm.

Headspace single-drop microextraction was performed with a commercially available 10-μL syringe containing a guided-PTFE plunger (Hamilton model 1701 RN, 10 AL). Iodine generation was carried out in a 40 mL amber-vial with a silicone rubber septum.

A domestic microwave oven, Samsung, Model M 9245 (Seoul, South Korea), with a 2450 MHz microwave frequency and an output power of 1000 W was used for pre-treatment of aqueous samples prior to iodate determination.

2.3. Water samples

Different natural water samples were analyzed to check the applicability of the proposed method. Rainwater was collected at the University of Vigo, placed at about 10 km far from the Vigo Ria (NE Atlantic Coast). The lake water sample was also collected in this University. Seawater was collected in Silgar Beach, located in Sanxenxo, inside the Pontevedra Ria. Spring water samples were collected at three different locations in Vigo. One of them (spring water III) has being recognized as an undrinkable water by the Galician Authority. Well water was also collected in Vigo.

2.4. Procedure for iodate determination

A 10 mL solution in 0.2 mol L^{-1} HCl is placed into a 40 mL amber-vial. After injecting 1 mL of KI 10^{-3} mol L^{-1}, a 2.5 μL drop of N,N′-dimethylformamide is exposed for 7 min to the headspace above a sample stirred at 1400 rpm. Then, 2 μL of the drop were retracted back into the microsyringe and subsequently placed onto the pedestal of the Nanodrop® spectrophotometer.

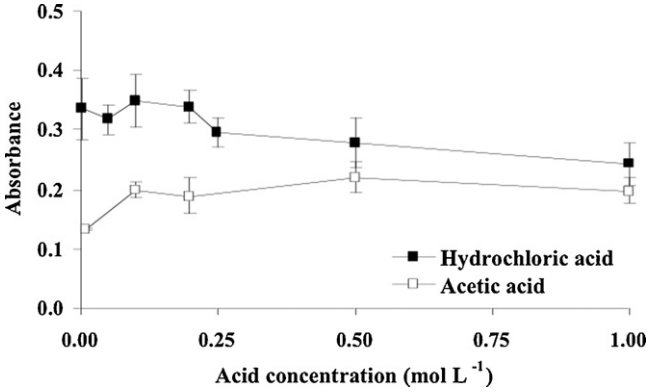

Fig. 1. Effect of the type and concentration of acid involved on the iodine generation from iodate.

3. Results and discussion

3.1. Optimization of SDME

The reaction between iodate and a weak reductant in acidic solution was applied for conversion of iodate into iodide. After this, iodine generation and further extraction into a microdrop of N,N′-dimethylformamide exposed to the headspace above the sample was performed.

Experimental conditions were studied following one variable at a time optimization.

3.1.1. Effect of the type and concentration of acid

The effect of different acids on iodine generation from iodate (i.e. H_2SO_4, HCl and CH_3COOH) was studied. H_2SO_4 was discarded because of the high blanks caused by this acid. The influence of the CH_3COOH and HCl concentration on iodine generation was tested from 0.002 to 1 mol L^{-1} (Fig. 1). An increase in the CH_3COOH concentration from 0.002 to 0.5 mol L^{-1} brought about an absorbance increase. In the case of HCl, results showed a slight decrease of the signal at high concentrations, although the signal achieved with HCl was higher than that using acetic acid in the whole studied range. Thus, 0.2 mol L^{-1} of HCl was fixed as optimum.

3.1.2. Effect of the type and concentration of reductant

Reduction of iodate to iodine is only achieved by weak reductants like iodide or thiocyanate:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (1)$$

$$6IO_3^- + 5SCN^- + 2H_2O \rightarrow 3I_2 + 5HCN + 5SO_4^{2-} \quad (2)$$

As can be seen above, the stoichiometry of reactions (1) and (2) shows a 6-fold increase on the generation of iodine when iodide is used in comparison with thiocyanate. Due to the low levels of iodate typically found in natural waters, an appropriate sensitivity of the method is mandatory. Therefore, iodide was selected as the best reductant of iodate, and its concentration was subsequently optimized in the range 10^{-4}–10^{-2} mol L^{-1} (Fig. 2). The analytical signal remained almost constant in the studied range, showing a quantitative reaction between iodate and iodide even at low KI concentrations. A 10^{-3} mol L^{-1} KI concentration was used.

3.1.3. Ionic strength of solution

An increase of the ionic strength of the sample usually enhances the mass transfer of volatile analytes to the headspace as a result of the increased polarity and modification of the solubility of the

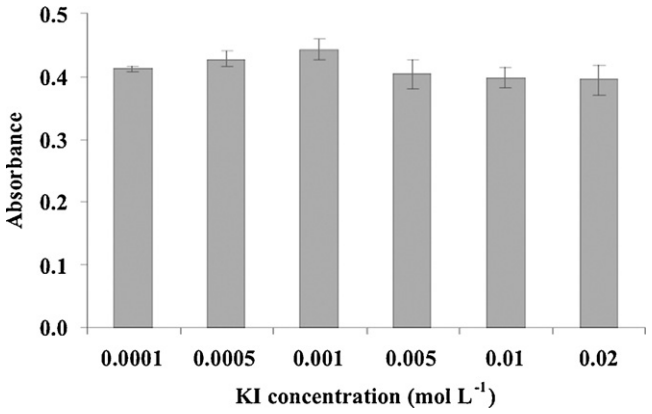

Fig. 2. Effect of the concentration of reductant on the iodine generation.

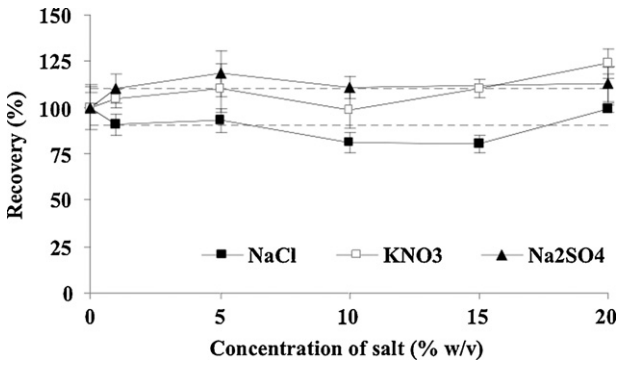

Fig. 4. Effect of the type and concentration of salt.

analyte [24,25]. However, no effect [6] or even the decrease on the analytical response by increasing the content of salt has been reported [26]. The salting-out effect was studied by addition of three different salts (Na_2SO_4, NaCl and KNO_3) to the sample solution. As shown in Fig. 3, they caused a little effect (between 80% and 124%) on the microextraction of iodine from iodate, even at very large amounts of salt (up to 20%, w/v). As pointed out in a previous work [5], a large enhancement of the signal (i.e. 2.7-fold increase) was achieved in the iodide determination by addition of Na_2SO_4 to the sample. In the present method there is an excess of iodine (used as a reductant of iodate) that reacts partially with the iodine generated *in situ*, forming triiodide:

$$I_2 + I^- \leftrightarrow I_3^- \quad (3)$$

The mass transfer of the iodine generated *in situ* to the headspace shifts the equilibrium (3) in the backward direction. However, the existence of this equilibrium may counteract the positive effect of the ionic strength of the sample. Consequently, no addition of salt to the sample solution was performed.

3.1.4. Mass transfer of iodine

HS-SDME strongly depends on the mass transfer of the volatile form of the analyte from the sample matrix to the headspace. Agitation of the sample is used by default when this mode of SDME is employed. Nevertheless, ultrasound waves are well known by their degassing properties and could also be employed with this purpose. On this basis, mass transfer of iodine was optimized by comparison of magnetic stirring (at 1400 rpm) and sonication. An increase of the analytical signal of almost 6-fold was observed when magnetic stirring was used. Adequate agitation of the sample solution by using a magnetic stirrer improves mass transfer in the aqueous phase and, unlike ultrasound waves, induces the convection in the headspace. Sonication of the sample gives rise to a random movement of the analyte in the headspace, which results in poor extraction efficiency. Therefore, magnetic stirring (1400 rpm) was selected for further experiments.

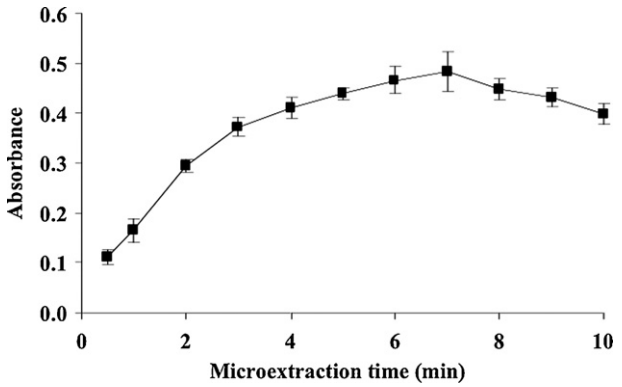

Fig. 3. Effect of the microextraction time.

3.1.5. Microextraction time

Microextraction time is a major parameter affecting the extraction efficiency. In HS-SDME the amount of analytes transferred to the microdrop reaches its maximum when equilibrium among the three phases involved is established. The effect of sampling time was examined in the range 0–10 min. Fig. 4 shows a sharp increase of the analytical signal with microextraction time up to 7 min and a slight decrease at longer exposures. This behaviour was also observed in a previous related work [5]. Thus, a 7 min time was selected.

3.2. Study of potential interferences

Two types of interferences, corresponding to species that can react with the reductant agent (i.e. KI) thus generating iodine and species that can react in solution with the iodine generated *in situ* were studied. In addition, different salts and organic matter as humic acid were also tested. An interference effect was established when a signal variation beyond ±10% was observed.

Tolerable concentration of species that may cause a positive interference effect on the determination of iodate were found to be 100 mg L^{-1} of As (V), Fe(III), Cu(II) and ClO^-; 10 mg L^{-1} of H_2O_2; 1 mg L^{-1} of Sb(V); 0.150 mg L^{-1} of NO_2^-, Cr(VI) and Ce(IV), and 0.040 mg L^{-1} of BrO_3^-. Bromate was the main positive interference in the determination of iodate. To minimize the interference owing to bromate, pre-reduction was mandatory while keeping iodate unmodified. Bromate was reduced by Fe(II) at room temperature within 20 min without altering substantially iodate. A domestic microwave oven was then used to accelerate the bromate conversion. An 80 s time of microwave irradiation working at 10% of the maximum power was enough to achieve the reduction of bromate and keeping iodate unchanged. Moreover, the interference owing to nitrite is also minimized in these conditions since the temperature of the sample is close to 80 °C after 80 s of microwave irradiation [27].

In respect to the species that can reduce the iodine generated *in situ*, the results indicated that at least 100 mg L^{-1} Sn(II); 0.100 mg L^{-1} As(III) and Sb(III); and 0.002 mg L^{-1} $S_2O_3^{2-}$ have no influence on the analytical signal.

The effect of three salts (Na_2SO_4, NaCl and KNO_3) and natural organic matter (as humic acid) was also studied. As it was mentioned above, the system can tolerate high concentrations of salt with little effects on the recovery of iodate (see Section 3.1.3). Humic acid did not interfere at least up to 5 mg L^{-1}.

Table 1
Comparison of the proposed method with other reported methods involving spectrophotometric detection for determination of iodate.

Method	LOD ($\mu g\,L^{-1}$)	Linear range ($\mu g\,L^{-1}$)	Repeatability (RSD, %)	Estimated analysis time (min)	Refs.
FI-UV–vis	330	875–7,000	0.66	1	[14]
FI-UV–vis	50	50–10,000	0.65–0.8	3	[16]
FI-UV–vis	175	175–17,500	1.2–2.2	3	[29]
Reverse FI-UV–vis	8	20–3,000	0.9	0.6	[30]
Kinetic UV–vis	20	30–1,200	0.92–2.12	3	[15]
IC-UV–vis	0.1	0.2–2,000	6.0	4[a]/17[b]	[20]
HPLC-UV	10	50–5,000	1.5–2.9	10	[18]
tICP-CZE-UV[c]	3.5	up to 5,000	1.08	8	[22]
tICP-CE-UV[d]	10	40–800	1.4	35	[21]
HS-SDME-microvolume UV–vis	1.1	7.5–175	4.2	7	This work

[a] For stock solutions.
[b] For environmental samples.
[c] Transient isotachophoresis-capillary zone electrophoresis with UV detection.
[d] Transient isotachophoresis-capillary electrophoresis with UV detection.

3.3. Analytical figures of merit

In order to evaluate the performance of the HS-SDME methodology, several analytical characteristics, such as linearity, limits of detection and quantification, repeatability and enrichment factor were evaluated under the optimized conditions.

The equation of the calibration line, calculated using five iodate standards in the concentration range 7.5–175 $\mu g\,L^{-1}$ was the following: $Y = 0.0027\ [IO_3^-] + 0.0127$, where Y is absorbance and $[IO_3^-]$ is the concentration of iodate ($\mu g\,L^{-1}$). The regression coefficient was $r = 0.9984$. The detection (LOD) and quantification limits (LOQ), calculated as $3\sigma/m$ and $10\sigma/m$ (σ being the standard deviation of 10 blank measurements and m the slope of the calibration line), were 1.1 and 3.4 $\mu g\,L^{-1}$ iodate, respectively. The proposed method revealed good repeatability, with a relative standard deviation (RSD) value of 4.2% ($n = 6$). The enrichment factor, defined as the ratio between the final analyte concentration in the extractant phase and the initial aqueous sample concentration, was calculated to be 396.

A comparison of analytical parameters obtained for the proposed method with related methods involving spectrophotometric detection is presented in Table 1. As can be seen, LOD of the developed method is improved as compared to those reported, as a result of the preconcentration obtained by HS-SDME. Acceptable repeatability and sample throughput are also achieved with the proposed method.

3.4. Analysis of samples and recovery study

The proposed method was applied to the determination of iodate in different natural waters. As a previous pre-treatment, samples were subjected to microwave irradiation for 80 s at 10% of the maximum power after addition of 0.025 mol L^{-1} Fe(II) (1 mL) in order to minimize interferent effects from bromate and nitrite.

All samples were analyzed in triplicate according to the proposed method. Results are presented in Table 2. Iodate concentrations were below the LOQ of the method in most water samples, the seawater sample being the only one that presented a detectable iodate content ($29.2 \pm 3.6\ \mu g\,L^{-1}$). This result is comparable to iodate concentrations typically found in surface seawater [19,28].

Water samples were spiked with 25 $\mu g\,L^{-1}$ of iodate in order to check for possible matrix effects and recoveries were estimated. Relative recoveries ranged from 94 to 104, with a mean value of 98%, then indicating that matrix had little effect on extraction (Table 2).

Table 2
Determination of iodate in environmental samples.

Sample	Iodate added ($\mu g\,L^{-1}$)	Iodate found ($\mu g\,L^{-1}$)	Recovery (%)
Mineral water	–	<LOQ[a]	
	25	24.6 ± 1.3	98.2 ± 5.0
Spring water I	–	<LOQ	
	25	23.6 ± 1.6	94.2 ± 6.5
Spring water II	–	<LOQ	
	25	25.3 ± 0.3	101.0 ± 1.3
Spring water III	–	<LOQ	
	25	25.8 ± 3.8	103.3 ± 14.5
Artificial lake water	–	<LOQ	
	25	24.3 ± 1.5	97.3 ± 6.1
Rain water	–	<LOQ	
	25	24.7 ± 2.6	98.8 ± 10.4
Seawater (surface)	–	29.2 ± 3.6	
	25	52.4 ± 1.4	96.6 ± 5.0

[a] LOQ = 3.4 $\mu g\,L^{-1}$.

4. Conclusions

In this work, the combination of liquid-phase microextraction with microvolume UV–vis spectrophotometry has been performed for the determination of iodate on the basis of the iodometric reaction. Vapor iodine generated *in situ* is extracted and preconcentrated onto a N,N′-dimethylformamide droplet after mass transfer of the volatile form of the analyte to the headspace. The proposed method, characterized by its simplicity and sensitivity, has been employed for the analysis of different natural water samples. Additional advantages of the developed method are low instrumental costs and easy operation.

Acknowledgements

Financial support from the Spanish Education and Science Ministry (project CTQ2009-06956/BQU) is gratefully acknowledged.

F.P.-P. thanks Xunta de Galicia for financial support as a researcher of the Maria Barbeito program.

References

[1] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta Part B 64 (2009) 1.
[2] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[3] A.L. Theis, A.J. Waldack, S.M. Hansen, M.A. Jeannot, Anal. Chem. 73 (2001) 5651.
[4] M. Thomas, Ultraviolet and visible spectroscopy, in: Analytical Chemistry by Open Learning, 2nd edition, Wiley, New York, 1996.
[5] F. Pena-Pereira, I. Lavilla, C. Bendicho, Anal. Chim. Acta 631 (2009) 223.
[6] I. Lavilla, F. Pena-Pereira, S. Gil, M. Costas, C. Bendicho, Anal. Chim. Acta 647 (2009) 112.
[7] F. Pena-Pereira, I. Lavilla, C. Bendicho, Food Chem. 119 (2010) 402.
[8] N. Sharma, A.K.K.V. Pillai, N. Pathak, A. Jain, K.K. Verma, Anal. Chim. Acta 648 (2009) 183.
[9] A.K.K.V. Pillai, et al., Talanta (2009).
[10] M. Anderson, B. De Benoist, I. Darnton-Hill, F. Delange, Iodine Deficiency in Europe—A Continuing Public Health Problem, World Health Organization, Geneva, 2007.
[11] M.S. El-Shahawi, F.A. Al-Hashemi, Talanta 43 (1996) 2037.

[12] O. Agrawal, G. Sunita, V.K. Gupta, Talanta 49 (1999) 923.
[13] A.A. Ensafi, G.B. Dehaghi, Anal. Sci. 16 (2000) 61.
[14] N. Choengchan, K. Uraisin, K. Choden, W. Veerasai, K. Grudpan, D. Nacapricha, Talanta 58 (2002) 1195.
[15] A. Afkhami, F. Mosaed, Anal. Sci. 18 (2002) 667.
[16] A.A. Ensafi, M.A. Chamjangali, Spectrochim. Acta Part A 59 (2003) 2897.
[17] O.V. Zui, A.V. Terletskaya, Fresenius' J. Anal. Chem. 351 (1995) 212.
[18] X.R. Xu, H.B. Li, J.D. Gu, K.J. Paeng, Chromatographia 60 (2004) 721.
[19] Z. Chen, M. Megharaj, R. Naidu, Talanta 72 (2007) 1842.
[20] Y. Bichsel, U. von Gunten, Anal. Chem. 71 (1999) 34.
[21] Z. Huang, K. Ito, A.R. Timerbaev, T. Hirokawa, Anal. Bioanal. Chem. 378 (2004) 1836.
[22] T. Wang, S. Zhao, C. Shen, J. Tang, D. Wang, Food Chem. 112 (2009) 215.
[23] J.H. Chen, K. Wang, S.J. Jiang, Electrophoresis 28 (2007) 4227.
[24] D.C. Leggett, T.F. Jenkins, P.H. Miyares, Anal. Chem. 62 (1990) 1355.
[25] Y. Yamini, M. Hojjati, M. Haji-Hoseini, M. Shamsipur, Talanta 62 (2004) 265.
[26] Q. Xiao, B. Hu, M. He, J. Chromatogr. A 1211 (2008) 135.
[27] T. Fujiwara, I.U. Mohammadzai, H. Inoue, T. Kumamaru, Analyst 125 (2000) 759.
[28] X. Hou, V. Hansen, A. Aldahan, G. Possnert, O.C. Lind, G. Lujaniene, Anal. Chim. Acta 632 (2009) 181.
[29] A.A. Ensafi, M.A. Chamjangali, Spectrochim. Acta Part A 58 (2002) 2835.
[30] Z. Xie, J. Zhao, Talanta 63 (2004) 339.