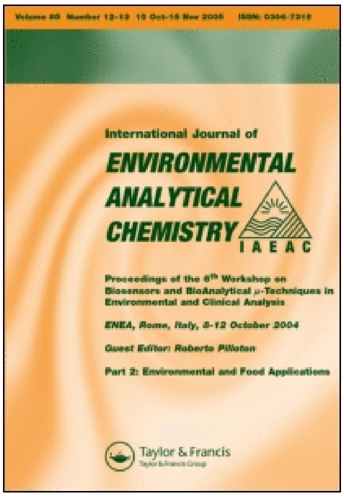

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Intercomparison Studies of Stripping Voltammetry and Atomic Absorption Spectrometry of Zn, Cd, Pb, Cu, Ni and Co in Baltic Sea Water

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For the determinations of trace metals in natural waters precaution steps concerning sampling, storage, pretreatment and analysis are demonstrated. Differential pulse stripping voltammetric (DPSV) and atomic absorption spectrometric (AAS) techniques are compared. Zn, Cd, Pb and Cu are determined by differential pulse anodic stripping voltammetry (DPASV) using either a hanging mercury drop electrode (HMDE) or an *in situ* plated mercury film electrode (MFE). A gold disc electrode (GDE) is also applied to Cu-determination. Differential pulse cathodic stripping voltammetry (DPCSV) is used for the determination of Ni and Co. Electrothermal AAS-methods are used for Cd, Pb, Cu, Ni and Co, while the flame AAS-method is employed for Zn. Analysis of coastal Baltic Sea waters gives similar results using the different modes of DPSV and AAS.

KEY WORDS: DPSV, AAS, Trace metals, Baltic.

INTRODUCTION

The concentrations of most heavy metals in sea water are low, often at sub-ppb level. The metal concentrations in open Baltic are low,[1-4] and many fall in the same ranges as in ocean water.[5] Therefore, Baltic Sea water samples require careful and skilful handling throughout the sampling and analytical procedures.

The most common analytical method used for trace metals is the atomic absorption spectrometric technique (AAS). The high salt matrix in sea water samples generally precludes direct usage of the AAS method.[6] Furthermore, the metals have to be concentrated prior to measurement. Both these problems are solved by using liquid/liquid extraction. Stripping voltammetry offers an alternative analytical technique for ultra trace metal analysis.[7,8]

Intercalibration studies of heavy metals in sea water samples usually show discrepancies in the concentrations determined,[9-11] which evidences the problems connected with heavy metal analyses at ultra trace levels. In our intercomparison study the analytical techniques mentioned above are used in varying modes.

EXPERIMENTAL

Sampling

Polyethylene gloves were worn during the whole sampling procedure. Surface water samples were taken directly into the sample bottle from the prow of the boat, and deeper samples were collected either by a plastic Ruttner sampler or by a go-flo sampler. The samples were acidified with HCl to pH 2 or deep-frozen in quartz bottles.

Washing

The vessels made of quartz, teflon and polyethylene were placed in 7 M HNO_3 for 24 hours, and then rinsed with ultra pure water three times. Drying and storage of the vessels took place in a dust-free environment. The water sample bottles were put into plastic bags and kept in a box up to the time of sampling.

Plastic labware used in the freon extraction method was washed in 4 M HCl at 60°C for five days and rinsed several times with water. Teflon separatory funnels and polyethylene bottles were subsequently filled with 0.2% surprapure HNO_3 and placed in a polyethylene container filled with dilute HCl until used. At the time of extraction they were rinsed with water immediately before use. Plastic pipette tips were washed in 4 M HCl for one day, rinsed several times with water and stored in beakers in a clean bench.

Chemicals

Hydrochloric acid, perchloric acid, nitric acid, sodium hydroxide and perhydrol (30% H_2O_2) were of suprapure grade (Merck), while methylisobutylketone (MIBK), ammonium pyrrolidine-dithiocarbamate (APDC), acetic acid, ammonia and dimethylglyoxime (DMG) were of p.a. quality. Freon (1,1,2-trichloro-trifluoromethane) was of spectroscopic grade (Merck). Standard metal solutions were prepared by dilution of commercially available standard solutions (BDH) or ampoules (Merck). Ultrapure water was obtained using a Milli-Q water purification system (Millipore Corporation) and subsequently double-distilled in quartz apparatus. In the freon method Milli-Q water was used without further purification. The difference of the preparation of ultrapure water depends on the fact that the freon method was carried out in one laboratory, and the MIBK method and the voltammetric analysis were done in another laboratory. Prior to voltammetric measurements the water was UV-irradiated for two hours.

Apparatus

The voltammetric measurements were performed with a polarographic analyser, PAR 174A, equipped with an X-Y recorder, Hewlett-Packard 7044 A. The time period for current sampling was changed to 20 ms in order to minimize disturbance from the net frequency (50 Hz). The voltammetric cell used was a quartz cell designed like the Metrohm model or a quartz beaker enclosed in a plexi-glass cylinder. The three-electrode system was fitted into the lid of the voltammetric cell, and the reference electrode was an Ag/AgCl electrode, dipped into the sample solution via a salt bridge. The counter electrode consisted of a Pt-wire and the working electrode was either a hanging mercury drop electrode (HMDE) or a mercury film electrode (MFE).

UV-irradiation was performed in a locally built device, depicted in Figure 1. The quartz tubes were placed around a 700 W UV-lamp (Original Hanau, West Germany).

The atomic absorption analysis of MIBK extracts was done with an atomic absorption spectrophotometer, Perkin-Elmer model 306 with a graphite furnace, HGA 74, connected to an automatic

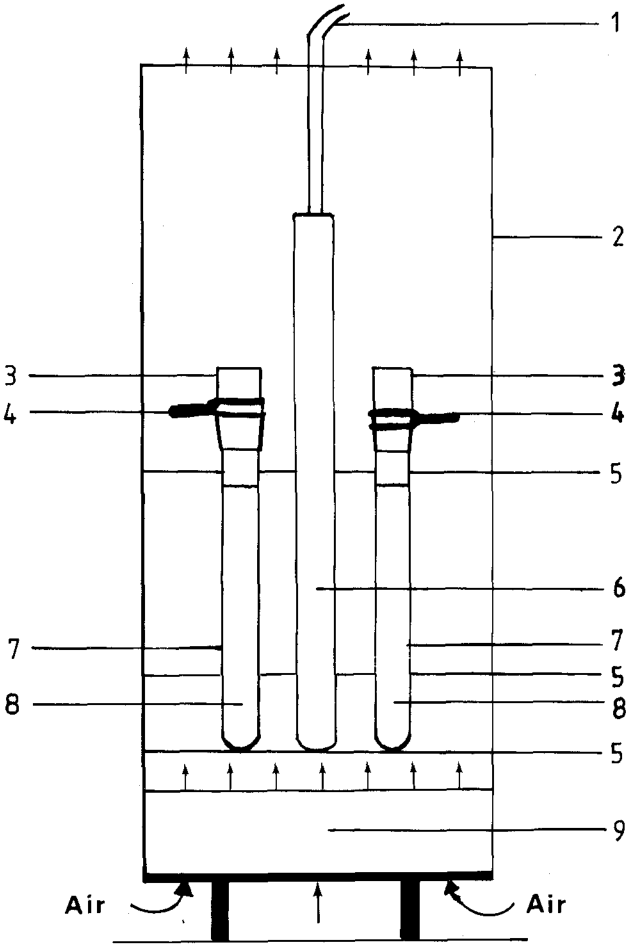

FIGURE 1 Device for UV-irradiation of water samples. 1. Electrical connection. 2. Stainless steel shield. 3. Ground quartz stopper. 4. Teflonized stainless steel spring-clip. 5. Steel-holder. 6. UV-lamp. 7. Quartz tube. 8. Sample solution. 9. Fan.

injection system, AS-1. The absorbance signal was registered on a Perkin-Elmer recorder, model 56.

In the freon method AAS measurements were carried out on a Perkin-Elmer 5000 model equipped with an HGA-400 graphite furnace. For the injections an AS-40 system was utilized. Peak absorbances were recorded by a PRS-10 printer.

All handlings of the samples were carried out in an air-filtered laboratory or in a clean-bench (Holten TL 2448).

PROCEDURE

Differential pulse stripping voltammetry (DPSV)

Prior to voltammetric analysis the sea water sample must be free from dissolved organic substances as they severely disturb the stripping step.[12] Perhydrol was added to the samples and UV-oxidation was performed for three hours. An aliquot was then accurately weighed into the voltammetric cell, and nitrogen gas was purged through the solution for ten minutes. Throughout all measurements the following experimental parameters were kept constant: scan rate $10\,mV\,s^{-1}$, pulse amplitude 50 mV and clock period ("drop time") 0.2 s.

HMDE: The following metals were analysed: Zn, Cd, Pb, Cu, Ni and Co. After out-gasing, the electrodeposition of the metals investigated took place under continuous stirring of the sample solution using a teflon imbedded magnet at a speed of 500 rpm. Unacidified samples were analysed for Zn. The deposition potential was set to $-1.2\,V$ for three minutes using a mercury drop area of $1.9\,mm^2$. After 15 seconds of quiescence the stripping scan was started from the initial potential and was swept to $-0.7\,V$. For Cd, Pb and Cu analysis was carried out on acidified samples, and they were deposited at 0.8 V for 8–15 minutes. The deposition time required depended on the metal concentration of the sample. The area of the mercury drop was $2.3\,mm^2$. Determinations of the blanks were performed using acidified ultrapure water. The determination of Ni was done by a cathodic stripping voltammetric procedure according to Pihlar et al.[13] Cobalt could also be analysed in the same cathodic sweep. Accumulation by adsorption of the $Me(DMG)_2$—complex at the HMDE took place for five minutes.

MFE: Cadmium, lead and copper were determined using an MFE. After the initial removal of oxygen, deaeration of the samples was continuously done through the whole deposition step. The working electrode used was a pyrolytic carbon film electrode,[14] the analytical performance for sea water samples being described elsewhere.[15]

GDE: The gold electrode was fitted to the piston of a Metrohm motor, model 628-10, the polishing and conditioning procedures following those of Golimowski *et al.*[16] The cathodic deposition of Cu was carried out at a potential of -0.2 V for five minutes, and the electrode rotated with a speed of 1500 rpm. The stripping procedure has to be done in a new medium, namely 0.1 M $HClO_4 + 2.5$ mM HCl,[17] and the potential scan started at $+0.1$ V and was swept to $+0.45$ V. The electrode surface was activated at $+1.7$ V for 30 seconds before the next analysis was initiated.

Atomic absorption spectrometry (AAS)

MIBK method: The samples were thermostated to room temperature. Usually no adjustment of pH took place, but if done, the pH was adjusted to 4–5 using either HCl or NaOH. The glass electrode must not be submerged into the sample solution due to the obvious risk of contamination. Therefore, during pH adjustment small sample aliquots were poured into separate beakers where pH was measured.

The MIBK extraction procedure was carried out in 10 ml quartz glass tubes using an IKA VIBRAX shaker (IKA-Werk, West Germany). The tubes were closed with ground stoppers of quartz, which were fixed during shaking by a piece of parafilm.

Amounts of 7 ml for Zn, Cu, Cd and Ni and 8 ml for Co and Pb of the sample solution were transferred to the quartz tubes by a Finnpipette. 300 μl of purified freshly prepared 2% APDC solution were added to each quartz tube. The added volume of MIBK was 1 ml for Zn and Cd and 0.7 ml for Co, Pb, Cu and Ni. The chelation/extraction procedure took place for ten minutes in the shaker. After phase separation the main part of the organic phase was transferred to a teflon cup fitting the sample exchanger of the automatic injection assembly of the atomic absorption spectrophotometer. Throughout, 50 μl were injected each time into the graphite furnace. For Zn determinations the MIBK was directly aspirated from the tube into the flame. The blanks were determined from extractions of ultrapure water, and the standards were prepared from metal stock solutions of appropriate concentrations made daily.

Freon method: The freon method was used to determine Cu, Cd and Pb. The procedure closely resembles the one described by Danielsson *et al.*[18] 200 ml aliquots were extracted into 2 × 20 ml freon by two repeated extractions with the aid of 8 ml of 1% APDC in ammonium acetate buffer. The metal complexes were destroyed with 100 μl of concentrated nitric acid and the metals reextracted into water. The concentration factor was 40. The 0.75 M ammonium acetate buffer, made from glacial acetic acid and 25% ammonia, gave the samples a pH of 4.9.

The buffer-APDC mixture was purified by freon extraction before use. Calibration was made using the method of standard additions directly to the samples in the separatory funnels. For blank determinations 200 ml acidified Milli-Q water was extracted.

RESULTS AND DISCUSSION

Coastal Baltic Sea water samples were collected off the Forsmark nuclear power plant, and the area can be regarded as a typical clean coastal region. The matrix of the samples can be considered to be constant as the salinity (5.5‰) does not vary to any particular extent. The concentrations were calculated by means of linear regression using two standard additions and with duplicate measurements made at each concentration level. At least two aliquots of each sample were analysed.

In Tables I–V the results with ranges are given. The tables also contain blank values if the metal in question was detected in the blank.

Cadmium

The cadmium concentration in unpolluted regions of the Baltic is about 5.10^{-10} M. Four different analytical performances were carried out, and they are summarized in Table I.

TABLE I

The concentration of Cd in two Baltic Sea water samples collected off the Forsmark nuclear power plant in 1982.

	Flameless AAS				DPASV			
	APDC/MIBK		APDC/Freon		HMDE		MFE	
Deep m	mean	range nM	mean	range nM	mean	range nM	mean	range nM
0.5	0.37	0.36–0.38	0.52	0.49–0.55	0.35	0.33–0.36	0.36	0.31–0.40
0.5[a]	0.58	0.57–0.59						
6	0.53	0.47–0.59	0.50	0.47–0.53	0.44	0.40–0.48	0.46	0.44–0.48
6[a]	0.59	0.58–0.60						
Blank	0.018		0.018		n.d.[b]		n.d.	

[a] pH adjustment to 4.5 using suprapure NaOH.

[b] n.d.—not detected.

The APDC/MIBK extractions are done either after pH-adjustment to pH 4.5 with NaOH or directly on acidified samples (pH 2.3). Sodium hydroxide, even of suprapure grade, is a latent contaminant as it usually contains traces of impurities. The results obtained after pH-adjustment are somewhat higher, which indicates a contamination originating from the NaOH. Therefore the chelation/extraction procedure should be employed directly on the acidified samples. The APDC/freon method gave a 40% higher value for the surface water than the other three techniques, but for the 6 m sample the results from all four methods agree well. Nevertheless, considering the concentration levels under investigation a disparity of 40% is quite tolerable. Consequently all four analytical performances can be applied to Baltic Sea water samples, even if the voltammetric method using the mercury film electrode is more preferable as it is time-saving and also has a better detection limit, enabling concentrations down to 0.5 ng/l to be determined with a precision of 20% RSD.[8]

Lead

Lead was determined with the same techniques as cadmium.

Spurious results are often obtained as lead is difficult to determine.[1] Elevated values are mostly due to airborne contamination. Of all metals analysed in this study, lead shows the greatest divergences between the methods. In Table II the concentrations determined differ maximally by a factor of 2. The divergence between analytical methods used for the same samples is usually much greater.[9, 11] Therefore the results are in acceptable agreement, and the four methods investigated are suitable for Baltic Sea water samples. As in the case of Cd, the DPASV-MFE mode is more sensitive and time-saving. The voltammetric techniques also possess the advantage of determining both metals in the same potential sweep. The blank value obtained using the APDC/MIBK system was somewhat high, which illustrates the risk of getting the samples contaminated.

TABLE II

The concentration of Pb in two Baltic Sea water samples collected off the Forsmark nuclear power plant in 1982.

	Flameless AAS				DPASV			
	APDC/MIBK		APDC/Freon		HMDE		MFE	
Deep m	mean nM	range nM	mean nM	range nM	mean nM	range nM	mean nM	range nM
0.5	0.73	0.68–0.77	0.48	—[a]	0.87	0.77–0.97	0.73	0.68–0.77
6	1.16	1.16–1.16	0.63	0.62–0.64	0.73	0.68–0.77	0.96	0.87–1.01
Blank	0.097		0.024		n.d.[b]		n.d.	

[a] Only one aliquot analysed.
[b] n.d.—not detected.

Copper

The determination of copper was carried out on the 1982 samples with four analytical techniques, and the 1983 sample was analysed with three methods. One of these used the rotating gold disc electrode (GDE) as working electrode. The results for copper are given in Table III, and a typical voltammogram using the GDE is shown in Figure 2. A better residual current is achieved with GDE than with the two types of mercury electrodes since these electrodes

TABLE III

The concentration of Cu in three Baltic Sea water samples collected off the Forsmark nuclear power plant in 1982/83.

		Flameless AAS				DPASV					
		APDC/MIBK		APDC/Freon		HMDE		MFE		GDE	
Date	Deep m	mean nM	range nM	mean nM	range nM	mean nM	range nM	mean nM	range nM	mean nM	range nM
3.6.82	0.5	18.7	17.5–19.8	16.5	16.1–16.9	19.8	19.2–20.5	14.0	13.7–14.3		
3.6.82	6	21.1	20.9–21.3	17.0	16.7–17.3	21.1	20.2–22.0	18.0	17.6–18.3		
23.3.83	0.5	36.7	35.6–37.6			33.8	32.3–35.6			33.3	32.9–33.5
Blank		1.9		1.6		n.d.[a]		n.d.		n.d.	

[a] n.d.—not detected.

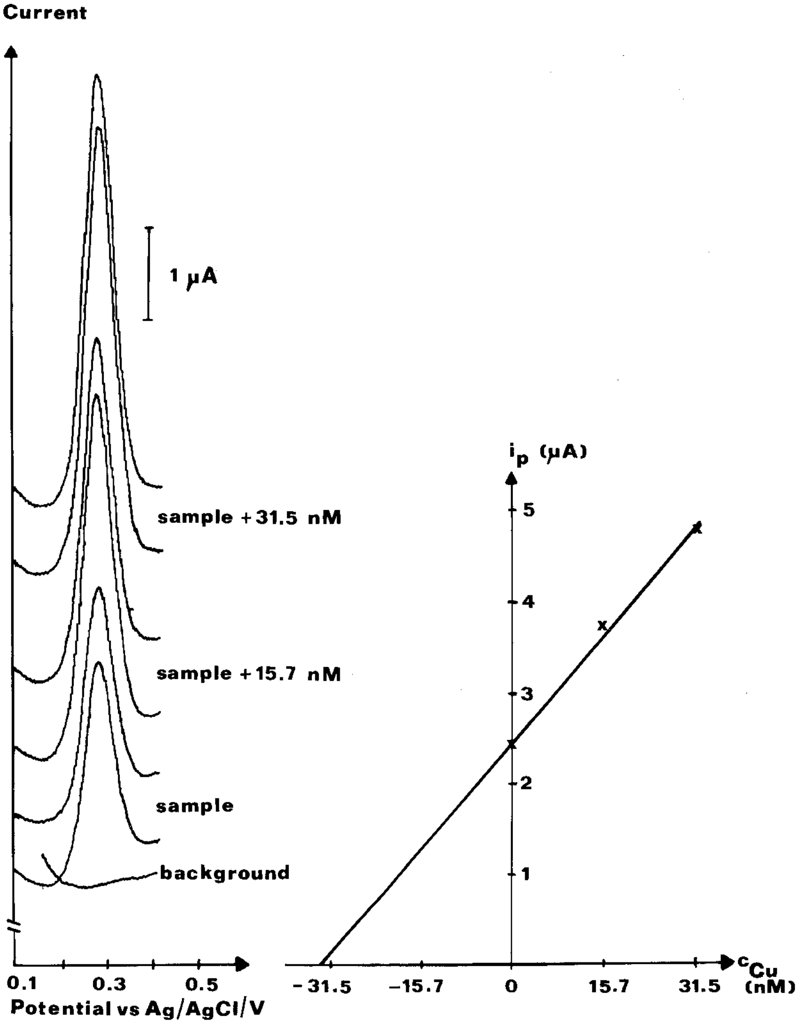

FIGURE 2 Voltammograms for Cu of a Baltic Sea water sample using DPASV-GDE and the standard addition curve of the sample.

give a sloping background which may cause problems when the voltammograms are evaluated for unknown concentrations. The HMDE method is applicable, even if the peaks of Cu and Hg coalesce somewhat. Nevertheless, the residual current can be estimated by stripping after deposition for two seconds. Formation of intermetallic compounds in connection with low solubility of copper in mercury gives distorted and irreproducible peaks using MFE.[19] Consequently, the use of MFE for copper determination should be avoided. The two AAS methods and the HMDE used on the 1982 samples gave similar results. Good agreement was also obtained on the 1983 sample with AAS using APDC/MIBK and the voltammetric techniques with both HMDE and GDE. Thus four of the analytical performances can be used for Baltic Sea water samples. The DPASV-GDE method has the benefit of being more time-saving.

Zinc

Zinc is probably the most difficult metal to analyse as it is a ubiquitous metal, and consequently usage of several chemicals and much handling of a sample invoke questionable results, as can be seen from the blank values in Table IV. Thus, the AAS method using the APDC/MIBK system gave a blank value half of that in the authentic samples. The flame was employed in the AAS measurements, since attempts using the flameless mode were unsuccessful because of non-reproducible absorbance peaks. The

TABLE IV

The concentration of Zn in a Baltic Sea water sample collected off the Forsmark nuclear power plant in 1983.

	Flame-AAS APDC/MIBK		DPASV HMDE	
Deep m	mean nM	range	mean nM	range
0.5	45.9	38.2–58.2	39.8	29.1–46.8
Blank	27.5 ± 0.5		4.6 ± 0.5	

major part of the zinc in the blank arises from the APDC solution. For the voltammetric method using HMDE the blank value was much lower, approximately 10% of the concentration in the sample. The blank solution consisted of a 5‰ NaCl solution, which worked as supporting electrolyte as acidified water could not be used because of the evolution of hydrogen.

Nickel

Nickel determinations were carried out with the APDC/MIBK system and with the DPCSV-HMDE technique.[20] The results are given in Table V. The concentrations obtained are higher with atomic absorption than with stripping voltammetry. The difference is less than 30%, which can be regarded as satisfactory. The blank does not contain any significant concentration of nickel, so this cannot explain the higher value for AAS. The voltammetric method is far more sensitive, and a low blank value could be demonstrated. The DPCSV-HMDE is therefore superior to the AAS method.

Cobalt

Cobalt is an essential metal for many organisms as it exists in the vitamin B_{12}, cobalamin. The concentration in natural waters is very low, $10^{-9}-10^{-10}$ M. The atomic absorption method used failed to

TABLE V

The concentration of Ni and Co in a Baltic Sea water sample collected off the Forsmark nuclear power plant in 1983.

	Flameless AAS APDC/MIBK			DPCSV HMDE			
	Ni		Co	Ni		Co	
Deep m	mean nM	range nM	mean nM	mean nM	range nM	mean nM	range nM
0.5	24.0	22.8–25.2	n.d[a]	18.7	16.8–21.2	0.50	0.48–0.52
Blank	n.d		n.d.	1.0		n.d	

[a] n.d.—not detected.

detect any cobalt in the Baltic Sea water sample (Table V). The stripping technique with prior accumulation of Co $(DMG)_2$ to the hanging mercury drop can be employed for quantitative determination. Cobalt is then determined simultaneously with nickel, and a typical voltammogram is displayed in Figure 3. The method has been used for cobalt analysis in sea water by Mart *et al.*[20] There is a difference of almost two orders of magnitude between the concentrations of Ni and Co, but despite that, peak separation is good enough to make detection of Co possible. However, a more sensitive current range has to be used, as depicted in Figure 3b.

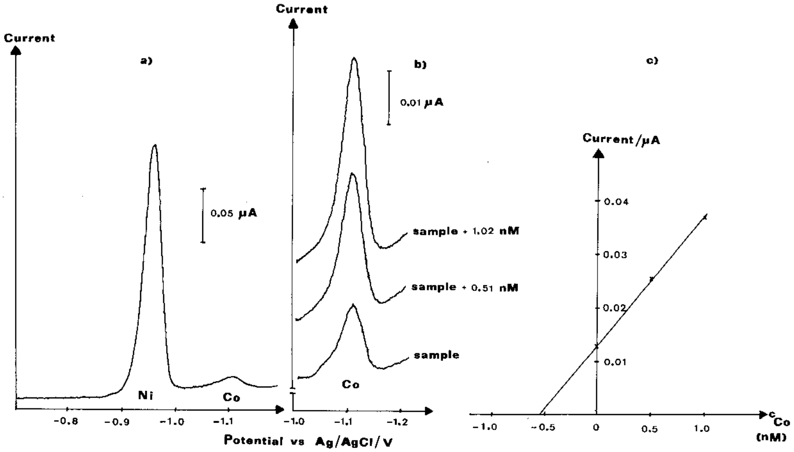

FIGURE 3 Voltammograms for Ni and Co of a Baltic Sea water sample using DPCSV-HMDE. (a) Ni and Co (b) Co (c) standard addition curve.

Comparison of analytical methods used

The most common method used for trace element analysis of sea water is the flameless atomic absorption spectrometry using the APDC/MIBK system for preconcentration. The chelation/extraction procedure is suitable for many transition metals. The injection of the MIBK phase into the graphite furnace has to be undertaken shortly after phase separation as many of dithiocarbamate complexes are not stable for any length of time. This problem can be circumvented if the metal chelates in the organic phase are decomposed by acid and back-extracted into an aqueous phase.[18,21,22] An additional preconcentration of the metals can then be achieved. Usually a great many samples have to be analysed in oceanographic investigations, which creates a storage problem. The second AAS method in our investigation employing the APDC/freon system was designed with this in mind as it makes the method superior to the APDC/MIBK system, even though it requires larger sample volumes. The major drawback of all AAS determinations applied to sea water samples concerns the numerous chemicals needed as they are latent sources of contaminants.

Voltammetric stripping techniques possess many advantages compared to the atomic absorption methods. Not only are they simpler, only one or two reagents need to be added, but the procedures are also time-saving. The instrumentation required is inexpensive in comparison with the equipment for AAS measurements. Stripping voltammetry can be used to determine the metals Zn, Cd, Pb, Cu, Ni, Co in natural waters and in some cases also Bi, Se, As and Hg. The AAS method can be used for a greater number of elements. Prior to stripping analysis the sample needs only to be UV-irradiated.

For both AAS and DPSV the metal concentrations have been evaluated by means of the standard addition method. The practical procedure of this technique for AAS measurements differs from that in DPSV determinations. In the AAS methods the sample is split up into separate quartz tubes or separatory funnels, and standards are added to separate tubes or vessels. In the voltammetric technique the additions are done stepwise into the same sample solution. Considered in this light, the stripping voltammetry is preferable.

CONCLUSIONS

The heavy metal concentrations found in the region off Forsmark nuclear power plant can be regarded as typical for clean Swedish coastal waters at the Baltic.[23] The atomic absorption methods using both the APDC/MIBK system or the APDC/freon with subsequent back-extraction procedure, are suitable for heavy metal analysis of sea water samples provided that all precautions are taken to prevent contaminants from entering during the analytical procedure. The stripping voltammetry is a more favourable method for Zn, Cd, Pb, Cu, Ni and Co than the AAS technique for trace metal analysis, and the DPSV method should be chosen if possible as it implies less handling of samples, is time-saving and requires relatively inexpensive instrumentation.

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