A Voltametric Study of Inorganic Selenium and some Organoselenium compounds at the Hanging Mercury Drop Electrode and its Analytical Applications

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Summary: In this paper, the differential pulse voltametric behaviour and resulting analytical applications of inorganic and different organoselenium compounds were investigated. Limits of detection and quantitation have been calculated for the differential pulse voltametric determination of the organoselenium compounds. Lastly in this paper high performance liquid chromatographic studies with an electrochemical detector for the estimation of organoselenium compounds is also investigated.

Introduction

The first polarographic work on selenium was reported by Schwaer and Suchy [1], who described three waves for Se(IV) in 1N hydrochloric acid. These authors attributed the waves to the stepwise reduction to the +2, elemental and -2 oxidation states respectively. In very dilute solution, the first two waves merged. They reported a single wave for the reduction of selenite ion to the element in ammonical solution. Lingane and Niedrach [2] found that the selenide ion gave adissolution wave at the dropping mercury electrode (DME) similar to that of sulphide ion. They also studied the polarography of selnite and selenate ions [3]. The selenite wave in an ammonical medium was attributed to reduction to the -2 oxidation state. Speranskaya [4] examined the reduction of Se(IV) in an acidic medium, reporting two waves, attributing the first wave to reduction to the elemental state and the second reduction of the elemnt to the -2 state. The second wave was accompanied by the reduction of hydrogen ion from the supporting electrolyte.

Among those who have contributed to the polarography of organic selenium compounds are Stricks and Mueller [5], who studied the polarography of two potential anti-radiation drugs, 2-aminoethanethiosulphuric acid and 2-aminoethaneselenosulphuric acid, and Griffin [6] who examined the selenium diaminobenzidine complex. The latter investigator studied the parameters for single-sweep polarographic analysis of the slenium diaminobenzidine complex and developed a technique for the determination of slenium with a sensitivity of 1 μ gdm^{-3} of the element. Polarographic investigations of organic selenium compounds has been extensively reported by Nygard [7-12]. In one of these investigation Nygard [12]
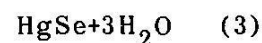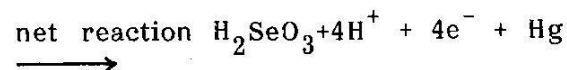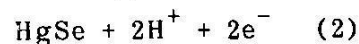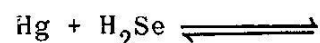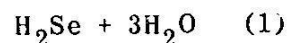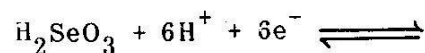
comprehensively studied the polarographic behaviour of diselenodiaceticacid. He showed that $(HOO\ CCH_2Se)$ and $HSeCH_2COOH$ form a reversible system at the dropping mercury electrode. The reversibility of the following electrode reaction was shown by a number of methods.
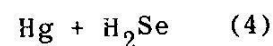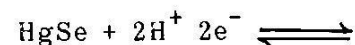
$$HgSeCH_2COOH + H^+ + e \rightleftharpoons$$
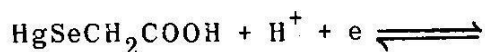
$$HSeCH_2COOH + Hg$$

The dissociation constant of the SeH group in $HSeCH_2COOH$ is 1.0×10^{-7}

The polarographic behaviour of slenium has been summarized as follows [13].
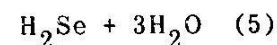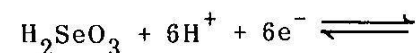
Ist wave $= -0.05V$ vs s.c.e., 0.2M HCl

$$H_2SeO_3 + 6H^+ + 6e^- \rightleftharpoons$$

$$H_2Se + 3H_2O \quad (1)$$

$$Hg + H_2Se \rightleftharpoons$$

$$HgSe + 2H^+ + 2e^- \quad (2)$$

net reaction $H_2SeO_3 + 4H^+ + 4e^- + Hg \longrightarrow$

$$HgSe + 3H_2O \quad (3)$$

2nd wave $= -0.54V$ s.c.e. in 0.2M Hcl

$$HgSe + 2H^+ \ 2e^- \rightleftharpoons$$

$$Hg + H_2Se \quad (4)$$

At higher pH

$-1.1V$ vs s.c.e. at pH 3, -1.6 vs s.c.e. at pH 8

$$H_2SeO_3 + 6H^+ + 6e^- \rightleftharpoons$$

$$H_2Se + 3H_2O \quad (5)$$

For the stripping voltametric determination of slenium, its reaction with mercury to form HgSe has been used [14-15]. At pH 1.5 - 4.5 and deposition potential (E_{el}) from -0.1 to -0.6V two peaks appear during the cathodic stripping at -0.7 and -0.95V [14]. The second peak is formed only after the whole electrode has been covered with the HgSe film, and the first peak corresponds to the reduction of HgSe. If the deposition is performed in 0.2M HCl at +0.05V on a mercury electrode [15], a film of adsorbed selenite complex is formed on the electrode, which may be cathodically stripped with the formation of a peak at about -0.1V. After deposition at -0.4V stripping peak of HgSe appear, allowing determination of 7×10^{-8}M Se(IV) using the first peak or 5×10^{-9}Se (IV) using the second peak when the I vs E curve is coulometrically evaluated. Interferences of Fe(III), Cu, Pb, Cd, As and TI have been reported.

This paper is concerned with the differential pulse stripping behaviour of inorganic selenium and the differential pulse voltametric behaviour of selected organoselenium compounds, in order to evaluate the application of these electrochemical techniques to the identification and determination of different chemicals forms of selenium singly and in mixtures with each other. The application of h.p.l.c. with u.v. and electrochemical detection to the organoselenium compounds was also briefly investigated.

Experimental

Apparatus

All experiments were performed using the Princeton Applied Research (PAR) Model 174 polarograph with a PAR Model 303 stationary mercury drop electrode. Voltammograms were recorded on PAR Model RE 0074x-y recor-

der. The electrode system was constructed with a platinum wire auxiliary electrode and a calomel reference electrode. A Kent Model EIL 7055 pH meter was used for pH measurement. All potentials are given versus s.c.e.

Reagents

All reagents were of anlaytical reagent grade and were used without further purification. The organoselenium compounds were synthesised and provided by the Organic Chemistry group in University College, Cork. Doubly distilled water was used throughout.

Standard solution preparation

Preparation of inorganic selenium standard solution

Stock solutions of 10^{-2}M inorganic selenium were prepared by dissolving 1.2897gms of Analar BDH selenious acid and making the volume up to 1000ml. 1000mg dm^{-3} solutions of inorganic selenium were also prepared from selenious acid by disssolving 1.6334 gms in 1000 ml of water.

Preparation of organoselenium stock solutions

Stock solutions of all organoselenium compounds were prepared by dissolving them in Analar methanol and diluting with deionized water to the required volume.

Supporting Electrolyte

A wide range of buffer solutions of pH 3-12 were prepared using acetate buffer (pH 3-5), phosphate buffer (pH 5-8) and borate buffer (pH 9-12) as described [16].

Procedure

For the differential pulse voltametric study of different organoselenium com-

pounds 10 ml of buffer was placed in a polagraphic cell, deareated for 4 minutes and the differential pulse voltametric behaviour of the buffer (supporting electrolyte) recorded after 30s quiescence time. The 100 µl of the organoselenium compounds was injected into the cell, deareated for 2 minutes and after 30s quiescence, the voltammogram was recorded.

For the on-line study of organoselenium compounds by reverse phase h.p.l.c., 70:30% (methanol:water) mobile phase was used with u.v. detection at 254 nm. As a supporting electrolyte ammonium acetate (0.5 gms) per 500 ml mobile phase was used.

Results and Discussion

Differential Pulse stripping voltametric behvaiour of Se(IV)

The effect of plating time on 10 µgdm^{-3} solution of Se(IV) was studied in 2M HCl supporting electrolyte and is shown in Table.1 The peak height increased with plating time for 120s. After 2 minutes there was no increase in peak height with plating time and broadening of the peak begins. After 4 minutes plating time two peaks are manifested, one at -0.55V and one at -0.78V suggesting multilayer formation. The second peak is formed only after the whole electrode has been covered with HgSe film and the cathodic peaks correspond to the reducjtion of HgSe. The first peak at -0.55V can be used for Se(IV) determinations by differntial pulse cathodic stripping voltammetry at the sub g dm^{-3} level.

Using the optimum conditions, the effect of concentration on the differentail pulse cathodic stripping voltametric behaviour of Se(IV) was studied at the µg dm^{-3} level. At lower concentrations only one peak is observed, while at concentrations higher than

Table-1: The effect of plating time on the differential pulse cathodic stripping voltammetric behaviour of Se (IV).

Initial potential = -0.4V;

Scan direction = -Ve;

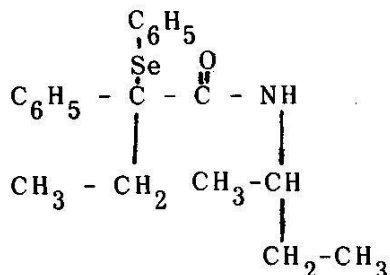Scan rate = 2 mVs^{-1}

Supporting electrolyte = 2M HCl;

Concentration = 10 ug dm^{-3}

Plating time (S)	Current (uA)
0	0.02
30	0.028
60	0.034
90	0.04
120	0.046
150	0.046

30 μg dm^{-3} two peaks are observed, showing multilayer formation phenomena. There is a linear relationship between concentration and current produced up to 200 g dm^{-3} in agreement with the results of Henze at al. [17].

Differential Pulse Voltammetric behaviour of organoselenium compound I

(N-sec butyl-2-phenylselenenyl-2-phenyl butyramide).

$$C_6H_5 - \overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CH_3 - CH_2}{|}}{C}} - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3-CH}{}}{C}} - NH$$

$$CH_2-CH_3$$

The effect of pH on the differential pulse voltametric behaviour of organoselenium compound I was studied and is summarized in Table 2. At pH 6 two cathodic peaks are observed for the differential pulse voltametric behaviour of this compound i.e. a small peak at an Ep of approximately -0.5V and a major one at Ep approximately -0.80V. At pH lower than 6 only one cathodic peak i.e at an Ep of approximately 0.80V is observed. As can be seen from Table 2 the optimum pH for the analytical application of the differential pulse voltametric behaviour of this compound is pH 4. The Ep values vary slightly with pH, i.e. as the pH is increased the Ep values move slightly toward more negative potentials.

After studying the effect of pH, pH 4 was chosen as the analytical optimum. The effect of inital potential was studied for the differential pulse voltametric behaviour of 10^{-6}M of the organoselenium compound I. the optimum initial potential for the differential pulse voltametric behaviour of this compound was found to be -0.2V. The effect of deposition time on the differential pulse voltametric behaviour of organoselenium compound I was studied at optimum pH and optimum initial potential. The cathodic peak showed an increase with deposition time. After 4 minutes deposition time a second peak is observed at -0.4V. The above observations show that this compouud is adsorbed on the electrode surface during deposition prior to electrolysis which gives the cathodic wave. The increase of the cathodic peak current with deposition time suggests that at the concentration under investigation there are vacant sites on the electrode surface where adsorption of the molecules take place giving enhancement to the cathodic peak. At and after 4 minutes deposition time vacant sites no longer exist on the electrode surface, and the first peak (-0.4V) is

Table-2: The effect of pH on the d.p. voltammetric behaviour
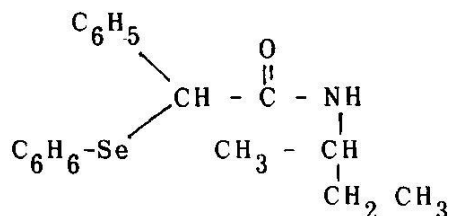of organoselenium compound I.

Scan rate = $20mV^{-1}$; Modulation amplitude = 100mV;
Scan direction = - ve; Pre-electrolysis time = 0 minute.

pH	Initial potential $E_{el}(V)$	Peak potential $E_p(V)$		Peak current $I_p(uA)$	
		1	2	1	2
3	+0.2	-	-0.78	-	0.26
4	+0.2	-	0.81	-	0.26
5	+0.2	-	-0.81	-	0.21
6	+0.15	-0.45	-0.76	0.03	0.22
7	+0.1	-0.56	-0.82	0.06	0.26
8	+0.01	-0.55	-0.82	0.06	0.24
9	0.0	-0.56	-0.80	0.04	0.24
10	0.0	-0.54	-0.80	0.02	0.18
12	-0.1	-0.52	-0.80	0.02	0.30

preseumbaly due to the reduction of weakly held or unadsorbed molecules.

The limit of detection and limit of quantitation of organoselenium compound I were determined using the optimum conditions, of pH, initial potential and scan rate and are 9×10^{-9} M and 3×10^{-8} M respectively.

Differential pulse voltametric behaviour of organoselenium compound II (N-sec-butyl-2-phenylselenenyl-2-phenylacetamide).

C$_6$H$_5$ \
           \
                O \
                ‖ \
          CH - C - NH \
                     | \
C$_6$H$_6$-Se   CH$_3$ - CH \
                         | \
                      CH$_2$ CH$_3$

The differential pulse voltametric behaviour of organoselenium compound II was studied through a wide pH range and is given in summarized form in Table 3. In acidic media only one cathodic peak is observed for this compound in the potential range - 0.74V to -0.80V. In alkaline media two cathodic peaks one at a potential of -0.42V and one at -0.78V are observed. The two peaks at pH 6 suggest that adsorption of this molecule occurs at the electrode in multilayer fashion in neutral and alkaline media.

As can be seen from Table 3, the optimum pH for the analytical application of differential pulse voltametric behaviour of this compound is 5. Further it can be seem from this Table that the differential pulse voltametric current of this compound is pH dependent. The cathodic current increases

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Table-3: The effect of pH on the d.p. voltammetric behaviour of organoselenium compound II

Scan rate = $10mV^{-1}$; Scan direction = - ve;
Modulation amplitude = 100mV; Solution concentration = $1.23 \times 10^{-6}M$

pH	Initial potential $E_{el}(V)$	Pre-electrolysis time (minutes)	Peak potential Ep(V)			Peak current I_p (uA)		
			1	2	3	1	2	3
3	+0.2	0	-	-0.74	-	-	1.2	-
	+0.2	2	-	-0.74	-	-	1.8	-
4	+0.1	0	-	-0.78	-	-1.5	-	
	+0.1	2	-	-0.78	-	-	2.3	-
5	+0.1	0	-	-0.8	-	-	3.7	-
	+0.1	2	-	-0.8	-	-	4.8	-
6	+0.1	0	-	-0.78	-	-	0.72	-
	+0.1	2	-	-0.78	-	-	1.0	-
7	+0.1	0	-0.42	-0.78	-	0.06	2.3	-
	+0.1	2	-0.42	-0.78	-	0.06	1.14	-
8	+0.1	0	-0.42	-0.78	-	0.04	1.7	-
	+0.1	2	-0.42	-0.78	-	0.04	2.1	-
9	0.0	0	-0.42	-0.78	-	0.04	1.8	-
	0.0	2	-0.42	-0.78	-	0.04	2.6	-
10	0.0	0	-0.42	-0.77	-	0.04	1.8	-
	0.0	2	-0.42	-0.77	-	0.04	2.5	-
11	-0.1	0	-0.42	-0.78	-1.03	0.04	1.7	0.08
	-0.1	2	-0.42	-0.78	-1.03	0.04	1.7	0.1
12	-0.2	0	-0.42	-0.78	-1.02	0.04	1.7	0.08
	-0.2	2	-0.42	-0.78	-1.02	0.04	2.5	0.1

with pH up to pH 5. After pH 5 cathodic current decreased up to pH 8, and then remains constant up to pH 12. The sudden drop in the cathodic current at pH 6 could be due to change in the medium, i.e. from acetate (pH 3 to 5) to phosphate (pH 6 to 8) buffer which may affect the adsorption of the molecule around the mercury drop and hence its desorption when the potential is made more negative.

The limit of detection and quanitation of organoselenium compound II were determined using the optimum conditions of pH initial potential and scan rate and are 3.6×10^{-8} and 1.2×10^{-7} M respectively.

Differential pulse voltametric behaviour of organoselenium compound III.

(N-isopropyl-2-phenylselenenyl-2-phenyl-acetamide)

$$C_6H_5 \diagdown$$
$$CH - \overset{\overset{O}{\|}}{C} - NH$$
$$C_6H_5 \diagup Se \quad CH_3 - CH - CH_3$$
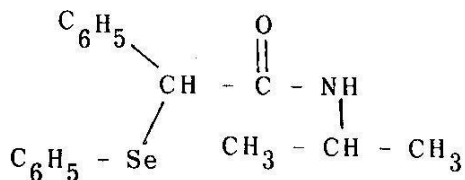
The Differential pulse voltametric behaviour of the organoselenium compound III was studied throughout a wide range of pH and is given in summarised form in Table 4. From Table 4 it can be seen that at 1 minute pre-electrolysis time the optimum pH for the analytical application of the differential pulse voltammetric behaviour of this compound is 6, while at 0 minute pre-electrolysis time, the optimum pH is 7.

At pH 3 two cathodic peaks were observed, one at Ep -0.79V and a small peak at Ep -0.95V. Both peaks show increase with pre-electrolysis

time. From pH 4 to pH 9, only one cathodic peak is observed at Ep-0.78V to -0.80V. In strongly basic solutions, that is pH 11 and 12, two cathodic peaks are observed, a small peak at Ep-0.40 to -0.42V and a major peak at Ep -0.78V to -0.79V.

The differential pulse voltametric behaviour of this compound is not dissimilar to the differential pulse voltametric behaviour of organoselenium compound II, which is expected due to the similar substitutents and sizes of the respective molecules. The appearance of the two cathodic peaks in strong alkaline media could be due to multilayer formation as has been observed for the other organoselenium compounds.

The limit of detection and limit of quantitation of organoselenium compound III were found out at optimum condition and are 1.4×10^{-8}M and 4.9×10^{-8}M respectively.

Differential pulse voltametric behaviour of organoselenium compound IV.

(Dphenyl diselenide)

$$C_6H_5 - Se - Se - C_6H_5$$
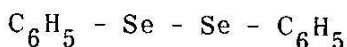
The differential pulse voltametric behaviour of the organoselenium compound IV was studied throughout the pH range and is given in summarized form in Table-5. As can be seen from Table 5, the optimum pH for the analytical application of the differential pulse voltametric behaviour of this compound is pH 7. Throughout the pH region only one main cathodic peak at Ep -0.76 to -0.80V is observed for the differential pulse voltametric behaviour of this compound.

The effect of deposition time was studied on the differential pulse volta-

Table-4: The effect of pH on the d.p. voltammetric behaviour of organiselenium compound III.
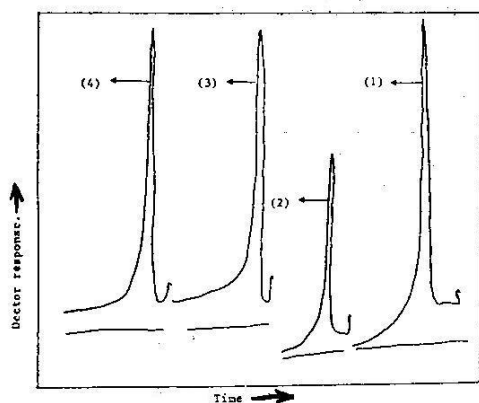
Scan rate = 10mV s^{-1}; Modulation amplitude = 100mV;
Scan direction = -ve; Solution concentration = 1.2 x 10^{-6}M

pH	Initial potential E_{el}(V)	Pre-electrolysis time (minute)	Peak potential Ep (V)			Peak current I_p (uA)		
			1	2	3	1	2	3
3	+0.2	0	-	-0.79	-0.85	-	0.8	0.08
	+0.2	1	-	-0.79	-0.85	-	1.12	0.12
4	0.2	0	-	-0.78	-	-	0.76	-
	+0.2	1	-	-0.78	-	-	0.96	-
5	+0.2	0	-	-0.79	-	-	1.0	-
	+0.2	1	-	-0.79	-	-	1.4	-
6	+0.1	0	-	-0.8	-	-	1.2	-
	+0.1	1	-	-0.8	-	-	1.6	-
7	+0.1	0	-	-0.8	-	-	1.32	-
	+0.1	1	-	-0.8	-	-	1.44	-
8	+0.1	0	-	-0.79	-	-	1.0	-
	+0.1	1	-	-0.79	-	-	1.3	-
9	0.0	0	-	-0.78	-	-	1.06	-
	0.0	1	-	-0.78	-	-	1.54	-
10	0.0	0	-0.4	-0.78	-	0.02	1.0	-
	0.0	1	-0.4	-0.78	-	0.02	1.4	-
11	-0.1	0	-0.42	-0.79	-	0.06	1.04	-
	-0.1	1	-0.42	-0.79	-	0.1	1.62	-
12	-0.1	0	-0.42	-0.78	-	0.06	1.08	-
	0.1	1	-0.42	-0.78	-	0.1	1.58	-

Table-5: The effect of pH on the d.p voltammetric behaviour of organoselenium compound IV.

Scan rate = 10mV s^{-1}; Modulation amlitude = 100mV;
Scan direction = -ve; Solution concentration = 1 x 10^{-6}M.

pH	Initial potential $E_{el}(V)$	Pre-electrolysis time minute	peak potential Ep(V)	Peak current $I_p(uA)$
3	+0.2	0	-0.76	0.56
3	+0.2	1	-0.76	0.76
4	+0.2	0	-0.8	0.88
4	+0.2	1	-0.8	1.00
5	+0.2	0	-0.8	0.86
5	+0.2	1	-0.8	1.10
6	+0.1	0	-0.8	0.88
6	+0.1	1	-0.8	1.14
7	+0.1	0	-0.79	0.93
7	+0.1	1	-0.79	1.24
8	+0.1	0	-0.79	0.8
8	+0.1	1	-0.79	1.04
9	0.0	0	-0.79	0.72
9	0.0	1	-0.79	1.05
10	0.0	0	-0.79	0.78
10	0.0	1	-0.79	1.09
11	-0.1	0	-0.78	0.58
11	-0.1	1	-0.78	0.83
12	-0.1	0	-0.78	0.8
12	-0.1	1	-0.78	1.09

(1) Organoselenium compound I;
(2) Organoselenium compound II;
(3) Organoselenium compound III;
(4) Organoselenium compound IV;
Column = Lichosorb R-P-18;

Mobile phase = methanol:water (70:30); Detector wavelength = 254 nm.

Fig.1: Chromatograms showing the detection of organoselenium compounds by u.v. detector.

metric behaviour of this compound. There is an increase in peak height with increasing deposition time. This preseumably is due to the adsorption behaviour of this compound. The cathodic peak is doubtlessly due to reduction of $C_6H_5 - Se - Se - C_6H_5$ to C_6H_5SeH.

The limit of detection and limit of quantitation of organoselenium compound IV were found out under optimum conditions and are 1×10^{-8} M and 3.39×10^{-8} M respectively.

H.p.l.c. study of organoselenium compounds

The aim of this study was an attempt to combine the selectivity of the chromatographic techniques with the sensitivity of the electrochemical method for the organoselenium compounds. Conditions for the elution of organoselenium compounds were optimized using h.p.l.c. with a reverse phase column and u.v. detector. The organoselenium compounds were injected (20 l) to the column and eluted with water :methanol (30:70) and detection was at 254 nm. Their chromatograms are shown in Fig.1. The eluent from the u.v. detector was then fed to the electrochemical detector. As a supporting electrolyte 0.5 grams of ammonium acetate was added to 500 ml of the mobile phase. The organoselenium compounds were then injected to the column. Every time u.v. signal was observed, no electrochemical signal was observed using the elctrochemical detector. Three types of indicator electrode, i.e. gold, platinum and glassy-carbon were tried at different potentials (both +ve and -ve), but no signal was observed under the above conditions.

Conclusion

For the differential pulse cathodic stripping voltametric behaviour of Se(IV) in 2M HCl two peaks are observed at μg dm^{-3} level, that is one at Ep-0.55V and the other at Ep -0.78V. The limit of detection of Se(IV) utilizing the first peak is 0.037 μgdm^{-3}. The limit of quantitation for Se(IV) by this method is 1.3μg dm^{-3}.

In the presence of equimolar concentrations of organoselenium compounds no stripping peak for Se(IV) is observed, only the cathodic peaks for the organoselenium compounds. This could be due to the preferential adsorption of organoselenium molecules around the mercury drop, inhibiting the formation of a film of HgSe and thus no stripping peak for Se(IV) is observed. The same behaviour was observed for the stri-

pping phenomena of As(III) in the presence of organoarsenic compounds [18].

Unlike organoarsenic compounds [18], the differential pulse voltametric behaviour of organoselenium compounds was unaltered throughout the pH range, i.e. the main cathodic peak is observed at Ep of approx. -0.8V. Therefore in this case it was impossible to resolve organoselneium compounds by application of differential pulse voltammetry. The conditions used for high performance liquid chromatography -u.v. detection were not particularly better with respect to resolution of the organoselenium compounds under investigation.

In conclusion, the technique of differntial pulse cathodic stripping voltammetry is very sensitive for the determination of inorganic Se(IV) providing organic forms of Se that can adsorb on the hanging mercury drop are absent in the environmental sample. Total organic Se (adsorbable on the hanging mercury drop electorde) can be determined down to 10^{-8}M concentrations by adsorption at +ve potentials followed by determination by differential pulse voltammetry at cathodic potentials.

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