J Radioanal Nucl Chem (2011) 287:211–216
DOI 10.1007/s10967-010-0670-x

Determination of arsenic (III) and arsenic (V) in freshwater biological samples from Thailand by solvent extraction and neutron activation

R. Zwicker · B. M. Zwicker · S. Laoharojanaphand · A. Chatt

Received: 15 June 2010 / Published online: 3 July 2010

Abstract Neutron activation analysis (NAA) methods were employed for the determination of total arsenic, and water soluble As(III) and As(V) compounds in freshwater fish/shellfish and plant samples from Southern Thailand. Total arsenic concentrations varied from 0.05 to 425 mg kg^{-1}. Water soluble arsenic species were separated by solvent extraction using ammonium pyrrolidinedithiocarbamate (APDC)/methylisobutylketone (MIBK) followed by NAA. The water soluble As(III) and As(V) levels varied from 0.07 to 26.4 and 0.03 to 22.9 mg kg^{-1}, respectively. The As(III) and As(V) detection limits were 0.007 for fish/shellfish, 0.005 for As(III) and 0.006 mg kg^{-1} for As(V) in plants. This separation method allows for the determination of water soluble As(III) and As(V) using commonly available and inexpensive laboratory equipment and chemicals, which can be coupled to a variety of quantification techniques.

Keywords As(III) · As(V) · Solvent extraction · Neutron activation · Thai fish and plants

Introduction

It is well recognized that bioavailability and toxicity of arsenic largely depend on its physico-chemical form. While total arsenic can be helpful in identifying target foods, risk factor cannot be predicted without the specific information on its chemical species. Arsenic can occur as arsenite as As(III), arsenate as As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AB), and arsenosugars. By far the most toxic as well as labile species of arsenic are As(III) and As(V) [1–3]. In an ambient environment, the two major sources of arsenic for humans are food and drinking water. While water primarily contains inorganic arsenic species, there are numerous organic arsenic compounds in food. Some of the dietary arsenic intake data in literature gives total arsenic and does not distinguish between inorganic and organic arsenic. While total arsenic can be helpful in identifying target foods, risk factor cannot be predicted without the specific information on its chemical species. There exists a need for speciation analysis of arsenic in food.

In general, speciation analysis consists of two steps. In the first step a chemical species is separated from the material followed by its detection and measurement in the second step. A number of techniques, such as hydride generation, thermal decomposition, liquid–liquid extraction, solid-phase extraction, coprecipitation, high performance liquid chromatography (HPLC) and other types of chromatography are used for the separation of various arsenic species. The elemental detection techniques generally employed are atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), atomic emission spectrometry (AES), and inductively-coupled plasma spectrometry (ICP), -AES (ICP-AES) as well as -mass spectrometry (ICP-MS) [4–6].

Neutron activation analysis (NAA) is also a very effective and sensitive element determination technique. Unlike some of the common techniques mentioned above, NAA has several unique features which can be advantageously employed in speciation analysis [7]. For example, it offers simultaneous multielement specificity, excellent

R. Zwicker · S. Laoharojanaphand
Thailand Institute of Nuclear Technology, 9/9 Moo 7 Tumbon Saimoon, Ongkharak, Nakhonnayok 26120, Thailand

B. M. Zwicker · A. Chatt (✉)
SLOWPOKE-2 Facility, Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3, Canada
e-mail: a.chatt@dal.ca

sensitivity, speciation of elements which are not chemically similar, and analysis of elements which are rather difficult to determine by many other techniques. In addition, it has some unique quality assurance capabilities which give excellent precision and accuracy. Chemical separation in conjunction with NAA has been used extensively in our laboratory for arsenic speciation of water and fish samples [8–11].

In many Asian countries arsenic contamination is considered as one of the major health hazards. It is particularly true in certain areas of Bangladesh and India. It is also a significant concern in Thailand. It is necessary to have simple, reliable and inexpensive methods using facilities available in Thailand for the determination of arsenic, and more importantly, inorganic arsenic species in food, water and environmental materials. There are many methods available in the literature but most are not that simple [6]. For the present study, NAA was selected as the arsenic determination technique since a medium-flux research reactor is available in Thailand [12]. Among the various techniques available for the separation of inorganic arsenic species, solvent extraction is widely used and was chosen for this work. A simple method consisting of solvent extraction and NAA for the quantitative determination of water soluble As(III) and As(V) in Thai fish/shellfish and plant samples is presented here.

Experimental

Reagents, standards and certified reference materials

All chemicals and reagents used were of high purity. The water used was deionized, distilled water (DDW). High-purity As_2O_3 (Aldrich) and KH_2AsO_4 (Sigma) were dissolved in DDW to prepare stock standard solutions of As(III) and As(V), respectively. These solutions were then used for studying recovery, precision, and optimization of the arsenic speciation procedure.

The National Research Council of Canada (NRCC) Certified Reference Materials (CRMs) DORM-2 (Dogfish Muscle) and TORT-2 (Lobster Hepatopancreas) and the U.S. National Institute of Standards & Technology (NIST) Standard Reference Materials (SRMs) 1946 (Lake Superior Fish Tissue) and 1947 (Lake Michigan Fish Tissue) were used to validate the methods used in this work.

Sample collection

Nine freshwater fish/shellfish and 5 plant samples were collected from Ron Phiboon District, Nakorn Si Thammarat Province (contaminated site) and Talay Noi Sanctury, Pattalung Province (non-contaminated site) in early 2008.

Table 1 Scientific and common names of samples collected from southern Thailand

Scientific name	Common name
Monopterus albus	Swamp Eel
Parambassis siamensis	Siamese Glassfish
Clarias batrachus	Batrachian Walking Catfish
Channa striata	Striped Snake-head Fish
Bagarius bagarius	Yellow Sisorid-Catfish
Pangasius sutchi	River Catfish
Anabus testudineus	Walking Fish
Pila ampullacea	Apple Snail
Macrobrachium lanchesteri	Lanchester's Freshwater Prawn
Ipomoea aquatica Forsk	Swamp Morning Glory
Zingiber montanum(Koen.) Theilade	Plai
Dryopteris amboninensis ktze.F	Oak Fern
Colocasia gigantea Hook. f.	Koon
Nymphaea	Water Lilly Stem

Both sampling areas are located in the southern part of Thailand. A list of the samples collected, including scientific names are given in Table 1. Pre-cleaned plastic bags were used for collecting only the edible parts of the samples. Samples were kept frozen until processing and analysis.

Lyophilization of samples

The samples were thawed at room temperature before weighing. Then they were weighed into pre-cleaned Teflon containers for freeze drying (Edwards Modulyo, −40 °C, 55 mbar). The freeze-dried samples were homogenized using a pre-cleaned porcelain mortar and pestle. The homogenized samples were then transferred and stored in pre-cleaned Nalgene bottles.

Preparation of comparator standards

Arsenic stock standard solution was prepared by diluting 1,000 mg kg^{-1} arsenic standard ICP solution purchased from SPC Science. A working standard of arsenic was prepared by diluting a required amount of this stock solution with DDW. The comparator standards were prepared by depositing microlitre portions containing nanogram quantities of arsenic onto sucrose powder in pre-cleaned polyethylene irradiation vials followed by drying under an IR lamp.

Determination of total arsenic

The total arsenic content of samples was determined by instrumental neutron activation analysis—Compton

suppression system (INAA-CSS). About 250-300 mg of CRM or freeze-dried sample was weighed into pre-cleaned polyethylene irradiation vials. They were irradiated (t_i) for 30 min and allowed to decay (t_d) for 17–24 h. A counting time (t_c) of 10 h was used for samples containing low levels of arsenic from the non-contaminated site and 1 h for samples with high levels of arsenic from the contaminated site.

General procedure for arsenic speciation

Approximately 1.0 g of a sample was placed in a centrifuge vial and 10 mL of extractant was added. The mixture was sonicated at 25–40 °C in an ultrasonic bath (Aquasonic VWR, Model 75HT, Fisher Scientific) for 1 h and then centrifuged (IEC Clinical Centrifuge, Damon/IEC Division, USA) for 20 min at 4,000 rpm. The extractant was then removed using a Pasteur pipette and the residue was re-extracted three more times following the same procedure. These four solutions were then combined.

The combined extractants were placed in a 125-mL separatory funnel to which 10 mL of 5% w/v complexing agent (APDC, Sigma) and 10 mL of the organic solvent (MIBK, HPLC grade, Sigma-Aldrich) were added. The mixture was then vigorously shaken on a wrist action shaker (Model 75, Burrel, USA) for 10 min and the phases were allowed to completely separate. The aqueous phase was then removed and re-extracted twice and all aliquots of MIBK were combined. About 1-mL aliquot of the aqueous phase containing the As(V) was transferred into a small-size vial and dried under an IR lamp prior to NAA. The vials were pre-cleaned by soaking them in 10% HNO_3 for one day, rinsing with DDW, and drying at room temperature. The As(III) in the combined MIBK phase was back-extracted with 10 mL of 4 M HNO_3 (Ultrapure grade, Sigma-Aldrich). Then an 1-mL aliquot of the HNO_3 phase containing As(III) was transferred into a small vial and dried under an IR lamp before NAA using a t_i of 30 min, t_d of 17 h, and t_c of 1 h. This solvent extraction method was optimized from work previously reported by several researchers [13–16].

Irradiation and measurement

Samples and comparator standards were irradiated in the inner sites of the Dalhousie University SLOWPOKE-2 Reactor (DUSR) facility at a neutron flux of 2.5×10^{11} cm^{-2} s^{-1}. The irradiated materials were counted in DUSR using the Compton suppression system (CSS) consisting of a 25% HPGe coaxial detector coupled to a digital gamma-ray spectrometer (Ortec DSPEC$^+$). The FWHM of the system was 1.75 keV at the 1332-keV photopeak of ^{60}Co, and peak-to-Compton ratio of 590:1 at the 662-keV of ^{137}Cs. The 559.1-keV γ-ray of ^{76}As($T_{1/2}$ = 26.3 h) was used for arsenic determination.

Results and discussion

Total arsenic levels measured in the Thai freshwater samples are presented in Table 2. It is evident that the values are generally low (0.05–1.67 mg kg^{-1}) for samples collected from the non-contaminated site. The total arsenic content of the samples from the contaminated site was much higher. They varied from a low of 5.75 mg kg^{-1} in Apple Snail to the highest concentration of 425 mg kg^{-1} in Edible Araceae as shown in Table 2. Previous publications have reported contamination in this area [17–21]. There are very few publications providing data on the concentration of arsenic in freshwater organisms and plants in Thailand [22, 23]. Most of the reports primarily focus on the arsenic levels in water, sediment and marine organisms in Thailand [24–26].

The accuracy of the INAA-CSS method for the determination of total arsenic was evaluated by analyzing three different CRMs. The averages of three measurements are presented in Table 3. The agreement between the measured and certified values is generally good and within ±4.6–13.5%.

Arsenic speciation of freshwater samples in this work was divided into two steps. In the first step, arsenic was extracted from the samples using sonication. The optimization of extraction efficiencies for water, methanol:water (1:1), and methanol:water (1:9) under sonication were evaluated using the two NRC CRMs as shown in Table 4. Extractants were selected based on similar work completed by Pizarro et al. [27]. It was observed that both water and methanol:water (1:9) mixture gave comparable as well as the highest overall extraction efficiency of arsenic for DORM-2 and TORT-2 (Table 4). Water was selected as the extractant over the methanol:water mixture for reasons such as usage of green chemistry, avoidance of mixed solvents, simplicity of the method, and purity, availability, transportability as well as cost of water.

The second step involved the extraction of As(III) from As(V) by APDC/MIBK. In previous work, chloroform was used instead of MIBK [16]. In this work MIBK was preferred since it presents a lower health hazard risk and also to prevent any possibility of creating complications with arsenic quantification. Chlorine sensitivity is rather high for NAA work, which would increase sample activity, resulting in higher detection limits for arsenic. This procedure is a quick, simple and inexpensive. The optimization of this technique was mentioned in a previous publication [14]. APDC complexes only As(III) at pH 3.5–5.0 as $As(PDC)_3$ which is extracted into the MIBK phase while As(V) remains in the aqueous phase.

Table 2 Total arsenic content (mean ± SD, mg kg^{-1}) in freshwater organisms and plant samples from non-contaminated and contaminated sites by NAA-CSS

Samples	Contaminated area (t_i = 30 min, t_d = 2 days, t_c = 1 h)	Non-contaminated area (t_i = 30 min, t_d = 2 days, t_c = 10 h)
1. Swamp Eel	12.07 ± 1.17	n/a
2. Siamese Glassfish	20.56 ± 1.10	n/a
3. Walking Fish	8.756 ± 0.16	n/a
4. Striped Snake-head Fish	23.92 ± 1.08 (sample A) 11.01 ± 0.16 (sample B)	0.12
5.Yellow Catfish	n/a	0.14
6. Batrachain Walking Catfish	n/a	0.05
7. River Catfish	n/a	0.43
8. Lanchester's Freshwater Prawn	n/a	0.40
9. Apple Snail	5.75 ± 0.72	1.67
10. Swamp Morning Glory	32.45 ± 0.59	n/a
11. Plai	8.57 ± 0.37	n/a
12. Oak Fern	2.62 ± 0.08	n/a
13. Edible Araceae	425.41 ± 0.39	n/a
14.Water Lilly Stem	n/a	0.15

n/a not available, certain species unavailable due to sampling location/time

Table 3 Total arsenic content in certified reference materials (n = 3) by INAA-CSS: t_i = 30 min, t_d = 2 days, t_c = 10 h

Certified reference materials	Arsenic content (mg kg^{-1} ± SD)	
	This work	Certified value
DORM-2 (Dogfish Muscle)	18.83 ± 0.04	18.0 ± 1.1
NIST 1946 (Lake Superior Fish Tissue)	0.83 ± 0.07	0.96 ± 0.01
NIST 1947 (Lake Michigan Fish Tissue)	2.51 ± 0.01	2.711 ± 0.03

Table 4 Extraction efficiency of total arsenic in CRMs for three different extractants by NAA-CSS: t_i = 30 min, t_d = 17 h, t_c = 30 min, n = 3

CRMs	Water mean ± SD (%)	MeOH:water (1:1) mean ± SD (%)	MeOH:water (1:9) mean ± SD (%)
DORM-2	95.29 ± 1.74	87.92 ± 4.33	94.09 ± 3.72
TORT-2	81.21 ± 3.99	76.57 ± 11.25	82.23 ± 0.51

For the determination of arsenic by NAA, samples should be irradiated for an extended period of time to limit counting statistics error by gamma spectrometry. Unfortunately, liquid samples generally cannot be irradiated for a long period of time due to a pressure build-up in the polyethylene vials. To avoid this problem liquid samples were evaporated to dryness by heating under an IR-lamp for about 3.5 h prior to irradiation. Since heating may cause the loss of As(III) during the evaporation of MIBK, a back extraction of As(III) from the MIBK phase using 4 M HNO_3 was applied [8]. The recovery of arsenic species by APDC/MIBK solvent extraction and back extraction of As(III) by 4 M HNO_3 and Compton suppression NAA was 97.8% for As(III) and 99.1% for As(V) as shown in Table 5. As(III) and As(V) concentrations in freshwater organisms and plants collected from the contaminated and non-contaminated sites are presented in Table 6. They were determined by solvent extraction using APDC/MIBK and the optimized conditions shown in Table 7.

Table 5 Percent recovery of As(III) and As(V) by solvent extraction and NAA-CSS, t_i = 30 min, t_d = 17 h, t_c = 30 min, n = 6

Arsenic species	Recovery, mean ± SD (%)
As(III)	97.8 ± 3.2
As(V)	99.1 ± 3.6

The As(III) and As(V) levels in the contaminated site varied from 0.07 to 26.4 and 0.03 to 22.9 mg kg^{-1}, respectively. These levels are much higher than those reported in the literature [28, 29]. The As(III) and As(V) levels of all samples collected from the non-contaminated site were at or below the detection limits of 0.007 for both As(III) and As(V) in fish/shellfish, 0.005 for As(III) and 0.006 mg kg^{-1} for As(V) in plants.

Based on total As determined in the fish/shellfish samples, the levels of water soluble As(III) and As(V) varied from 5.3 to 11.5 and 6 to 27.9%, respectively. Our results are comparable to those found by Zheng et al. [30]. They found 9.9–33.5% of As(III) and 2.4–39.6% of As(V) in

Table 6 As(III) and As(V) in Thai freshwater organisms and plants by solvent extraction and NAA-CSS: $t_i = 30$ min, $t_d = 17$ h, $t_c = 1$ h

Samples	Contaminated site		Non-contaminated site	
	As(III) (mg $kg^{-1} \pm$ SD)	As(V) (mg $kg^{-1} \pm$ SD)	As(III) (mg kg^{-1})	As(V) (mg kg^{-1})
1. Swamp Eel	0.91 ± 0.16	1.70 ± 0.22	<0.007	<0.007
2. Siamese Glassfish	1.11 ± 0.01	1.59 ± 0.22	n/a	n/a
3. Walking Fish	0.68 ± 0.12	0.57 ± 0.02	n/a	n/a
4. Striped Snake-head Fish	2.74 ± 0.05 (sample A) 0.71 ± 0.03 (sample B)	6.67 ± 0.34 (sample A) 1.71 ± 0.11 (sample B)	<0.007	<0.007
5.Yellow Catfish	n/a	n/a	<0.007	<0.007
6. Batrachain Walking Catfish	n/a	n/a	<0.007	<0.007
7. River Catfish	n/a	n/a	<0.007	<0.007
8. Lanchester's Freshwater Prawn	n/a	n/a	<0.007	<0.007
9. Apple Snail	0.55 ± 0.02	n/a	<0.007	<0.007
10. Swamp Morning Glory	26.40 ± 1.61	22.91 ± 2.63	n/a	n/a
11. Plai	0.27	0.49	n/a	n/a
12. Oak Fern	0.07 ± 0.04	0.03 ± 0.01	n/a	n/a
13. Edible Araceae	8.75 ± 0.58	5.43 ± 0.03	n/a	n/a
14.Water Lilly Stem	n/a	n/a	<0.005	<0.006

n/a not available, certain species unavailable due to sampling location/time

Table 7 Optimized conditions for arsenic speciation by solvent extraction using APDC/MIBK

Factors	Condition
APDC concentration	5%
Extraction time	10 min
Number of re-extraction	3 times
pH	5.5

freshwater fish but only 6–25% was AB, while DMA was the predominant arsenic species (46%). Slejkovec et al. reported only 5.75% of the total arsenic was As(III) and that AB was the major arsenic species (92–100%) among the four arsenic species determined in freshwater fish [29]. Soeroes et al. also reported that AB was the major As species found in catfish along with trace amounts of several other As species, including As(III) and As(V) [31].

The percent of As(III) and As(V) in plant samples analyzed in this work ranged from 2.06 to 81.35% and 1.14 to 70.6%, respectively. This agrees well with Schaeffer et al. who reported that arsenate was the major arsenic species 49–77% in freshwater plants [28]. Koch et al. found 8–71% of As(III) and 25–88% of As(V) in plants [32]. This illustrates that the primary As species among freshwater fish and plants is variable, and that the concentration of As(III) and As(V) varies over a large range.

Adverse health effects from the ingestion of arsenic are dependent on the consumption of both water and food products. If both the drinking water and food products contain elevated levels of arsenic, the risk of adverse health effects is compounded. The concern is further complicated in this case since the risk is not only dependent on the arsenic concentration, but also the arsenic species. The method reported here determines the concentration of water soluble As(III) and As(V) in the samples. The inorganic forms of As(III) as arsenite and As(V) as arsenate are considered the toxic forms of arsenic, while the former is more toxic [1, 2]. Since arsenite and arsenate are more water soluble than most other methylated or organoarsenic species, it is fair to assume that the As(III) and As(V) determined in these samples are primarily arsenite and arsenate. Although this method is incapable of identifying different compounds containing As(III) and As(V) species, it does give an indication of the associated health concern by providing some information on the potential concentration of the most toxic form of arsenic.

In addition to the health related information, the primary goal of this work was to develop a simple and inexpensive separation method, while utilizing the equipment available for arsenic quantification in Thailand. Many research facilities have very modest equipment budgets or lack of access to more sophisticated and expensive separation equipment (e.g. HPLC) limiting their ability to perform any arsenic speciation work. The separation method reported here allows for the determination of water soluble As(III) and As(V) using commonly available and inexpensive laboratory equipment and chemicals, which can be coupled to a variety of quantification techniques.

Conclusions

A simple method consisting of solvent extraction and NAA was optimized and applied to the quantitative determination of water soluble As(III) and As(V) in Thai fish/shellfish and plant samples. It provides good recovery and detection limits for water soluble As(III) and As(V) species by APDC/MIBK solvent extraction and back extraction of As(III) by 4 M HNO_3 and NAA-CSS for both fish and plant samples. This method can be used in most laboratories. The NAA quantification work can be performed in any country with a research reactor (such as Thailand) or by another equivalent quantification technique.

Acknowledgement The authors wish to thank all individuals involved in sample collection and preparation. Financial supports provided by the International Atomic Energy Agency (IAEA) in the form of a Fellowship to R. Zwicker and the Natural Sciences and Engineering Research Council (NSERC) of Canada Discovery Grant to A. Chatt are gratefully acknowledged. Also thanks are due to TINT for a study leave to R. Zwicker and to the DUSR for providing training and equipment.

References

1. Yamauchi H, Fowler BA (1994) In: Nriagu JO (ed) Arsenic in the environment, part II: human health and ecosystem effects, vol 27. Wiley, New York, pp 35–53
2. Shiomi K (1994) In: Nriagu JO (ed) Arsenic in the environment, part II: human health and ecosystem effects, vol 27. Wiley, New York, pp 261–282
3. Sharma VK, Sohn M (2009) Environ Intern 35:743–759
4. Gong Z, Lu X, Ma M, Watt C, Le XC (2002) Talanta 58:77–96
5. McSheehy S, Szpunar J, Morabito R, Quevauviller P (2003) Trends Anal Chem 22:191–209
6. Francesconi KA, Kuehnelt D (2004) Analyst 129:373–395
7. Chatt A (2003) In: Tomar BS, Saxena MK, Manchanda VK, Manihar SB (eds) Proc BRNS-DAE National Symp on Nuclear and Radiochemistry (NUCAR 2003). BARC, Mumbai, India, pp 19–22
8. Shi Y (2000) PhD Thesis, Dalhousie University, Halifax, Canada, 2000
9. Menendez W (2010) PhD Thesis, Dalhousie University, Halifax, Canada, 2010
10. Shi Y, Acharya R, Chatt A (2004) J Radioanal Nucl Chem 262:277
11. Menendez Sanchez W, Zwicker B, Chatt A (2010) J Radioanal Nucl Chem 282:133
12. Laoharojanaphand S, Dharmavanij W, Busamongkol A, Pareepart R, Wimolwattanapun W, Chantarachot W (2008) J Radioanal Nucl Chem 278:675
13. Brooke PJ, Evans WH (1981) Analyst 106:514
14. Subramanian KS, Meranger JC (1981) Anal Chim Acta 124:131
15. Mok WM, Wai CM (1987) Anal Chem 59:233
16. Yusof AM, Ikhsan ZB, Wood AKH (1994) J Radioanal Nucl Chem 179:277
17. Williams M, Fordyce F, Paijitprapapon A, Charoenchaisri P (1996) Environ Geol 27:16–33
18. Williams M (1997) DFID-TDR project R6491, BGS Overseas Geol Series Tech Rep WC/97/49
19. Williams TM, Rawlins BG, Smith B, Breward N (1998) Environ Geochem Health 20:169–177
20. Zhang J, Chen X, Parkpian P, Tabucanon MS, Mongkolsuk S (2001) Geogr Inform Sci 7:69–78
21. Wiwanitkit V (2008) Toxicol Environ Chem 90:1043–1046
22. Jankong P, Chalhoub C, Kienzl N, Goessler W, Francesconi KA, Visoottiviseth P (2007) Environ Chem 4:11–17
23. Rattanachongkiat S, Millward GE, Foulkes ME (2004) J Environ Monit 6:254–261
24. Tupwongse V, Parkpian P, Watcharasit P, Satayavivad J (2007) J Environ Sci Health Part A 42:1041–1092
25. Sompongchaiyakul P, Sirinawin W (2006) Asian J Water Environ Pollut 4:17–24
26. Oshikawa S, Geater A, Chongsuvivatwong V, Chakraborti D (2007) J Environ Sci Health Part A 42:1753–1761
27. Pizarro I, Gomez M, Camara C, Palacios MA (2003) Anal Chim Acta 495:85–98
28. Schaeffer R, Francesconi KA, Kienzl N, Soeroes C, Fodor P, Varadi L, Raml R, Goessler W, Kuehnelt D (2006) Talanta 69: 856–865
29. Slejkovec Z, Bajc Z, Doganoc DZ (2004) Talanta 62:931–936
30. Zheng J, Hintelmann H (2004) J Anal At Spectrom 19:191–195
31. Soeroes C, Goessler W, Francesconi KA, Kienzl N, Schaeffer R, Fodor P, Kuehnelt D (2005) J Agri Food Chem 53:9238–9243
32. Koch I, Wang L, Ollson CA, Cullen WR, Reimer KJ (2000) Environ Sci Technol 34:22–26