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Comparative determination of microelements in Baltic seawater and brown algae samples by atomic absorption spectrometric and inductively coupled plasma methods

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Abstract. A variety of spectroscopic methods (ETAAS, FAAS, ICP–MS, ICP–OES) were comparatively characterized with respect to analysis of brown alga *Fucus vesiculosus* and Baltic seawater samples (with a specific low salinity). Attention was focused on the determination of Pb, Cd, Cu, Zn, Mn, Cr, and As in algae samples. Methods of atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) are well suited for the determination of Mn, Zn, As, and Cu, to a lesser extent for that of Pb and Cd. The brackish Baltic seawater has its peculiarities relative to the effectiveness of analysis methods. The contents of arsenic (2.12 ± 0.03 μg L^{-1}) and cadmium (0.061 ± 0.003 μg L^{-1}) were determined directly from seawater by AAS using a palladium modifier. The enrichment factors for microelement content in seaweeds (characterizing the increase of element concentration from seawater to algae) have no constant value for different algae samples and therefore algae cannot be used as quantitative bioindicators for analytical characterization of seawater.

Key words: atomic absorption spectrometry, brown algae, inductively coupled plasma, microelements, seawater analysis.

INTRODUCTION

The use of various spectrometric techniques such as atomic absorption spectroscopic (AAS) and inductively coupled plasma (ICP) methods for analysis of seawater, marine organisms, and sediments has attracted much attention in

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recent years. However, this important field of environmental analysis has some specific difficulties, due mainly to the very low concentrations of several elements in highly chloride conditions [1]. Besides, there are some accompanying minor problems such as reproducibility and precision resulting also from the multielement composition of seawater as well as marine organisms.

AAS and ICP have been thoroughly compared with other instrumental methods. To choose a suitable method for the investigation of biological objects it is especially important to compare such sensitive multielemental methods as inductively coupled plasma–mass spectrometry (ICP–MS) and instrumental neutron activation analysis (INAA) [2]. It is also of importance to collate AAS and ICP because both have a potential for analysis of marine objects.

A number of preconcentration methods were proposed already years ago [3] to overcome the above problems. Several techniques, including solvent extraction, use of chelating resins, solid-phase extraction, ion exchange, and coprecipitation, have been slightly modified later and are used today as very effective concentrating methods for microelemental analysis. For example, in coprecipitation concentration factors can reach 5000–40 000, and a number of metal hydroxides have been widely used and applied to the preconcentration of trace metal ions from different media [1, 4–8]. In addition, some specific sorbents and carriers such as iminodiacetate resins [9], colloidal palladium modifier [10], commercial C18 cartridges [11], and C_{60} fullerene [12] are used for the preconcentration of inorganic ions from natural waters.

For the analysis of Baltic seawater samples collected from different regions it is possible to make use of the natural concentrating ability of the brown marine alga *Fucus vesiculosus* (bladder wrack). This seaweed is of wide distribution in the Baltic Sea and has been used as an indicator species for monitoring the concentration of heavy metals and arsenic in different Baltic Sea regions [13–16]. Taking into consideration the average content of microelements of seawater [17] and *Fucus vesiculosus* biomass [18] (both from the Atlantic), the following high order values of the enrichment factor for the selected elements can be calculated: 10^4 for As, Cr, Cu, and Pb; 10^5 for Cd; 10^6 for Mn and Zn. These elements are of highest interest from the viewpoint of environmental research and monitoring. They will be treated in the present study as well. However, it is not clear how constant the enrichment factors are for these (and other) elements of algae samples from different habitats and from the same sampling site.

During the last decade one of the most promising possibilities for the determination of microelements by electrothermal atomic absorption spectrometry (ETAAS) in the environment, including seawater, was the use of a colloidal palladium modifier [10, 19]. In this work, the possibility of using this modifier for the analysis of some microelements in a brackish Baltic seawater sample was also investigated.

Although ICP and AAS have been widely used for the analysis of seawater and marine algae, especially in the last decades, no comparative multielemental research of these methods has been carried out. Hence, this study aimed at assessing the feasibility of the methods for analysis of marine objects and the stability of the results obtained. Of special interest was the determination of such frequent pollutants present in seawater as As and Cd by ETAAS. Another aim was to test the stability of enrichment factors (from seawater to algae) in the environment of a Baltic Sea city, as well as possibilities of using these factors for seawater monitoring.

EXPERIMENTAL

Instrumentation

Spectra AA 220F and 220Z atomic absorption spectrometers (Varian, Mulgrave, Australia) equipped with a side-heated GTA-110Z graphite atomizer, a Zeeman-effect background correction, and an integrated autosampler were used. Graphite tubes with coating and platforms made of pyrolytic graphite were used throughout the work. Argon of 99.998% purity (AGA, Helsinki, Finland) was used as the purge gas. Acetylene of 99.998% purity (AGA, Helsinki, Finland) was used as the fuel gas in flame atomic absorption spectroscopy (FAAS).

An Anton Paar Multiwave 3000 (Graz, Austria) microwave oven with teflon bombs was used for the microwave-assisted acid digestion.

For ICP–MS investigations an Agilent ICP–MS 7500a (Agilent Technologies Inc., USA) instrument with Agilent ICP–MS ChemStation software and for ICP–optical emission spectroscopy (OES) investigations an ICP–OES Vista MPX (Varian, Mulgrave, Australia) instrument were used.

Reagents and samples

Nitric acid (65%), “suprapure” grade (Merck, Darmstadt, Germany), hydrochloric acid (36–38%) “for trace metal analysis” (Baker, Phillipsburg, USA), and hydrogen peroxide (35%), “puriss.” (Riedel-de Haën, Seelze, Germany) were used. Polyvinyl pyrrolidone (PVP) K-90 ($M_r \approx 360\,000$) “for molecular biology” and palladium(II) chloride anhydrous (“purum”, 60% Pd) were purchased from Fluka (Buchs, Switzerland). Ethanol (96.8% v/v) was from Moe Joogid (Tallinn, Estonia). Water was purified to 18.2 $\mathrm{M\Omega\,cm^{-1}}$ resistivity using a Milli-Q water purification system (Millipore, Bedford, USA).

The stock atomic spectroscopy standard solutions (1000 $\mathrm{mg\,L^{-1}}$) of Pb, Cd, Cu, Zn, Mn, Cr, and As (Fluka) and Multielement Quality Control Standard 26 (High-purity standards, Charleston, USA) were gradually diluted with 4% HNO_3 before use.

In the case of ICP–MS, various multielement standard and quality control solutions, containing 10 $\mathrm{mg\,L^{-1}}$ of each element (AccuStandard, USA), were used. For ICP–MS single element standard solutions, containing 1000 $\mathrm{mg\,L^{-1}}$ of each element, were purchased from Merck.

The samples of the brown alga *Fucus vesiculosus* were collected from coastal regions of Tallinn, Estonia, in summer 2005. Seaweeds were collected from five habitats to characterize the varying concentration of these significant microelements in seaweeds and seawater near Tallinn. The fresh samples were washed with MilliQ water and dried first at room temperature and then in a microwave oven at 105 °C till constant weight. After drying the samples of algae were homogenized using an agate mortar and treated as described in Analytical procedures.

Seawater samples were collected from seven characteristic places in the coastal waters around Tallinn into pre-cleaned high-density polyethylene bottles. After collection, the seawater samples were acidified to pH lower than 2.0 by adding concentrated nitric acid in order to avoid metal adsorption onto the inner bottle walls. The acidified seawater samples were then filtered through a 0.45 μm polycarbonate membrane Nucleopore filter (Millipore).

Analytical procedures

Instrumental parameters and temperature programs for atomic absorption measurements used are given in Tables 1 and 2, respectively. The total volume of the solution pipetted into the atomizer was always 20 μL (10 μL of the sample solution plus 10 μL of the modifier solution). At least two replicates were measured for each solution. As a rule, the reproducibility of the measurements was better than ±10%.

Table 1. Instrumental parameters used for the determination of Cd, Pb, As, and Cr by ETAAS and Zn, Cu, and Mn by FAAS (peak area quantitation)

	ETAAS				FAAS		
	Pb	Cd	As	Cr	Zn	Cu	Mn
Wavelength, nm	283.3	228.8	193.7	357.9	213.9	324.8	279.5
Bandwidth, nm	0.5	0.5	0.2	0.2	1.0	0.2	0.2

Table 2. Temperature programs used for the determination of Cd, Pb, As, and Cr* by ETAAS [20]

Step	Temperature, °C	Time, s	Ar flow rate, L min^{-1}
1. Drying	85 (Cr); 110 (Cd, Pb, As)	5.0	3.0
2. Drying	95 (Cr)	40.0	3.0
	110 (Cd, Pb, As)	20.0	
3. Drying	120 (Cr); 130 (Cd, Pb, As)	10.0	3.0
4. Pyrolysis	700 (Cd, Pb); 1300 (As)	10.0	3.0
	1000 (Cr)	5.0	
5. Pyrolysis	700 (Cd, Pb); 1300 (As)	25.0	3.0
	1000 (Cr)	1.0	
6. Pyrolysis	700 (Cd, Pb); 1300 (As)	6.2	0
	1000 (Cr)	2.0	
7. Atomization	1800 (Cd); 2000 (Pb); 2600 (As)	0.7	0
	2600 (Cr)	0.8	
8. Atomization	1800 (Cd); 2000 (Pb); 2600 (As, Cr)	2.0	0
9. Cleaning	2200 (Cd); 2300 (Pb); 2600 (As, Cr)	2.0	3.0

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* Cr was determined using a pyrolytical coated cuvette without a modifier.

Table 3. Comparative analysis of certified reference material* (n = 3)

Element	Found, µg/g		Certified, µg/g
	By ETAAS	By ICP–OES	
As	26.4 ± 2.1	22.3 ± 2.0	24.0 ± 3.2
Cd	2.63 ± 0.25	2.53 ± 0.21	2.7 ± 0.3
Cr	94.0 ± 6.4	90.0 ± 5.2	84.0 ± 9.4
Cu	79.1 ± 3.3**	80.2 ± 3.0	83.6 ± 4.1
Mn	1230.3 ± 21.0**	1228 ± 25	1240 ± 60
Pb	73.0 ± 3.8	70 ± 4	77.2 ± 1.7
Zn	439 ± 13**	430 ± 12	439 ± 26

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* Certified Reference Material LG6187 (River Sediments).

** Analysed by FAAS.

The algae samples (0.1–0.2 g) were mineralized with 3 mL of concentrated HNO_3 and 1 mL of concentrated H_2O_2 in teflon bombs in a microwave oven at temperatures up to 180 °C for 30 min. After cooling down the bombs the solutions were transferred to volumetric flasks and diluted (to 25 mL) with MilliQ water. At least two weights and two blanks were performed per each sample.

The colloidal Pd modifier was synthesized according to the procedure described in [19]. To 4 mL of the $PdCl_2$ solution containing 50 mg of Pd in 1 mol L^{-1} HCl, 1 mL of water, 20 mL of an aqueous solution of 2.5 mg mL^{-1} PVP, and 25 mL of ethanol were added. The solution was refluxed for 30–60 min (on an electric hotplate) in a flow of argon.

For direct determination of As and Cd in the Baltic seawater sample by ETAAS using a colloidal palladium modifier the seaweed samples were diluted with Milli-Q water (1 : 5) and the same processing program (Tables 1 and 2) was used as for the analysis of seaweeds.

The accuracy of the methods used was validated by the analysis of standard certified reference material (CRM) (Table 3). For ICP–OES and ICP–MS analyses also CRM TM-28.2 (low level fortified standard for trace elements – lake water) and QCS 26 were used.

RESULTS AND DISCUSSION

Analysis of Baltic seawater

The results of the analysis of seawater samples from seven geographic points around Tallinn are presented in Table 4. There are only a few effective methods for direct multielemental analysis of seawater samples: mainly INAA and ICP–MS. Quite poor analytical data are available about Baltic seawater of different regions, particularly the Gulf of Finland.

When comparing ICP and INAA it may be pointed out that the results of the present study are in accordance with earlier conclusions [2] and with our earlier

Table 4. Analysis of seawater by ICP–MS*

Element	Unit	Detection limit	Concentration of elements around Tallinn**						
			1	2	3	4	5	6	7
B	µg L^{-1}	<1	880	850	890	810	780	850	765
Be	µg L^{-1}	<0.01	0.08	0.38	0.12	0.05	<0.05	0.08	<0.05
Na	mg L^{-1}	<0.01	1620	1580	1620	1520	1460	1600	1599
Mg	mg L^{-1}	<0.001	220	220	220	200	190	220	203
Al	µg L^{-1}	<0.2	46	27	110	45	45	63	7.5
K	mg L^{-1}	<0.1	66	65	69	61	58	65	65.5
Ca	mg L^{-1}	<0.03	85	85	90	81	75	81	83.5
V	µg L^{-1}	<0.02	0.28	0.24	0.43	0.35	0.22	0.25	0.5
Cr	µg L^{-1}	<0.1	1.4	2.7	0.71	1.5	2.1	<0.5	<0.05
Fe	µg L^{-1}	<10	280	180	230	200	150	110	54.5
Mn	µg L^{-1}	<0.02	27	11	39	14	9.4	8.8	1.1
Co	µg L^{-1}	<0.01	0.26	0.26	0.36	0.19	0.19	0.23	0.1
Ni	µg L^{-1}	<0.1	2.5	2.5	2.6	2.1	2.6	2	1
Cu	µg L^{-1}	<0.1	13	49	16	5.7	5.7	3.6	1.6
Zn	µg L^{-1}	<0.2	8.9	40	14	5	5	4.2	3.8
As	µg L^{-1}	<0.1	1.5	0.93	1.8	1.1	1.1	0.82	1.75
Se	µg L^{-1}	<0.4	<2	<2	<2	<2	<2	<2	<2
Sr	µg L^{-1}	<0.02	1360	1330	1430	1270	1220	1350	1360
Mo	µg L^{-1}	<0.01	1.2	1.2	1.6	1.2	1.1	1.1	1.45
Cd	µg L^{-1}	<0.01	0.05	0.05	0.05	<0.05	<0.05	0.25	–
Sb	µg L^{-1}	<0.01	0.24	0.25	0.96	0.24	0.14	0.21	0.45
Ba	µg L^{-1}	<0.03	25	21	31	22	22	22	23
Tl	µg L^{-1}	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	–
Pb	µg L^{-1}	<0.02	0.53	1.3	2.2	0.59	0.13	0.38	0.15
Th	µg L^{-1}	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.15
U	µg L^{-1}	<0.01	0.62	0.63	0.61	0.61	0.54	0.58	0.5

* Results of 1 : 5 diluted natural water analysis (n = 3). Sodium was determined by diluting 1 : 10.
** In characteristic sites from Suurupi to Tsitre.

results of analysis of seawater samples from the same Baltic region [21]. It was found that ICP–MS is preferable for the analysis of light metals (Na, Mg, Ca, K) and microelements (Cu, Pb, Ni, Sr, and Ba). The determination of some lanthanides (Sm, Eu, Tb, Yb, Lu), Th, and Au is much more accurate and sensitive by INAA. For the quantification of Sb, U, Zn, and As, the potentials of both the methods are well comparable. Direct determination of Hg in a normal (without any preconcentration) seawater sample is impossible by either method due to its very low concentration (≈0.03 µg L^{-1}) but it is possible in brown algae samples by INAA [21].

In this work, the determination of As and Cd in the Baltic seawater sample by ETAAS using a colloidal palladium modifier was carried out. The content of arsenic in the Baltic seawater sample (Kakumäe region) was 2.12 ± 0.03 µg L^{-1} and that of cadmium 0.061 ± 0.003 µg L^{-1}. Direct analysis of these elements in the Baltic seawater sample by AAS has not been performed before. A favourable condition for the analysis is the low salinity of the Baltic seawater; but, for example, in the case of Mediterranean seawater the determination of arsenic is complicated [10].

Analysis of algae by AAS and ICP–OES

The content of six microelements (Pb, Cu, Zn, Cr, Mn, As) in the brown alga *Fucus vesiculosus* is presented in Fig. 1. The results of analysis of the elements content by AAS and ICP–OES are given as parallel measurements for the same algae sample.

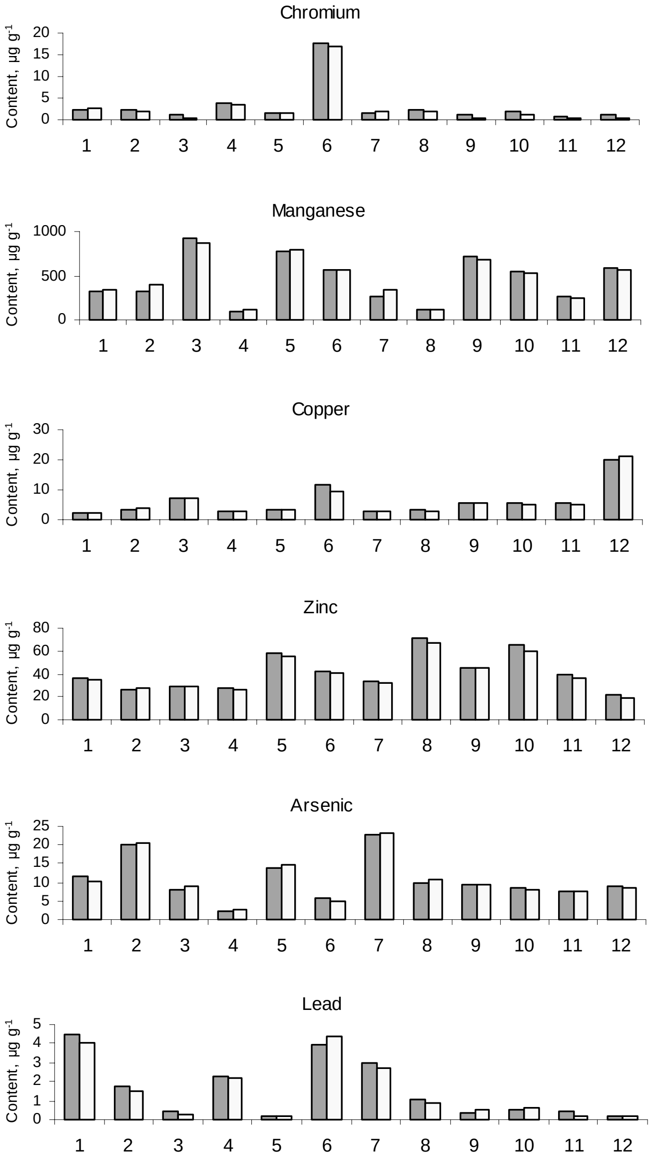

Fig. 1. Comparative determination of microelements by AAS (■) and ICP (□) in *Fucus vesiculosus* (from 12 sampling sites around Tallinn, extent 50 km of coastal line from Suurupi to Tsitre). RSD of neither method exceeded 1.5%.

The microelemental composition of seaweed samples varies greatly by habitat and average age of the algal tissues analysed. Regardless of the great variation of concentrations, the elements may be determined equally well by AAS and ICP–OES (Fig. 1). In general, the variation of the composition of seaweeds by habitat, season, and age is well known [18, 21–23]. Our results confirm the instability of inorganic ions content in algal biomass. This is why the powerful concentrating ability of seaweeds may be only very poorly used for monitoring seawater composition.

Comparison of ETAAS (or FAAS), ICP–OES, and ICP–MS

The methods were used for comparative analysis of the concentration of seven important microelements from solutions of algal samples (Table 5). In some

Table 5. Comparison of different methods for the determination of microelements in *Fucus vesiculosus* from solutions of algae samples ($n = 4$)

	Detection limit	Element concentrations in solutions from different sampling sites				
		1	2	3	4	5
Pb, μg L^{-1}						
ETAAS	1.2	4.46 ± 0.12	1.06 ± 0.04	3.21 ± 0.09	5.62 ± 0.08	2.81 ± 0.11
ICP–OES	10	5.22 ± 0.12	1.33 ± 0.51	2.34 ± 0.67	2.28 ± 0.64	0.43 ± 0.21
ICP–MS	0.02	6.91 ± 0.13	1.83 ± 0.04	4.91 ± 0.04	7.61 ± 0.06	3.22 ± 0.09
Cd, μg L^{-1}						
ETAAS	0.021	3.82 ± 0.02	3.93 ± 0.03	3.01 ± 0.04	6.91 ± 0.03	4.60 ± 0.04
ICP–OES	10	BDL	BDL	BDL	BDL	BDL
ICP–MS	0.01	4.52 ± 0.02	2.52 ± 0.02	3.61 ± 0.02	8.80 ± 0.01	5.23 ± 0.02
Cu, mg L^{-1}						
FAAS	0.005	0.434 ± 0.021	0.177 ± 0.022	0.057 ± 0.012	0.074 ± 0.012	0.047 ± 0.028
ICP–OES	0.005	0.396 ± 0.031	0.185 ± 0.028	0.049 ± 0.015	0.071 ± 0.016	0.048 ± 0.033
ICP–MS	0.1×10^{-3}	0.462 ± 0.004	0.224 ± 0.007	0.059 ± 0.010	0.088 ± 0.007	0.049 ± 0.009
Zn, mg L^{-1}						
FAAS	0.003	0.525 ± 0.013	0.188 ± 0.019	0.264 ± 0.019	0.531 ± 0.016	0.447 ± 0.016
ICP–OES	0.010	0.480 ± 0.015	0.161 ± 0.018	0.229 ± 0.017	0.500 ± 0.017	0.377 ± 0.019
ICP–MS	0.2×10^{-3}	0.587 ± 0.005	0.192 ± 0.006	0.269 ± 0.006	0.530 ± 0.005	0.449 ± 0.004
Mn, mg L^{-1}						
FAAS	0.003	4.44 ± 0.02	5.21 ± 0.01	7.33 ± 0.01	3.85 ± 0.04	6.01 ± 0.04
ICP–OES	0.010	4.23 ± 0.04	4.99 ± 0.04	6.83 ± 0.05	3.50 ± 0.04	5.73 ± 0.04
ICP–MS	0.02×10^{-3}	4.54 ± 0.01	5.47 ± 0.01	7.50 ± 0.01	3.95 ± 0.02	6.08 ± 0.04
Cr, μg L^{-1}						
ETAAS	0.5	15.92 ± 0.09	10.19 ± 0.11	7.51 ± 0.08	11.22 ± 0.02	8.97 ± 0.02
ICP–OES	10	8.42 ± 0.24	3.84 ± 0.19	2.42 ± 0.08	4.06 ± 0.14	4.64 ± 0.09
ICP–MS	0.1	14.21 ± 0.02	8.92 ± 0.08	7.00 ± 0.04	9.62 ± 0.11	n.d.
As, μg L^{-1}						
ETAAS	0.62	70.7 ± 0.1	79.3 ± 0.1	64.4 ± 0.1	106.7 ± 0.1	97.7 ± 0.1
ICP–OES	20	64.40 ± 0.13	74.1 ± 0.1	70.7 ± 0.1	104.4 ± 0.1	97.7 ± 0.1
ICP–MS	0.1	94.1 ± 0.1	105.0 ± 0.1	93.6 ± 0.1	143.0 ± 0.1	101.0 ± 0.2

BDL – below detection limit.

n.d. – not determined.

cases, the methods were unsuitable for analysis, especially ICP–OES for the analysis of Cd, Cr, and Pb (which were below the detection level). Evidently, the determination of Pb is complicated in all the cases studied. The results of As content determination by ICP–MS differ from other results and need further investigation. In general, however, the results are acceptable and the methods investigated can be used for such kind of analyses.

Validation of data

It can be seen that the data obtained (Table 3) correspond well to the reference data for all four CRMs and for all analytes studied. The accuracy of the analytical results for the algae samples was checked using recovery of spikes. For this purpose, spikes of the analytes were added to the digests of biological materials before the measurements. Recoveries for the spikes for all analytes studied were in the range 91–113% (Table 6). Detection and quantitation limits and uncertainties for the method developed are given in Tables 7 and 8.

Table 6. Recoveries of the spikes for two algae samples ($P = 0.95$; $n = 4$)

Analyte	Found in original sample, μg L^{-1}	Spike added, μg L^{-1}	Total concentration found, μg L^{-1}	Spike found, μg L^{-1}	Recovery, %
Furcellaria lumbricalis, Viimsi 2003					
Cd	4.48 ± 0.04	5	9.44 ± 0.09	4.96	99
Pb	9.12 ± 0.33	10	19.02 ± 0.08	9.90	99
As	21.16 ± 0.10	10	31.64 ± 0.71	10.5	105
Se	3.01 ± 0.10	20	22.87 ± 0.21	22.7	113
Furcellaria lumbricalis, Viimsi 2005					
Cd	1.03 ± 0.03	5	5.57 ± 0.06	4.54	91
Pb	3.79 ± 0.04	10	13.18 ± 0.49	9.39	94
As	21.71 ± 0.34	10	31.4 ± 1.1	9.69	97
Se	2.25 ± 0.09	20	23.9 ± 1.4	21.65	108

Table 7. Metrological parameters for the ETAAS method developed

Parameter	Analyte			
	Pb	Cd	As	Se
Detection limit (3SD), μg L^{-1}	1.2	0.021	0.62	1.1
Quantitation limit (10SD), μg L^{-1}	2.8	0.057	1.15	2.6
Measurement expanded, μg L^{-1}	4.1*	1.3*	5.8*	3.6*
Uncertainty, % ($k = 2$)	8	11	15	12
Measurement expanded, μg g^{-1}	3.0**	1.0**	20.0**	2.0**
Uncertainty, % ($k = 2$)	11	9	8	15

Note: Measurement expanded uncertainties were calculated from CRM* – TM-28.2 (low level fortified standard for trace elements – lake water) and spiked algae sample**.

Table 8. Metrological parameters for the FAAS method developed

Parameter	Analyte			
	Cu	Zn	Mn	Cr
Detection limit (3SD), mg L^{-1}	0.005	0.003	0.003	0.06
Quantitation limit (10SD), mg L^{-1}	0.011	0.007	0.010	0.14
Measurement expanded, mg L^{-1}	0.1	0.1	0.1	2.0
Uncertainty, % ($k = 2$)	6.1	8.1	6.8	7.6
Measurement expanded, μg g^{-1}	5.0	20.0	5.0	25
Uncertainty, % ($k = 2$)	6	8	8	10

Note: Detection and quantitation limits were calculated from blanks and an R-chart.

CONCLUSIONS

In general, the data obtained proved the high potential of modern AAS and ICP methods for fast and accurate determination of some toxic elements in the brown alga *Fucus vesiculosus* and Baltic seawater. However, of the seven important (polluting) microelements (Pb, Cd, Cu, Zn, Mn, Cr, As) some complications may occur in the case of Pb and Cd (for ICP–OES) due to their too low concentration levels in brown algae samples. On the other hand, some elements (As, Cd) may be determined directly from Baltic seawater by AAS using a colloidal palladium modifier, thanks to the low natural salinity of this brackish sea. ICP–MS is one of the best and most universal methods for the quantification of microelements and light metals in seawater and brown algae.

The microelement composition of algae varies strongly by samples. Although the enrichment factors of elements (from seawater to algae) are high, they have no constant value for the algae of different habitats and ages. The poor correlation between the content of microelements in seawater and algal biomass does not allow trustworthy characterization of the marine environment by using enrichment factors.

REFERENCES

1. Doner, G. & Ege, A. Determination of copper, cadmium and lead in seawater and mineral water by flame atomic absorption spectrometry after coprecipitation with aluminum hydroxide. *Anal. Chim. Acta*, 2005, **547**, 14–17.
2. Ayrault, S. Multi-element analysis of plant and soil samples. In *Trace and Ultratrace Elements in Plants and Soil* (Shtangeeva, I., ed.). WIT Press, Boston, 2005, 1–32.
3. Mizuike, A. *Enrichment Techniques for Inorganic Trace Analysis*. Springer, New York, Berlin, 1983.
4. Kujirai, O. & Yamada, K. Application of cobalt ammine for the simultaneous determination of traces of As, Fe, Ti, V and Zr in high-purity cobalt metal by lanthanum hydroxide coprecipitation and inductively coupled plasma-atomic emission spectrometry. *Fresenius J. Anal. Chem.*, 1996, **354**, 428–431.

5. Divrikli, U. & Elci, L. Determination of some trace metals in water and sediment samples by flame atomic absorption spectrometry after coprecipitation with cerium(IV) hydroxide. *Anal. Chim. Acta*, 2002, **452**, 231–235.
6. Duan, T., Kang, J., Chen, H. & Zeng, X. Determination of ultra-trace concentrations of elements in high purity tellurium by inductively coupled plasma mass spectrometry after $Fe(OH)_3$ coprecipitation. *Spectrochim. Acta, Part B*, 2003, **58**, 1679–1685.
7. Saracoglu, S., Soylak, M. & Elci, L. Separation/preconcentration of trace heavy metals in urine, sediment and dialysis concentrates by coprecipitation with samarium hydroxide for atomic absorption spectrometry. *Talanta*, 2003, **59**, 287–293.
8. Nakajima, J., Hirano, Y. & Oguma, K. Determination of lead in seawater by flow-injection on-line preconcentration-electrothermal atomic absorption spectrometry after co-precipitation with iron(III)hydroxide. *Anal. Sci.*, 2003, **19**, 585–588.
9. Warnken, K. W., Tang, D., Gill, G. A. & Santschi, P. H. Performance optimization of a commercially available iminodiacetate resin for the determination of Mn, Ni, Cu, Cd and Pb by on-line preconcentration inductively coupled plasma-mass spectrometry. *Anal. Chim. Acta*, 2000, **423**, 265–276.
10. Volynsky, A. B., Akman, S., Dogan, C. E. & Koklu, U. Application of colloidal palladium modifier for the determination of As, Sb and Pb in a spiced sea water sample by electrothermal atomic absorption spectrometry. *Spectrochim. Acta, Part B*, 2001, **56**, 2361–2369.
11. Otero-Romaní, I., Moreda-Piñeiro, A. & Bermejo-Barrera, A. Evaluation of commercial C18 cartridges for trace elements solid phase extraction spectrometry determination. *Anal. Chim. Acta*, 2005, **536**, 213–218.
12. Muñoz, J., Gallego, M. & Valcárcel, M. Speciation analysis of mercury and tin compounds in water and sediments by gas chromatography-mass spectrometry following preconcentration on C_{60} fullerene. *Anal. Chim. Acta*, 2005, **548**, 66–72.
13. Fuge, R. & James, K. H. Trace metal concentrations in *Fucus* from the Bristol Channel. *Mar. Pollut. Bull.*, 1974, **5**, 9–12.
14. Forsberg, Å., Söderlund, S., Frank, A., Petersson, L. R. & Pedersén, M. Studies on metal content in the brown seaweed, *Fucus vesiculosus*, from the Archipelago of Stockholm. *Environ. Pollut.*, 1988, **49**, 245–263.
15. Rönnberg, O., Adjers, K., Ruokolahti, C. & Bondestam, M. *Fucus vesiculosus* as an indicator of heavy metal availability in a fish farm recipient in the Northern Baltic Sea. *Mar. Pollut. Bull.*, 1990, **21**, 388–392.
16. Stengel, D. B., Macken, A., Morrison, L. & Morley, N. Zinc concentrations in marine macroalgae and a lichen from western Ireland in relation to phylogenetic grouping, habitat and morphology. *Mar. Pollut. Bull.*, 2004, **48**, 902–909.
17. Emsley, J. *The Elements*. Clarendon Press, Oxford, 1993.
18. Amer, H. A., Ostapczuk, P. & Emons, H. Quality assurance in measuring the elemental composition of the alga *Fucus vesiculosus*. *J. Environ. Monit.*, 1999, **1**, 97–102.
19. Volynsky, A. B. & Krivan, V. Colloidal palladium – a promising chemical modifier for electrothermal atomic absorption spectrometry. *Spectrochim. Acta, Part B*, 1997, **52**, 1293–1304.
20. Viitak, A. & Volynsky, A. B. Simple procedure for the determination of Cd, Pb, As and Se in biological samples by electrothermal atomic absorption spectrometry using colloidal Pd modifier. *Talanta*, 2006, **70**, 890–895.
21. Truus, K., Vaher, M., Koel, M., Mähar, A. & Taure, I. Analysis of bioactive ingredients in the brown alga *Fucus vesiculosus* by capillary electrophoresis and neutron activation analysis. *Anal. Bioanal. Chem.*, 2004, **379**, 849–852.
22. Hou, X. & Yuan, X. Study on the concentration and seasonal variation of inorganic elements in 35 species of marine algae. *Sci. Total Environ.*, 1998, **222**, 141–156.
23. Vasconcelos, M. T. S. D. & Leal, M. F. C. Seasonal variability in the kinetics of Cu, Pb, Cd and Hg accumulation by macroalgae. *Mar. Chem.*, 2001, **74**, 65–85.

Balti mere vetikate ja merevee mikroelementide võrdlev analüüs AAS- ning ICP-meetodite abil

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On iseloomustatud võrdlevalt erinevaid spektroskoopilisi meetodeid (elektrotermiline aatomiabsorptsioonspektroskoopia (ETAAS), leek-aatomiabsorptsioonspektroskoopia (FAAS), induktiivsidestunud plasma-massispektromeetria (ICP–MS), induktiivsidestunud plasma-optiline emissioonspektroskoopia (ICP–OES)) pruunvetikate *Fucus vesiculosus* ja Läänemere veeproovide analüüsi aspektist. Enam on tähelepanu pööratud selliste aktuaalsete saasteelementide nagu Pb, Cd, Cu, Zn, Mn, Cr ja As määramisele vetikaproovides. On näidatud, et AAS- ja ICP-meetodid sobivad hästi Mn, Zn, As ja Cu, kuid vähemal määral Pb ja Cd määramiseks. Riimveelise Läänemere veeproovidel on analüüsi efektiivsuse seisukohast teatud eelised, võimaldades määrata pallaadiummodifikaatorit, kasutades ülimadalaid arseeni (2,12 ± 0,03 µg L^{-1}) ja kaadmiumi (0,061 ± 0,003 µg L^{-1}) kontsentratsioone otse mereveest. Mikroelemendi rikastusfaktor uuritud pruunvetikates, mis iseloomustab vetikate kontsentreerimisvõimet (arv, mis näitab, mitu korda on elemendi sisaldus vetikate biomassis kõrgem kui ümbritsevas merevees), pole erinevate vetikaproovide jaoks konstantse väärtusega, mistõttu pole see faktor kvantitatiivse bioindikaatorina merevee analüütiliseks iseloomustamiseks kasutatav.