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Original Research

Trace Metal Determinations Using Voltammetric (DPV-HMDE) and Atomic Absorption Spectrometry (F-AAS and ET-AAS) in Bottom Sediment, Cod, Herring, and Cormorant Tissue Samples

Irena Baranowska[1]*, Bartosz Kowalski[1], Halina Polkowska-Motrenko[2], Zbigniew Samczyński[2]

[1]Department of Inorganic, Analytical Chemistry and Electrochemistry, Chemical Faculty,
Silesian University of Technology, Strzody 7, 44-100 Gliwice, Poland
[2]Institute of Nuclear Chemistry and Technology, Laboratory of Nuclear Analytical Techniques,
Dorodna 16, 03-195 Warsaw, Poland

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Abstract

We developed a voltammetric method using hanging mercury drop electrode (HMDE) for the determination of copper, zinc, lead, and cadmium, and an atomic absorption spectrometry method with flame and electrothermical atomisation for the determination of cobalt, copper, cadmium, lead, zinc, ferrum, manganese, and nickel. These methods were applied for the determination of elements in bottom sediment and animal tissue samples – candidates for certificate reference materials. The mineralisation procedure using a closed microwave-assisted system, which allowed for total decomposition of samples, was applied. For accurate testing of developed methods for elemental determination, Buffalo River sediment (NIST) and fish muscle (ERM) certified reference materials were used. Limits of detection (LOD) and limits of quantification (LOQ) varied depending on technique used. For F-AAS, LOD values were between 2.2-12 mg·kg^{-1}, for ET-AAS 0.10-0.35 mg·kg^{-1}, and 0.014-0.021 mg·kg^{-1} for HMDE. LOQ values varied between 6.5-30 mg·kg^{-1}, 0.31-1.1 mg·kg^{-1}, and 0.042-0.063 mg·kg^{-1}, for F-AAS, ET-AAS, and HMDE, respectively. Linearity ranges also varied for each technique: 0.005-1.0 mg·kg^{-1} for HMDE, 0.35-50 mg·kg^{-1} for ET-AAS, and 6.5-500 mg·kg^{-1} for F-AAS technique. Homogeneity within and between bottles was calculated for each element. Variances did not differ in a statistically significant way, which is why materials can be considered homogenous.

Keywords: metal determination, bottom sediment, animal tissues, DPV-HMDE, F-AAS, ET-AAS

Introduction

Two years ago a consortium consisting of several Polish universities (including the Silesian University of Technology and Institute of Nuclear Chemistry and Technology) were established. The goal of this consortium was to implement a project called MODAS (production and attestation of new types of reference materials crucial for achieving European accreditation for Polish industrial laboratories). This project has sought the development and validation of new refer-

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*e-mail: irena.baranowska@polsl.pl

ence materials that are essential for Polish laboratories, which deal with industrial analytics, for European accreditation. Within this project new materials will be produced – candidates for certified reference materials with different matrices. Among these materials are: the soil in which the analytes are stable organic compounds such as PAH or PCB; bottom sediment, where the analytes are metals, pharmaceuticals, and other residues; and herring, cod, and cormorant tissues, where the analytes are metals and persistent organic compounds. At this stage, the materials are already produced and the certification process is ongoing.

The certified reference materials are of great importance. They allow validation laboratory methods (accuracy), and are necessary when estimating uncertainty of measurement, recovery test, and calibration. Certified reference materials are also needed to check out the skills of a new laboratory or new laboratory analysts.

Production of CRMs is a laborious and time-consuming process. First of all, the selection of the right amount of material is needed. Then homogenization, initial homogeneity, and dosage into suitable containers needs to be carried out. In the next step sterilization should take place, plus homogeneity and stability. The last step is interlaboratory comparison, which is an essential element of the certification process of the material. Within the consortium, each team is responsible for a different part of the preparation of these materials.

In this work we would like to concentrate on studies of the determination of select metals in bottom sediment, and cod, cormorant, and herring tissues using voltammetric (DPV-HMDE) and spectroscopic methods (F-AAS and ET-AAS). The literature still shows research that focuses on determination of different elements in bottom sediments. Some of the research has concentrated on distribution, mobility, or fractionation of some elements in bottom sediments [1-5]. However, most of the publications describe multi-elemental monitoring studies. The most commonly used technique has been ICP with different detectors: MS [1, 2, 6-8], AES [3, 9, 10], and OES [11]. Moreover, XRF techniques with different modification were also used, as these methods can be applied directly with solid samples [5, 12-15]. One publication described the INAA method for determining elements in bottom sediment [16], and five used the AAS method [4, 14, 17-19]. To our knowledge, there have been only two publications in recent years that have applied electrochemical methods for element determination in bottom sediments [20, 21]. There is also one publication that compared results from different techniques: F-AAS, ET-AAS, and XRF [16].

Furthermore, research that focuses on determination of elements in animal tissues were also conducted. There are only a few articles that describe determination of metals in the same tissues as described in this work. Two publications we found described elemental determination in cod [22, 23], herring [23, 24], and cormorant [25, 26] tissues. However, there are still works that described the determination of trace elements in other tissues. The most popular are fish tissues from lakes and seas all over the world [27-33]. Nevertheless, a few applications were applied to determine elements in other organism tissues from water [34, 35] and land [36].

The methods proposed were not hitherto applied for preparation of certified reference materials for bottom sediments, cod, cormorant, and herring tissue samples.

Experimental Procedures

Reagents and Reference Solutions

Nitric acid (HNO_3), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2) were all suprapure grade (NORMATOM TRACE A, VWR, UK). Hydrofluoric acid (HF) was bought from Merck (SUPRAPUR, Germany) and boric acid was bought from ACROS ORGANICS (EXTRA PURE, USA).

Aqueous stock solutions of Cd(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II) were prepared by dilution of the respective standards 1000 $mg\cdot l^{-1}$ (Merck, Germany). All solutions were prepared using double-distilled water (Millipore).

Certified reference materials: RM-8704 Buffalo River Sediment (NIST, USA) and ERM-BB422 (ERM, Belgium) were used for the accuracy measurements.

Instrumentation

Determination of metals was carried out using atomic absorption spectrometry on an AAS 30 Carl Zeiss (Jena, Germany), both using flame atomisation (F-AAS) with acethylene-air flame and electrothermal atomisation (ET-AAS). Select metals were determined under the specific wavelengths: Cd 228.8 nm, Cu 324.8 nm, Co 240.7 nm, Fe 248.3 nm, Mn 279.5 nm, Ni 232.0 nm, Pb 283.3 nm, and Zn 213.9 nm. Except for Cd and Co, all metals were determined using F AAS. For determination of Cd, Co, Fe, Mn, Pb, and Zn, the ET-AAS technique was also used. The ash and atomisation temperatures were specific for each element: Cd (460ºC, 1750ºC), Co (800ºC, 2300ºC), Fe (1000ºC, 2100ºC), Mn (1050ºC, 1900ºC), Pb (700ºC, 1900ºC), and Zn (700ºC, 2000ºC). Determining Cd, Cu, Pb, and Zn also was performed using the voltammetric technique of hanging a mercury drop electrode (DPV-HMDE, Eco-Trybo, Czech Republic) with Ag/AgCl (in saturated KCl) as a reference electrode and a platinum wire as an auxiliary electrode. Before the experiment, solutions were deoxygenated with argon for five minutes, and then after each standard addition were deoxygenated for two minutes. The specific conditions for determination of elements are presented in Table 1. An additional step was added for cod, cormorant, and herring tissues. Because elements in these samples were at lower concentration levels, in order to detect those elements a wait time of 100 s before analysis was applied to concentrated elements on the mercury drop.

A Multiwave 3000 (Anton Paar GmbH, Germany) was used for mineralisation of samples. This closed microwave-assisted system allowed for rapid sample decomposition at high pressure.

Table 1. Conditions of determination of Zn, Cd, Pb, and Cu using DPV-HMDE.

	Zn	Cd	Pb	Cu
Measuring potential	-921 mV	-560 mV	-364 mV	+59 mV
Electrolyte	0.1 M HCl – addition of ammonium buffer to adjust pH to 4	0.1 M HCl (pH 1)		
Starting potential	-1200 mV			
Ending potential	+150 mV			
Scan rate	25 mV/s			

Sample Preparation

The bottom sediment was taken from the Vistula River in Torun. After removing gravel and leaves, the collected fresh material was freeze-dried, ground, and sieved through a nylon sieve, and a fraction of particle size below 90 μm was separated. The particle size distribution of the collected fraction was tested microscopically and by laser diffraction method. The obtained powdered material was homogenized by mixing in a homogenizer for 16 hours and distributed into bottles made of amber glass. All bottles with the candidate CRM were sterilized by electron beam irradiation with a dose of 28 kGy in order to ensure long-term stability of the material. The same procedure (after liofilisation) was applied for the fish and cormorant tissues.

The 400 mg of bottom sediment and RM-8704 were weighed and mineralised with the mixture comprised of HNO_3:HCl:HF (5:2:4, v/v), which allowed for the complete digestion of samples (even the silica). To remove additive hydrofluoric acid, boric acid (H_3BO_3) was used. The mineralisation samples were then transferred into 50 mL volummetric flasks. The complete mineralisation programme is presented in Table 2.

The 450 mg of ERM-BB422 and all tissue samples were mineralised. These samples did not contain silica, therefore another mineralisation programme was applied. The best results were achieved where the mineralisation mixture was comprised of HNO_3:H_2O_2 (9:1.5; v/v) (Table 3).

Table 2. Mineralisation and complexation programme for bottom sediment samples.

Power [W]	Ramp [min]	Hold [min]	Fan
1200	15	40	1
0	-	15	3
Complexation			
1400	5	15	1
0	-	15	3

Table 3. Mineralisation programme for tissue samples.

Power [W]	Ramp [min]	Hold [min]	Fan
600	10	20	1
800	5	15	1
0	-	15	3

Results

Different mineralisation programmes were tested to obtain results with good precision and accuracy. These programmes comprised several mixtures of acids (HNO_3, HCl, HF, H_2SO_4) and H_2O_2 in various combinations. The mixtures without HF acid were unable to decompose silica, which was present in bottom sediment samples. The results for some elements, like Fe and Mn, were lower than the real values of even 10%, when silica were not digested. Therefore, only mixtures with HF acid can be used for those samples. The results of best accuracy were achieved using the programme presented in Table 2. With tissue samples there were not such problems, because these samples did not contain silica. However, the organic matrix was greater than in bottom sediment, which was a problem when determining elements using the DPV-HMDE method. Therefore, a mineralisation programme (Table 3) that contained 9 ml of HNO_3 with the addition of H_2O_2 was applied. With this programme organic matter was removed and electrochemical determination could be applied (Fig. 1).

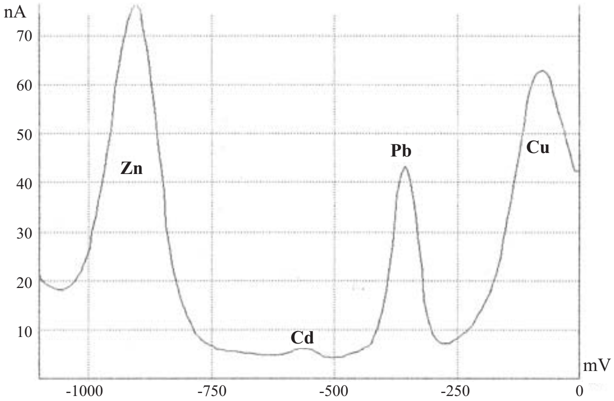

Fig. 1. Voltammogramme of bottom sediment sample (after mineralisation) at pH 4.

Table 4. Results achieved for the Buffalo River sediment material with uncertainty values.

Element	Certification results from RM-8704 Report	F-AAS	ET-AAS	HMDE
	[mg·kg^{-1}]			
Cd	2.94±0.29	-	2.53±0.41	2.64±0.34
Co	13.57±0.43	-	14.29±1.23	-
Fe	39700±1000	37592±3134	38185±4513	-
Mn	544±21	537±14	530±52	-
Ni	42.9±3.7	46.1±5.2	-	-
Pb	150±17	154±14	145±27	140±23
Zn	408±15	396±22	-	390±31

Table 5. Results achieved for the fish tissue material with uncertainty values.

Element	Certification results from ERM-BB422 Report	ET-AAS	HMDE
	[mg·kg^{-1}]		
Cu	1.67±0.16	-	1.53±0.21
Fe	9.4±1.4	8.2±2.0	-
Mn	0.368±0.028	0.457±0.113	-
Zn	16.0±1.1	-	14.3±2.5

The optimal mass for mineralisation of bottom sediment samples was 400 mg and 450 mg for tissue samples. Each round of samples was comprised of six mineralisation samples and two blank samples. For the accuracy measurements we used a certified reference material like Buffalo River sediment (RM-8704, NIST) and fish tissue (ERM-BB422, ERM). Appropriate masses of these certified materials (400 mg and 450 mg) were mineralised using adequate mineralisation procedure. The results obtained for the Buffalo River sediment material with different techniques are presented in Table 4 and for fish tissue in Table 5.

For all obtained values the expanded uncertainty (*U*) was calculated as:

$$U = ku_{(xi)}$$

...where k is the coverage factor, which for the probability level 95% is 2, and $u_{(xi)}$ is standard uncertainty calculated as a standard deviation.

All certified values were in agreement with values obtained using developed methods. As can be seen in Tables 4 and 5, the accuracy and precision of proposed analytical methods is satisfactory. For RM-8704, besides Co and Ni, other elements were determined using two techniques (with Pb even three). The values obtained with different techniques can confirm that determined values are close to the real ones. This could be very useful when applying this procedure for the determination of bottom sediments samples – candidates for certified reference materials.

In ERM-BB422 only four elements from those under consideration were presented. There is a lack of certified reference materials for the fish tissue in the market, which is the next reason for production of such materials. Elements in this CRM were at very low levels, which is why only ET-AAS and DPV-MDE techniques could be applied for verification of developed procedures. However, the values achieved were in agreement with those from CRM. The uncertainty values were higher because of lower concentrations (near the LOQ levels).

The results achieved for the bottom sediment samples (from the Vistula River) are candidates for certified reference materials as presented in Table 6.

The results achieved for the cod, cormorant, and herring tissue samples are candidates for certified reference materials as presented in Table 7.

Calibration curves for elements determined using F-AAS and ET-AAS were determined using linear regression:

Table 6. Results achieved for bottom sediment samples with uncertainty values (n=6).

Element	F-AAS	ET-AAS	HMDE
	[mg·kg^{-1}]		
	(uncertainty %)		
Cd	-	1.91 (15)	1.82 (13)
Co	-	7.74 (5)	-
Cu	38.2 (5)	-	39.1 (6)
Fe	25721 (9)	24973 (10)	-
Mn	1014 (7)	981 (8)	-
Pb	38.1 (12)	36.9 (9)	40.4 (8)
Zn	318 (8)	-	304 (7)

Table 7. Results (mg·kg^{-1}) achieved for tissue samples with uncertainty (%) values (n=6).

Sample	Method	Cu	Fe	Mn	Pb	Zn
Cod tissue	ET-AAS	-	11.3 (12)	0.87 (9)	-	-
	HMDE	1.25 (10)	-	-	0.17 (17)	-
Cormorant tissue	F-AAS	17.6 (8)	299 (5)	-	-	65.8 (6)
	ET-AAS	-	282 (7)	2.32 (8)	2.87 (13)	-
	HMDE	17.0 (6)	-	-	2.62 (7)	62.3 (5)
Herring tissue	F-AAS	-	180 (8)	-	-	107 (5)
	ET-AAS	-	168 (9)	5.31 (7)	-	-
	HMDE	3.2 (8)	-	-	-	99 (7)

Table 8. LOD and LOQ values determined with different techniques.

Element	LOD			LOQ		
	[mg·kg^{-1}]					
	F-AAS	ET-AAS	HMDE	F-AAS	ET-AAS	HMDE
Cd	-	0.12	0.017	-	0.36	0.051
Co	-	0.28	-	-	0.84	-
Cu	2.2	-	0.021	6.5	-	0.063
Fe	12	1.3	-	36	3.9	-
Mn	2.9	0.10	-	8.8	0.31	-
Ni	12	-	-	35	-	-
Pb	8.1	0.35	0.014	24	1.1	0.042
Zn	10	-	0.019	30	-	0.057

$$y = ax + b$$

...where y is the peak area, a is the slope, x is the respective concentration, and b is the intercept.

For determining elements with DPV-HMDE, the standard addition method was used. The limit of detection (LOD) and limit of quantification (LOQ) were determined using the parameters of standard curves. The LOD values were determined as:

$$\mathrm{LOD} = 3.3s/a$$

...where s is the standard deviation of intercept (S_b) and a is the slope.

The LOQ values were calculated as:

$$\mathrm{LOQ} = 3\mathrm{LOD}$$

The LOD and LOQ values were determined for different techniques (Table 8). Linearity levels are presented in Table 9.

For homogeneity within and between bottles, additional measurements were made. From six bottles six samples were taken for mineralisation and the results for each element were calculated using analysis of variance. In each case the result was the same and variances did not differ in a statistically significant way. Therefore, the bottom sediment samples are homogenous for the 400 mg mass and the tissue samples are homogenous for the 450 mg mass and

Table 9. Linearity levels for selected elements with different techniques.

Element	F-AAS	ET-AAS	HMDE
	[mg·kg^{-1}]		
Cd	-	0.4-10	0.06-1.0
Co	-	0.9-25	-
Cu	6.5-100	-	0.07-1.0
Fe	40-500	3.9-50	-
Mn	9-100	0.35-10	-
Ni	35-500	-	-
Pb	25-300	1.1-50	0.05-1.0
Zn	30-300	-	0.06-1.0

can be considered in subsequent operations as candidates for certified reference materials.

The proposal presented in this article for the use of three different techniques for the determination of the selected elements enables customers to select the appropriate technique to determine elements in candidates for certified reference materials, and not only the most commonly used ICP technique. In addition, verification of the results using three analytical techniques is useful for determining the reliability of the results of analyses.

Conclusions

New candidates for certified reference materials (for elements) have been proposed. These materials were prepared from bottom sediment from the Vistula River (Torun) and cod, cormorant, and herring tissues.

A sample mineralisation programme was optimised and applied to 400 mg samples to achieve total decomposition. Without decomposition of silicates, adsorption of some elements can occur, which leads to even more than 10% lower values.

Three analytical techniques were successfully introduced for the determination of several elements. Beside Co and Ni, every element can be determined by at least two techniques for bottom sediment samples, which confirms that values achieved are close to the real values.

For accuracy testing certified reference materials RM-8704 from NIST and ERM-BB422 from ERM were used. Values obtained for this material by applying analytical procedures showed that good accuracy was achieved and those methods could be applied for new bottom sediment and tissue samples.

Produced materials can be considered as homogeneous within and between bottles, as no statistically significant differences from variances were observed. Further studies on the metal content of the aforementioned samples have been carried out by other members of the consortium with the use of other techniques for interlaboratory comparison.

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