



DETERMINATION OF CADMIUM AND LEAD IN THE LOW NG/L RANGE BY STRIPPING POTENTIOMETRY EMPLOYING MEDIUM EXCHANGE IN BATCH MODE AND MULTIPLE STRIPPING IN A HANGING STRIPPING MEDIUM DROP

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Summary—A novel three-in-one electrode assembly, permitting medium exchange under a controlled potential in batch mode by exploiting electrolytic conductance through a drop hanging under the electrode, has been used for the simultaneous determination of cadmium(II) and lead(II) at trace levels. Potentiostatic reduction and amalgamation of these ions are carried out in the sample and the subsequent stripping, in the stripping potentiometry mode, in a drop of a suitable medium. Several such media have been investigated, a mixture of 2.5*M* acetic acid and 7.5*M* ammonium acetate having been found to be the most suitable with respect to sensitivity, potential resolution and trace metal purity. The quiescent conditions in the drop of medium facilitated multiple stripping and thus increased sensitivity. Detection limits for cadmium(II) and lead(II) were found to be around 0.5 ng/l. (5 and 2.5*pM*) for an electrolysis time of 10 min. The relative precision at the concentration level 20 ng/l. was 6.4% for cadmium and 5.4% for lead. The procedure has been used for the determination of cadmium(II) and lead(II) in reference seawater samples.

A major advantage of electrochemical stripping techniques is their high sensitivity.¹ This advantage is, however, often counterbalanced by the poor selectivity due to the Nernstian behaviour of the stripping peaks. Since the potentials for the stripping peaks depend on the complexing properties of the stripping medium,² increased separation between two overlapping peaks can often be obtained by suitable choice of this medium. This can be achieved either by adding complexing agents to the sample and then performing the stripping in the sample, or by medium exchange after electrolysis and prior to stripping. The second approach is often preferable since it permits unrestricted choice of the stripping medium, *i.e.*, it is not necessary to take complexing agents, *e.g.*, chloride ions, which may already be present in the sample, into consideration. Obviously, this latter approach is also not affected by trace analyte impurities in the complexing agent(s) exploited, since these are not present during the electrolysis phase of the analysis. This aspect is particularly important in the ultra-trace concentration range.

Medium exchange in electrochemical strip-

ping analysis in batch mode³⁻⁷ has been performed by continuously replacing the sample with the stripping medium, *e.g.*, by using one pump sucking out the sample, and another pump delivering, at the same flow rate, the stripping medium. More frequently flow systems, permitting medium exchange, have been exploited.¹ Apart from being slow, the first batch approach also requires that large volumes of stripping medium are pumped into the sample vessel in order to achieve, *e.g.*, a 99% removal of the sample. To a lesser extent this is also true for the flow system approach. Furthermore, when solutions with different gas solubility are mixed in a flow system, bubbles are frequently formed. These are likely to break the contact between the working, reference and counter electrodes causing spontaneous chemical stripping.

In this article a third approach to medium exchange in stripping analysis is demonstrated. It is based on the use of a novel "three-in-one" electrode which, when lifted out of a solution, leaves a droplet, permitting electrical conductance between the working, reference and

counter electrodes, hanging under it.⁸ Consequently, the electrode can, under potentiostatic control, be moved from the sample solution to the stripping medium. The droplet hanging under the electrode has, moreover, been used for sensitivity enhancement. After immersion in the stripping medium the electrode is lifted out of the solution. In this way quiescent conditions at the working electrode surface are obtained almost instantaneously making multiple stripping, *i.e.*, consecutive oxidation and re-reduction of the analytes, possible.

The high sensitivity methodology described in this article has been applied for the determination of lead(II) and cadmium(II) in seawater.

EXPERIMENTAL

Instrumentation and software

A Radiometer PSU20 combined potentiometric and constant current stripping unit connected to an IBM compatible personal computer was used for all measurements. The real time measurement rate of the stripping unit was 90 kHz and the potential resolution 2 mV. Modification from the standard rate of 30 kHz was made by the instrument manufacturer. A Radiometer SAC80 sample changer and a Radiometer ABU93 triburette was also connected to the system. All equipment was controlled by the personal computer through the Radiometer TAP2 Trace Talk Method Builder and Commander software package. All control of instrumental parameters, including electrolysis potentials and times, stirring rates, stripping current magnitudes and stripping peak integration, calculation of sample concentrations, as well as control of the sample changer and burettes were pre-programmed into the TAP2 program and automatically executed without operator assistance.

Electrode

A Radiometer prototype three-in-one electrode, based on the design described by Jagner and co-workers,⁸ was used for all measurements. A schematic drawing of the electrode assembly is shown in Fig. 1. The electrode had a 3-mm diameter glassy carbon disk as working electrode and Ag/AgCl electrodes in 3M hydrochloric acid as reference and counter electrodes. The inner solution of 3M acid was separated from the working electrode and the sample by means of a solid ionic conductor. The electrode design permitted medium exchange under elec-

trode potential control in batch mode. All potentials referred to below are *vs.* Ag/AgCl in 3M hydrochloric acid.

Cleaning of sample vessels

Prior to use the polyethylene sample vessels were cleaned in 4M hydrochloric acid for one week and then carefully rinsed in Millipore water.

Chemicals

All chemicals used were of analytical grade except the mineral acids which were freshly distilled. Millipore water was used for the preparation of all samples and solutions. The ammonium acetate solution used as stripping medium was prepared by mixing concentrated acetic acid with 25% w/w ammonia to give an acetate concentration equal to 7.5M and an acetic acid concentration equal to 2.5M. The density of the mixture was 1.11 g/ml, pH = 5 and the viscosity 0.01 Pa sec at 25°.

Seawater samples

The seawater reference samples used in this investigation were obtained from the National Research Council of Canada. The samples had been acidified with nitric acid to pH = 1.6 at sampling. Prior to analysis by stripping potentiometry 20 mg/l. of mercury(II) was added to the samples.

Electrolysis and medium exchange

Prior to each measurement a fresh mercury film was pre-plated onto the glassy carbon by

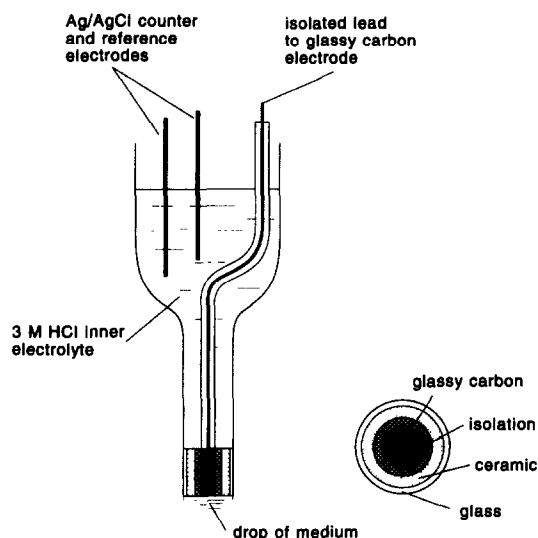


Fig. 1. Schematic drawing of the electrode assembly.

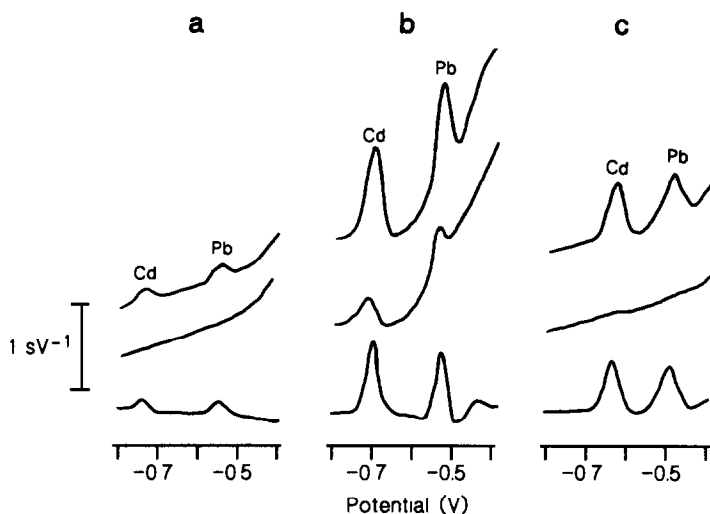


Fig. 2. Stripping potentiometry curves obtained after electrolysis for 10 min in a sample containing 100 ng/l. of cadmium(II) and lead(II) and subsequent stripping in (a) 5M hydrochloric acid, (b) 4M calcium chloride, (c) 2.5M acetic acid/7.5M ammonium acetate, using an oxidative current equal to 1.0 μ A. The upper curves are the stripping signals obtained from the sample, the middle curves those obtained from the background and the lower curves are the background corrected signals.

means of electrolysis for 30 sec at a stirring rate of 1,000 rpm at a potential of -1.20 V in 20 ml of a solution containing 0.10M hydrochloric acid and 200 mg/l. of mercury(II). The sample changer then moved the electrode into the sample (20 ml) at a controlled potential of -0.30 V. Reduction and simultaneous amalgamation of cadmium(II) and lead(II) was performed by a pulsed potential sequence composed of -1.20 V for 29 sec followed by -2.00 V for 1 sec, the latter potential being applied in order to remove species that might have adsorbed onto the electrode surface.⁹ The potential sequence was repeated until the total time of electrolysis was reached after which the sample changer moved the electrode to the stripping solution at a potential of -0.90 V. After stirring at 1,000 rpm for 10 sec the stirrer was stopped for 5 sec, the electrode lifted and stripping, in the pre-chosen potential range, initiated 5 sec later. In the multi-stripping mode the reset potential of -0.90 V was applied immediately after the end of the strip and this potential was kept for 4 sec before the next strip was started. Prior to background measurement the electrode was again immersed in the stripping medium, a potential of -0.30 V was applied for 5 sec at a stirring rate of 1,000 rpm in order to remove the cadmium(II) and lead(II) ions from the vicinity of the electrode surface. The same measurement procedure as that used for measurement of the sample was then applied. Finally the electrode was moved into a

washing solution, standard additions of cadmium(II) and lead(II) were made, either by the syringe burets or manually, and the measurement cycle repeated.

RESULTS AND DISCUSSION

Choice of stripping medium

In order to obtain maximum sensitivity in the determination of lead(II) and cadmium(II) the stripping medium must, of course, be capable of separating the lead and cadmium stripping peaks but, at the same time, also separate these peaks from the copper peak since copper is likely to be present in most samples. Furthermore, the stripping medium should have a high salt content so that the dissolved oxygen concentration is small and the viscosity high resulting in a low chemical stripping rate.¹⁰ Furthermore, the stripping medium should contain a minimum of lead(II) and cadmium(II) impurities. On investigating a large number of electrolytes fulfilling the first two requirements, including alkali metal nitrates, perchlorates, halides and sulphates, it was revealed that these salts did not fulfil the purity requirements. Attempts to purify these salts by means of solvent extraction, ion exchange, co-precipitation and electrolysis on mercury pool cathode did not give satisfactory results considering the extreme purity requirements. It was thus concluded that only reagents which can be prepared

by distillation could be considered as stripping media.

Figure 2(a) shows the sample, the background and the background corrected stripping curves obtained using 5M hydrochloric acid as stripping medium and an oxidative current equal to 1.0 μA . The curves have been obtained by one sample and one background strip subsequent to 10 min of electrolysis in a sample containing 100 ng/l. of cadmium(II) and lead(II), 0.015M hydrochloric acid and 10 mg/l. of mercury(II). Figures 2(b) and (c) shows the stripping curves obtained under the same experimental conditions, the stripping media being 4M calcium chloride and 2.5M acetic acid/7.5M ammonium acetate.

From Figs. 2(a)–(c) it can be seen that the sensitivity for lead(II) and cadmium(II), expressed as msec l./ng, is less in hydrochloric acid than in calcium chloride and acetic acid/ammonia media. This is due to the oxidative contribution of the protons in this highly acidic medium which, of course, also makes the background smaller. From the background stripping curves in these figures it can also be seen that calcium chloride contains significant concentrations of lead(II) and cadmium(II) impurities while this is not the case with the two other media.

From Figs. 2(a)–(c) it is obvious that all stripping media investigated are capable of resolving the cadmium and lead stripping peaks. Their possibility to resolve also the copper stripping peak was investigated by repeating the experiments in Figs. 2(a)–(c) with the exception that 10 $\mu\text{g/l.}$ of copper(II) was added to the sample prior to electrolysis. The background corrected stripping curves thus obtained are shown in Fig. 3, the potential differences between the lead and copper peaks being approximately 150 mV for hydrochloric acid and calcium chloride and approximately 320 mV for acetic acid/ammonia. Consequently the latter is the best suited medium for trace cadmium(II) and lead(II) determinations. From Fig. 3 it can also be seen that the potential for the copper stripping peak is much more negative in chloride-containing media than in acetic acid/ammonia. The reason for this is that in these media copper is oxidised to copper(I) chloride species.

Effect of stripping current

In stripping potentiometry an oxidative stripping process can be achieved either solely by

oxidants, *e.g.*, dissolved oxygen or mercury(II) ions, diffusing towards the electrode or by a combination of this chemical process and an applied oxidative current.¹¹ A third alternative is to apply a reducing current to partly counteract the chemical process and thereby slow down the stripping rate and thus increase the sensitivity. This mode is, however, seldomly used in practice since it normally yields poor precision. Analogously, improved precision is often obtained by combining chemical and constant current stripping. The influence of combined chemical and constant current stripping when using acetic acid/ammonia as stripping medium was studied by electrolysis for 10 min in a sample containing 50 ng/l. of cadmium(II) and lead(II), 0.015M hydrochloric acid and 10 mg/l. of mercury(II). Stripping was then performed with oxidative currents equal to 0, 0.5, 1.0 and 5.0 μA , the precision of the current being $\pm 0.05 \mu\text{A}$. The background corrected stripping curves thus obtained are shown in Fig. 4. From these curves the contribution of the chemical oxidation component in the stripping process, caused by the diffusion controlled flow of oxidants (predominantly dissolved oxygen) to the electrode surface, can be determined and expressed in μA . Denoting this current i and plotting α vs. the (stripping signal)⁻¹, where α is the applied oxidative current, a chemical stripping current equal to 0.52 μA was obtained from the intercept. No significant difference was

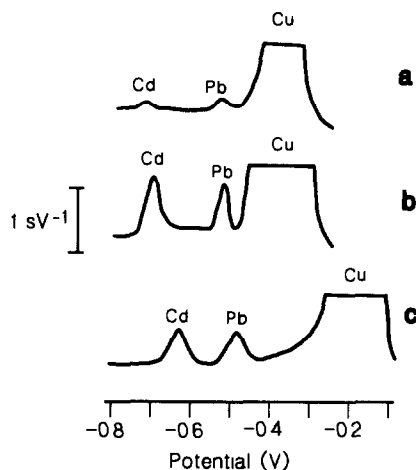


Fig. 3. Background corrected stripping potentiometry curves obtained after electrolysis for 10 min in a sample containing 100 ng/l. of cadmium(II) and lead(II) and 10 $\mu\text{g/l.}$ of copper(II) and subsequent stripping in (a) 5M hydrochloric acid, (b) 4M calcium chloride, (c) 2.5M acetic acid/7.5M ammonium acetate using a constant current equal to 1.0 μA .

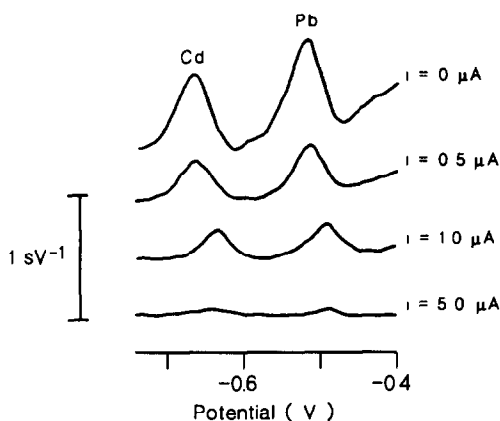


Fig. 4. Background corrected stripping potentiometry curves obtained after electrolysis for 10 min in a sample containing 50 ng/l. of cadmium(II) and lead(II) and subsequent stripping in 2.5M acetic acid/7.5M ammonium acetate using four different oxidative currents.

obtained between the results for lead and cadmium.

By repeating the experiments shown in Fig. 4 it became apparent that the best precision was obtained with stripping currents equal to 1.0 and 5.0 μA . An oxidative current equal to 1.0 μA was thus chosen as an optimum compromise between precision and sensitivity in the analytical applications below. When using this current, approximately two thirds of the electrons involved in the oxidation of the amalgamated metals emanate from the applied current and the rest from the chemical stripping process.

Multiple stripping

Increased sensitivity in stripping potentiometry, *i.e.*, an increased stripping time per ng/l. of the element(s) studied, can be achieved either by increasing the electrolysis time or by applying a multiple stripping procedure. In the latter case the oxidised elements should be, preferably quantitatively, re-reduced and simultaneously amalgamated immediately after an oxidative strip. Then another strip can be initiated and the results from several strips accumulated in the analyser.¹¹ Obviously quantitative re-amalgamation can be achieved only if the oxidised elements remain in the immediate vicinity of the electrode surface after a strip. One prerequisite for achieving this is that the solution surrounding the electrode is quiescent. In this respect the stripping medium drop, hanging under the electrode, is almost ideal since convection in this drop stops almost immediately after the electrode is taken out of the bulk of the solution.

Another prerequisite is that the oxidised species do not diffuse away from the electrode surface. Consequently, a stripping medium with a high viscosity, as the acetic acid/ammonium acetate solution used in this investigation, is desirable.

Since the multiple stripping procedure does not compensate for the noise due to imperfections in the A/D converter it is desirable to use background corrected curves. The accumulated background curves have the same A/D converter noise as the accumulated sample curves and, therefore, background subtraction eliminates this noise resulting in lower detection limits.

In order to investigate the efficiency of re-amalgamation in multiple stripping, a sample containing 100 ng/l. of cadmium(II) and lead(II), 0.015M hydrochloric acid and 10 mg/l. of mercury(II) was electrolysed for five minutes prior to stripping in acetic acid/ammonia solution. Stripping was achieved in the potential range -0.90 to -0.35 V with oxidative currents equal to 1 or 5 μA . The accumulated results from 1, 5, 10 and 20 stripping/re-amalgamation procedures were registered. Also the time for re-amalgamation, *i.e.*, the time of electrolysis at -0.90 V prior to the next strip, was varied as 0.25, 1 and 4 sec.

The average re-amalgamation efficiency, f , obtained after N strips was calculated for $N = 5, 10$ and 20 as

$$S_N = S_1 \sum_{j=0}^{N-1} f^j \quad (1)$$

where S_N denotes the accumulated signal after N strips and S_1 the stripping signal obtained after the first strip. The results are summarised in Table 1. From this it can be seen that the most critical parameter is the time for potentiostatic re-amalgamation. It can also be seen that the magnitude of the stripping current is of less importance for the re-amalgamation efficiency. As expected the efficiency for lead is slightly higher than that for cadmium since the cadmium(II) ions diffuse away from the electrode surface while lead is being stripped. From a practical point of view this difference is negligible. From the data in Table 1 it was decided to use eight strips, each with a re-amalgamation time of 4 sec, in the multi-stripping applications below. Since the background correction is not perfect it was also decided to use only seven background strips in order to avoid occasional over-correction.

Table 1. Re-amalgamation efficiency

No. of strips <i>N</i>	Stripping current μA	Re-amalgamation time sec	Stripping time for the first strip S_1 , cf. Eqn. (1) msec		Accumulated stripping signal, S_N , cf. Eqn. (1) msec		Average re-amalgamation efficiency, f , in each strip according to Eqn. (1)	
			Cd	Pb	Cd	Pb	Cd	Pb
			5	1.0	0.25	13.4	13.9	39.9
10	1.0	0.25	13.4	13.9	62.7	74.0	0.81	0.85
20	1.0	0.25	13.4	13.9	98.5	118.4	0.87	0.90
5	1.0	1.00	13.4	13.9	49.8	51.2	0.85	0.85
10	1.0	1.00	13.4	13.9	76.8	81.4	0.87	0.87
20	1.0	1.00	13.4	13.9	119.2	140.7	0.90	0.92
5	1.0	4.00	13.4	13.9	54.6	56.9	0.90	0.90
10	1.0	4.00	13.4	13.9	89.4	97.7	0.91	0.92
20	1.0	4.00	13.4	13.9	144.1	160.6	0.93	0.94
5	5.0	1.00	4.0	4.1	14.0	13.9	0.82	0.80
10	5.0	1.00	4.0	4.1	24.0	25.9	0.88	0.89
20	5.0	1.00	4.0	4.1	42.5	46.9	0.93	0.94

Sensitivity, precision and reagent blank

In order to investigate the sensitivity, a water sample to which 0.015M hydrochloric acid and 10 mg/l. of mercury(II) had been added was electrolysed for 10 min prior to stripping in 2.5M acetic acid/7.5M ammonium acetate medium with an oxidative current of 1.0 μA . Eight strips, from -0.90 to -0.35 V, were accumulated from which seven accumulated background strips were subtracted. The measurements were repeated after the addition of 10 and 20 ng/l. of cadmium(II) and lead(II), respectively. The background corrected stripping curves thus obtained are shown in Fig. 5. Fig. 6 shows, at ten times smaller scale, the eight accumulated sample stripping curves, the seven accumulated background curves and the background corrected curve obtained in the analysis of a sample to which 20 ng/l. of cadmium(II) and lead(II) had been added. On plotting the lead stripping signals *vs.* the concentration of lead(II) added, a regression line with a correlation coefficient equal to 0.9997 and an intercept on the concentration axis equal to -3.8 ng/l. was obtained. The corresponding data for cadmium were 1.0000 and -0.12 ng/l., respectively. The sensitivity was 1.68 msec l./ng for lead and 1.44 msec l./ng for cadmium.

The origin of the blank value for lead(II) of 3.8 ng/l. was investigated by doubling the concentrations of hydrochloric acid and mercury(II) in the sample. No significant increase in the blank value was obtained. The possibility that the blank values originated from continuous contamination from the laboratory atmosphere or by leaching of lead(II) from the electrode was investigated by seven consecutive analyses of the sample to which 20 ng/l. of

lead(II) and cadmium(II) had been added. No significant increase in the lead and cadmium stripping signals were registered. Thus it was concluded that the blank value emanated from contamination of the Millipore water. The mean value obtained for the cadmium stripping signal was 25.6 msec and that obtained for lead 32.8 msec, the relative standard deviations being 6.4 and 5.4% ($n = 7$), respectively. The ratio between the cadmium and lead signals had a relative standard deviation equal to 6.1%.

The minimum detection limit that can be

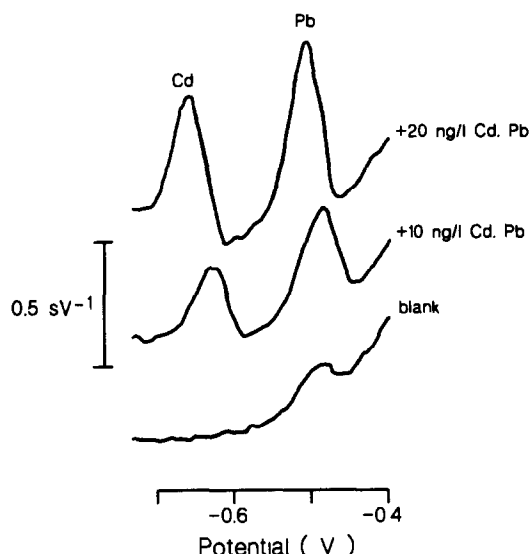


Fig. 5. Stripping potentiometry curves obtained after electrolysis for 10 min in samples to which 0, 10 and 20 ng/l. of cadmium(II) and lead(II) had been added. Stripping in 2.5M acetic acid/7.5M ammonium acetate using a constant current of 1.0 μA . Seven accumulated background strips have been subtracted from eight accumulated sample strips. The accumulated sample and background strips for the sample containing 20 ng/l. are shown in Fig. 6 together with the background corrected curve at ten times smaller scale.

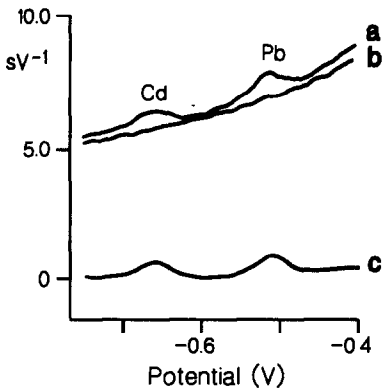


Fig. 6. Eight accumulated sample strips (a), seven accumulated background strips (b) and background corrected stripping curve (c) obtained after electrolysis for 10 min in a sample to which 20 ng/l. of cadmium(II) and lead(II) had been added. Stripping in 2.5M acetic acid/7.5M ammonium acetate using a constant current of 1.0 μ A (cf. Fig. 5).

obtained in practice with the proposed method was determined by electrolyzing for 20 min a Millipore water sample containing 0.015M hydrochloric acid and 10 mg/l. of mercury(II) prior to stripping in acetic acid/ammonia solution. Eight sample and seven background strips were accumulated in the potential region -0.90 to -0.50 V. The measurements were repeated after the addition of 1, 2 and 4 ng/l. of cadmium(II) and the background corrected stripping curves are shown in Fig. 7. The regression line obtained when plotting the cadmium signals vs. the concentration of cadmium(II) added had a correlation coefficient equal to 0.9990 ($n = 4$) and an intercept on the concentration axis equal to 0.081 ng/l. The sensitivity was 2.8 msec l./ng. The stripping

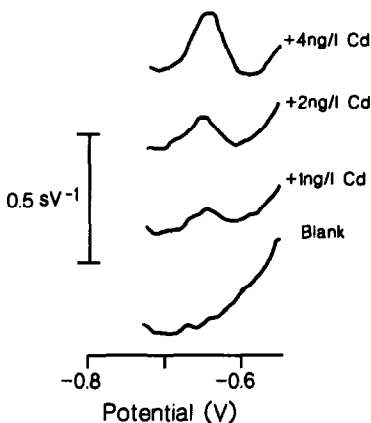


Fig. 7. Stripping potentiometry curves obtained after electrolysis for 20 min in samples to which 0, 1, 2 and 4 ng/l. of cadmium(II) had been added. Stripping in 2.5M acetic acid/7.5M ammonium acetate using a current equal to 1.0 μ A. Seven accumulated background strips have been subtracted from eight accumulated sample strips.

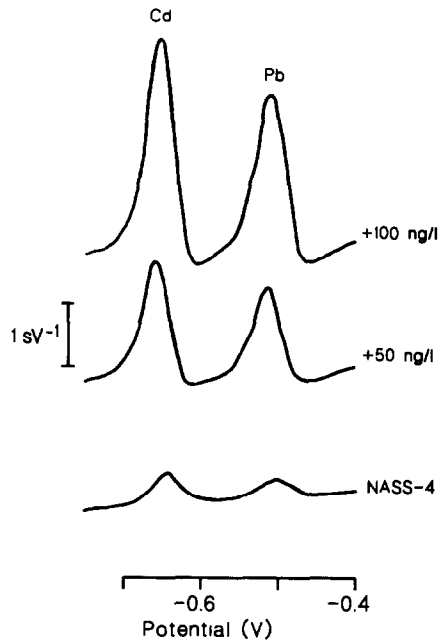


Fig. 8. Stripping potentiometry curves obtained in the analysis of NASS-4 reference seawater with certified values for cadmium(II) and lead(II) equal to 16 ± 3 and 13 ± 5 ng/l. respectively. Electrolysis in the sample for 10 min prior to stripping in 2.5M acetic acid/7.5M ammonium acetate using a constant current equal to 1.0 μ A. Seven accumulated background strips have been subtracted from eight accumulated sample strips. Standard additions of 50 and 100 ng/l. of cadmium(II) and lead(II).

signal after the addition of 4 ng/l. of cadmium(II) was 11.2 msec. Empirically it has been shown that the detection limit in stripping potentiometry when using a 90 kHz instrument and a single strip is approximately equal to a stripping signal of 0.2 msec. When using multiple stripping involving eight strips the estimated signal for the detection limit is approximately 0.5 msec (cf. Fig. 7) which corresponds to a detection limit of 0.2 ng/l. of cadmium(II) for a total electrolysis time of 20 min. Since the sensitivity for lead(II) is slightly higher than that for cadmium (see Fig. 5) a similar detection limit is valid for lead(II). In practice this is, however, difficult to obtain since contamination problems are much more serious for lead(II) than for cadmium(II).

Analysis of seawater samples. Linear range

Figure 8 shows the stripping potentiometry curves obtained in the analysis of NASS-4 reference seawater sample after electrolysis for 10 min and subsequent stripping in 2.5M acetic acid/7.5M ammonium acetate with an oxidative current of 1.0 μ A. Seven accumulated

background strips were subtracted from eight accumulated sample strips. Also shown in Fig. 8 are the stripping curves obtained after additions of 50 and 100 ng/l. of cadmium(II) and lead(II). Evaluation by means of standard addition gave a value for cadmium(II) equal to 16 ng/l. and for lead(II) equal to 12 ng/l., the certified values being 16 ± 3 and 13 ± 5 ng/l., respectively. The correlation coefficients for both plots were 1.0000 ($n = 3$). From these correlations it can be concluded that the linear range for the proposed procedure extends to 120 ng/l. of the elements. Separate experiments show that the linear range is 0–500 ng/l. of lead(II) and cadmium(II).

The results obtained in the analysis of CASS-2 nearshore reference seawater was 18 ng/l. of cadmium(II) (certified 19 ± 4) and 24 ng/l. of lead(II) (certified 19 ± 6) and in the analysis of SLEW-1 estuarine reference water 15 ng/l. of cadmium(II) (certified 18 ± 3) and 31 ng/l. of lead(II) (certified 28 ± 7).

CONCLUSION

The combination of a novel three-in-one electrode, permitting medium exchange in batch mode and quiescent conditions during stripping, with a 90 kHz stripping potentiometry analyser makes it possible to determine cadmium(II) and lead(II) in the low ng/l. con-

centration range. The detection limits obtained in this study are the lowest so far reported for stripping potentiometry or stripping voltammetry without prior enrichment by means of *e.g.*, solvent extraction or ion exchange.

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