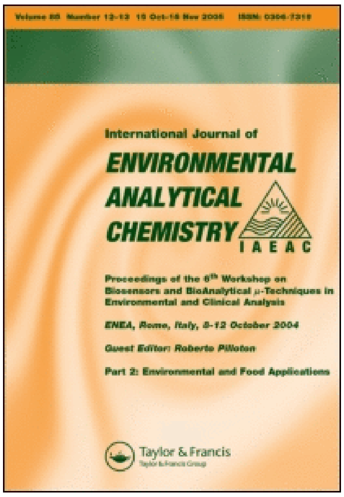

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Drabæk, I. , Madsen, P. Pheiffer and Sørensen, J.(1983) 'Analysis of Sea Water by Potentiometric Stripping Analysis', International Journal of Environmental Analytical Chemistry, 15: 3, 153 — 163
To link to this Article: DOI: 10.1080/03067318308071915
URL: http://dx.doi.org/10.1080/03067318308071915

Intern. J. Environ. Anal. Chem., 1983, Vol. 15, pp. 153–163
0306-7319/83/1503-0153 $18.50/0

Printed in Great Britain

Analysis of Sea Water by Potentiometric Stripping Analysis

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(*Received January 18, 1983*)

The application of potentiometric stripping analysis to sea water for the determination of Pb, Cd and Zn has been demonstrated.

The precision was evaluated by several duplicate determinations and was found to be in the range of 5–16% relative, depending on the concentration level. The accuracy of the method was evaluated by comparison with other conventional methods, i.e., atomic absorption spectroscopy and anodic stripping voltammetry, and good agreement was found. Where statistical comparisons could be performed between the methods, no significant difference was found.

KEY WORDS: Analysis, seawater, potentiometric stripping, precision, accuracy, atomic absorption, anodic stripping voltammetry, comparison.

INTRODUCTION

Recently, a new electrochemical method for the determination of Pb, Cd, Zn and Cu has been introduced: potentiometric stripping analysis (PSA), e.g.[1,2] In some ways PSA resembles anodic stripping voltammetry (ASV). The analytical device is based on a 3-electrode system: (1) a glassy carbon electrode (serves as cathode), (2) a saturated calomel electrode (SCE), (which is the reference electrode) and (3) the counter electrode during electrolysis made of platinum.

Analysis of metal ions in a sample solution is started by electrochemical formation of a mercury film on the glassy carbon electrode. Subsequently, the metal ions are reduced and amalgamated in the mercury film during the electrolysis step (plating). When the plating is terminated, the metals are stripped from the mercury film back into the solution by chemical oxidation. During this step the potential of the carbon electrode (against SCE) versus time is recorded. The metals are identified by their stripping potentials and the quantitative determination is obtained by measuring the stripping time for each metal.

Until now, only a limited number of publications concerning the application of the PSA method have appeared. The sample matrices have been sea water,[3] blood and serum,[4] mussel and bovine liver.[5]

At the Danish Isotope Centre (DIC), the method has been used on a routine basis for 2–3 years. Sea water and sediments have been the matrices. The work on sediments is described elsewhere,[6] and the present paper deals exclusively with the experiences obtained in the analysis of sea water.

EXPERIMENTAL

Instrumentation

The basis of the instrumentation is provided by the Radiometer ISS820 Ion Scanning System consisting of an REA120 Ion Scanning Module plugged into an REC80 Servograph and a TTA80-IS Titration Cell Assembly. Three Radiometer standard electrodes are used, i.e., glassy carbon F3500, SCE K4040 and Pt P1312. The entire system is thoroughly described in several references (e.g., refs. [7,8]). All the instrumentation is placed in a clean bench ensuring laminar flow of HEPA filtered air over the working area.

Chemicals

All chemicals used are of Analytical Grade except sodium acetate and the mineral acids which are of Suprapure Grade (Merck). Commercial stock solutions for atomic absorption spectroscopy (Merck/BDH) are used as standards.

Samples

Sea water samples were filtered (0.45 μm) and acidified with 3 ml/l of conc. HNO_3 (Merck Suprapure) immediately after sampling.

Analytical procedure for determination of Cd and Pb in sea water

25 ml of the acidified sea water is placed in the analyzer. A Hg(II) solution, usually 100 μl of a solution containing 1000 ppm Hg, but depending on the metal concentration, is added together with an internal standard (Cu).

To increase precision, especially at the lower concentration levels encountered in relatively non-polluted sea water, preparation, regeneration and precoating of the working electrode are carried out prior to each analysis. Likewise, adequate cleaning of all the equipment is a prerequisite. With respect to plating, a normal procedure using 10 precoating-stripping cycles is employed.[2] Simultaneously, the sample is deaerated by purging with helium.

After precoating and deaeration of the sample, analysis is performed at −0.95 V vs SCE with an appropriate plating time (1–32 min). The method of standard addition is used. Analysis is performed in a cyclic mode and standards are added immediately after recording the stripping curve.

Analytical procedure for determination of Zn in sea water

Prior to plating, the same analytical steps as for Cd and Pb analysis are applied, the only exception being the use of Pb instead of Cu as the internal standard. Furthermore, gallium and sodium acetate are added, the former to prevent the formation of the intermetallic zinc–copper compound and the latter to adjust pH to 4.7 which is favourable for Zn determination. Plating is carried out at −1.25 V vs SCE. Again the method of standard addition is applied.

RESULTS AND DISCUSSION

A large number of sea water samples from different locations in an arctic marine area has been analyzed. In this area tailings from a lead–zinc mine are discharged. It should therefore be noticed that some of the results presented below greatly exceed concentrations for normal, uncontaminated sea water. However, the wide range of measured concentrations provides a beneficial background for investigation of the analytical method.

Determination of Cd, Pb and Zn in sea water

In Figures 1 and 2 are shown typical stripping curves for Cd, Pb and Zn obtained from a 25-ml sea water sample. The sample was analyzed as previously described. The concentrations found were: Pb(II), 7.1 μg/l; Cd(II), 0.2 μg/l and Zn(II), 4.1 μg/l. Internal standard to correct for variations in oxidation rate was applied in the analyses (Cu in Figure 1 and Pb in Figure 2) and is clearly warranted, the corrections amounting to 7%. The precision of the method was estimated by several duplicate determinations on different samples. The results are shown in Table I.

The detection limit in potentiometric stripping analysis depends on the plating time, the Hg(II) concentration and the speed of the recorder. No ultimate detection limit can be defined, but obviously the decrease in precision at lower concentration levels indicates the approach of a practical detection limit for our system.

The relatively high decrease in precision for Pb (i.e., 5.2% to 16.5%; cf. Table I) stems from the fact that the pairs used for the estimation of the precision in the concentration range 1–15 μg/l are all grouped in the lower end of the interval (mean = 3.5 μg/l).

The accuracy of the potentiometric stripping analysis was investigated by comparison with other conventional techniques, i.e., atomic absorption spectroscopy (AAS) and anodic stripping voltammetry (ASV). In order to make statistical tests on the results (i.e., a paired *t*-test) the standard deviations on single determinations for each population of results must be assumed equal. This is clearly not fulfilled as far as the absolute standard deviation (cf. Table I) is concerned. However, the assumption that the relative standard deviations are equal seems more reasonable. The criterion of the constant standard deviation can then be satisfied by a logarithmic transformation of the data. The comparisons were made on both identical samples (comparison with AAS) and parallel samples

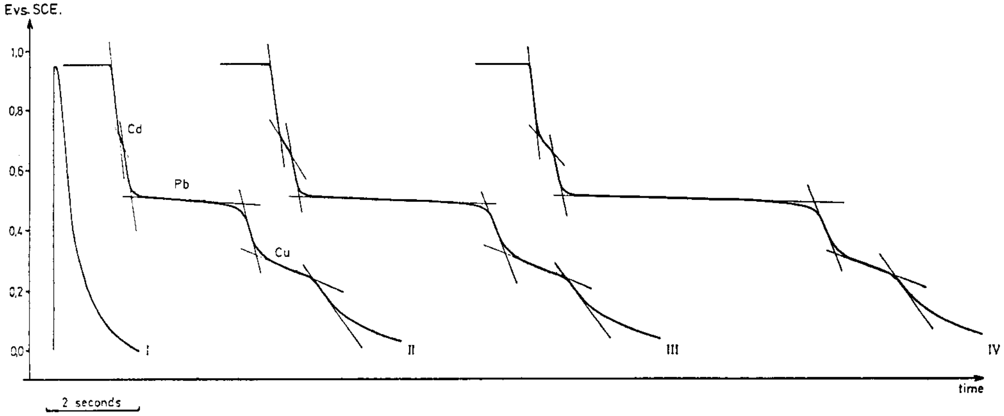

FIGURE 1. Potentiometric stripping curve for a 25-ml sea water sample. I = background, II = curve before standard addition, III and IV = curve after each addition of 5 ng Cd(II) and 100 ng Pb(II). 25 ng Cu(II) was used as internal standard. Plating time 32 min at −95 V vs. SCE.

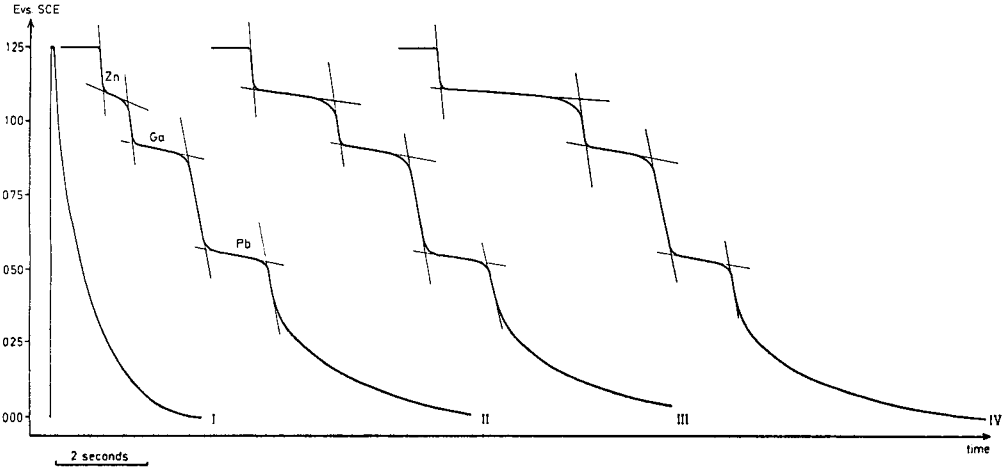

FIGURE 2. Potentiometric stripping curve for a 25-ml sea water sample. I = background, II = curve before standard addition, III and IV = curve after each addition of 250 ng Zn(II). 250 ng Pb was used as internal standard and 250 ng Ga(II) was added as a Cu(II) scavenger. Plating time 16 min at −1.25 V vs. SCE.

TABLE I

Relative precision (in %) of the potentiometric stripping analysis.[a]

Concentration level	Pb	Cd	Zn
>15 µg/l	5.2 (19)	—	4.7 (20)
1–15 µg/l	16.5 (13)	6.3 (11)	9.4 (15)
0.1–1 µg/l	—	10.3 (5)	—
0.03–0.1 µg/l	—	16.0 (7)	—

[a] Relative precision estimated from several duplicate determinations. Numbers in parentheses denote numbers of pairs used for the estimation.

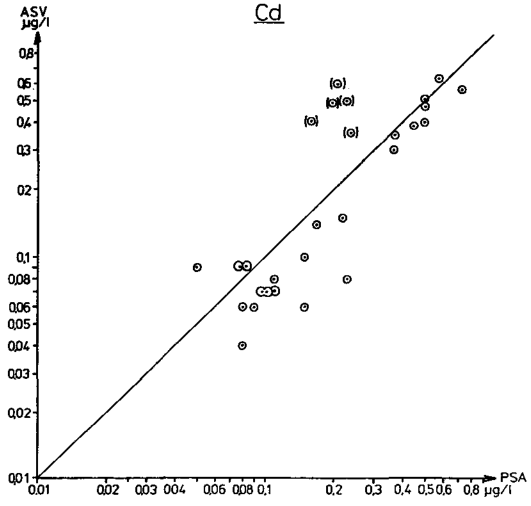

FIGURE 3. Comparison between results obtained by anodic stripping voltammetry and potentiometric stripping anslysis on parallel sea water samples.

Results enclosed in parentheses are suspected to be wrong.

Cd: $\bar{d} = \log x - \log y = 0.489$ $S_{\bar{d}} = 0.130$.

(comparison with ASV). The results are reproduced in a log–log delineation in Figures 3–8.

Our hypothesis is that the difference between the results obtained

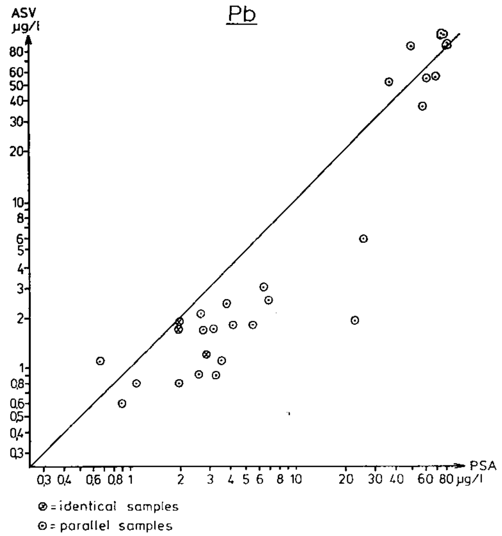

FIGURE 4. Comparison between results obtained by anodic stripping voltammetry and potentiometric stripping analysis on parallel sea water samples.

Pb: $\bar{d}=\overline{\log x-\log y}=0.066$ $S_{\bar{d}}=0.100$.

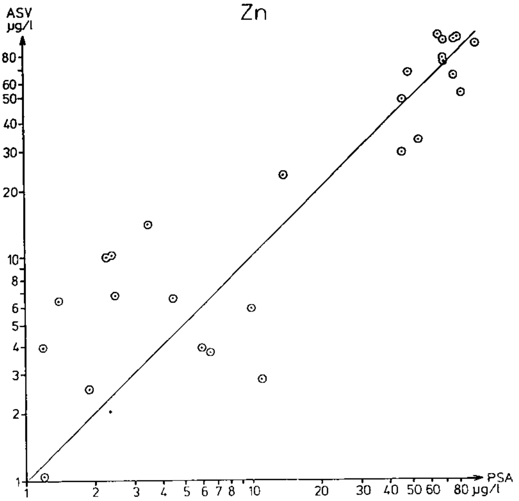

FIGURE 5. Comparison between results obtained by anodic stripping voltammetry and potentiometric stripping analysis on parallel sea water samples.

Zn: $\bar{d}=\overline{\log x-\log y}=-0.144$ $S_{\bar{d}}=0.143$.

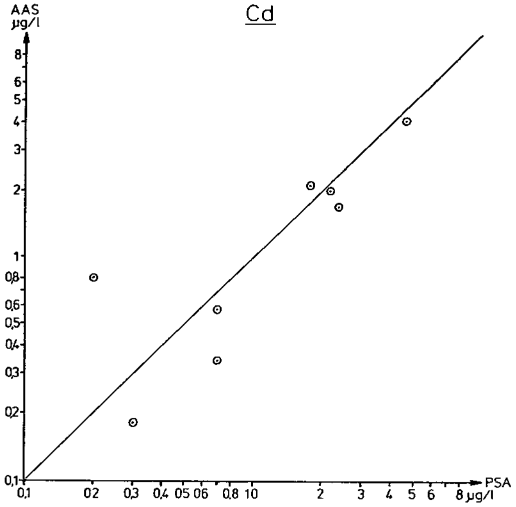

FIGURE 6. Comparison between results obtained by atomic absorption spectroscopy and potentiometric stripping analysis on identical sea water samples.

Cd: $\bar{d} = \overline{\log x - \log y} = 0.059$ $S_{\bar{d}} = 0.227$.

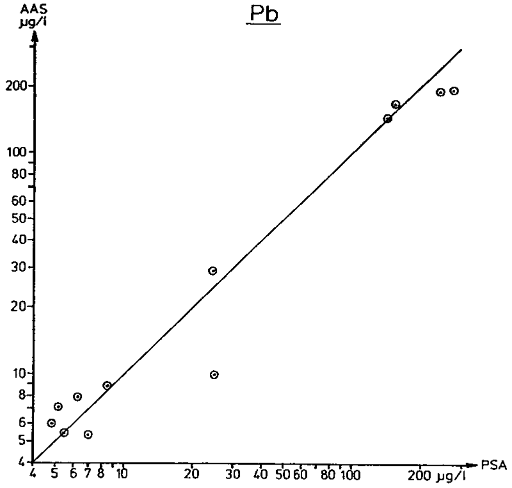

FIGURE 7. Comparison between results obtained by atomic absorption spectroscopy and potentiometric stripping analysis on identical sea water samples.

Pb: $\bar{d} = \overline{\log x - \log y} = 0.068$ $S_{\bar{d}} = 0.097$.

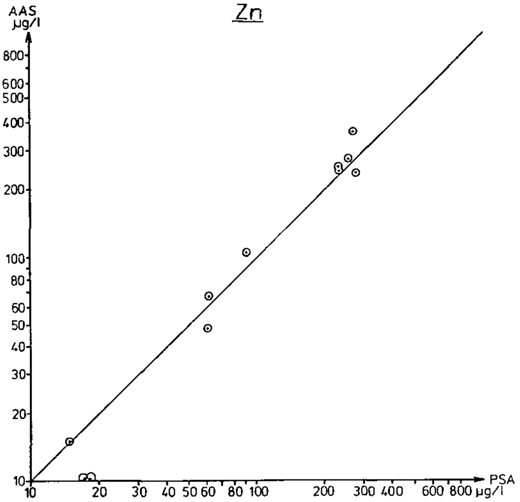

FIGURE 8. Comparison between results obtained by atomic absorption spectroscopy and potentiometric stripping analysis on identical sea water samples.
Zn: $\bar{d} = \log x - \log y = 0.093$ $S_{\bar{d}} = 0.111$.

by the different methods might be assumed to be zero, i.e., the methods produce the same results on identical samples. This can be tested using a paired t-test, the test parameter being the mean difference between the logarithmized analysis results, $\bar{d}$, weighted with the estimated standard deviation on this mean difference, $S_{\bar{d}}$. The test parameter follows a t-distribution with $n-1$ degrees of freedom, n being the number of samples. The values of the mean differences of the logarithmized data are shown in Table II. For the comparisons made on identical samples (PSA vs AAS), the test parameter is shown (cf. Figures 6–8). According to the fractiles in the t-distribution, the hypothesis that the PSA and the AAS will give the same results can be accepted for Zn, Cd and Pb on at least a 40%, 80% and 40% significance level, respectively.

For the comparisons between PSA and ASV on parallel samples, no test was performed because variations in metal contents between the parallel samples also contribute to the estimated standard deviation on the mean difference. In fact this is clearly seen in Figures 3–5, the dispersion around the line $x = y$ obviously being greater than the ones illustrated in Figures 6–8. Part of this can be

TABLE II

Comparison of PSA and ASV or AAS on sea water samples.[a]

Element	Methods	n	$\bar{d}=\overline{\log x}-\overline{\log y}$	$S_{\bar{d}}$	$T=\bar{d}/S_{\bar{d}}$
Cd	PSA/ASV	28	0.066	0.100	
Pb	PSA/ASV	28	0.489	0.130	
Zn	PSA/ASV	27	−0.144	0.143	
Cd	PSA/AAS	8	0.059	0.227	0.2599
Pb	PSA/AAS	12	0.068	0.097	0.6993
Zn	PSA/AAS	11	0.093	0.111	0.8229

[a] n is number of analyses; x is PSA results; y is ASV or AAS results; S_d is standard deviation of $\bar{d}$, and T is test parameter for the paired t-test.

explained by the low concentrations encountered in this comparison, which decreases the precision of the analysis results. Generally, bearing in mind the former and the fact of the possible contamination risk when dealing with parallel samples, a fairly good agreement can be said to be seen.

The PSA results for Pb seem to be systematically higher than the ASV results (Figure 4). This tendency has previously been reported as a possible Sn(IV) interference[3] although the three results of ours obtained on identical samples (Figure 4) and the satisfactory agreement in Figure 7, also on identical samples, support the hypothesis that contamination is the main cause of the deviating results.

Occasionally, when determining Zn by the PSA method, a shift in stripping potential is observed, causing a faulty result. The reason for this has not yet been fully recognized, but probably an unidentified substance complexing with the Zn(II) is the main cause. The problem is partly alleviated by using all-glass equipment.

CONCLUSIONS

It has been shown that potentiometric stripping analysis provides a simple instrumental approach to accurate and precise determination of Cd, Pb and Zn in sea water. One of the major advantages of potentiometric stripping analysis is the simple instrumentation required and the straightforward result calculation. The minimization of sample treatment also makes this form of analysis very suitable for trace element determination.

Acknowledgement

The authors wish to thank K. Pedersen (GREENEX) for kindly making the results of sea water analysis performed by the Danish Isotope Centre and the Danish Water Quality Institute available.

We further wish to thank G. Asmund (Geological Survey of Greenland) for providing the anodic stripping voltammetry results.

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