Monograph

Inorganic Adsorptive Stripping Analysis

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Metrohm

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Contents

Page

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Introduction

The technique of anodic stripping voltammetry (ASV) is now widely used for the trace analysis of metal ions in a variety of matrices, e.g., electronic grade materials[1], milk[2], human whole blood[3], soils and sewage sludges[4], ground and spring waters[5], etc. Part per billion (ppb) and sub ppb concentrations of metal ions such as Cd, Cu, Pb, Zn are determined by ASV after controlled electrolytic accumulation of the metal ions at indicator electrodes such as the hanging mercury drop electrode (HMDE) or mercury film electrode (MFE). ASV is, however, limited to a smaller group of elements than can be determined by rival analytical techniques such as atomic absorption spectroscopy (AAS), i.e., ASV is limited to certain elements in Groups Ib, IIb, IIIb, IVb, Vb of the Periodic Table and can be supplemented by the application of the technique of cathodic stripping voltammetry (CSV) for certain elements in Groups VIb and VIIb such as S, Se[6], Cl[7], Br[7], and I[8]. These latter elements can, at anodic potentials, electrolytically form partially insoluble compounds with mercury which will adsorb on the mercury surface and can subsequently be stripped by imposition of a cathodic voltage scan.

Recently, analytical application of the technique of adsorptive stripping voltammetry (AdSV) has extended the range of inorganic species that can be determined by stripping voltammetry at ppb and sub ppb concentrations. AdSV involves the analyte being concentrated onto the electrode surface by adsorption *without* electrolysis, followed by direct current, differential pulse or square wave voltammetric determination of the surface active species which is usually a chelate of the metal ion to be determined. The current can arise from reduction of the element or ligand in the adsorbed complex or by catalytic evolution of hydrogen. The entire adsorbed monolayer is reduced during the potential scan, causing the voltammetric determinations to have particularly low detection limits. In recent years, papers on a diverse group of elements have been published such as La (Group IIIa)[9], Zr (IVa)[10], V (Va)[11], Mo (VIa)[12], Fe[13] and Pt[14] (VIII), Cd (IIb)[15], Al (IIIb)[16], Ge (IVb)[17] and Se (VIb)[18]. Very low detection limits of the order of 10^{-10} to 10^{-11} mol/L have been quoted (Table 1) for the determination of metal ions that cannot be conveniently measured by ASV due to low solubility in mercury, irreversible metal/metal ion couple (e.g., Fe(0)/Fe(II)), high negative redox potential or formation of intermetallic compounds (e.g., Ni-Zn). These detection limits are comparable to those obtained by AAS with a carbon furnace or inductively coupled plasma mass spectrometry (ICP-MS).

From the viewpoint of selectivity, there are several types of interference. Firstly, a non-selective ligand such as a catechol can give rise to surface active chelates with other metal ions in the sample which will limit the surface area of the working electrode available for the determination of the analyte chelate. Competitive adsorption of this kind can be minimised by using a shorter accumulation period. When these other sur-

Table 1 Limits of Detection for the Determination of Selected Elements by AdSV

Element	Electrolyte	Compound adsorbed	Working electrode	Limit of detection	Ref.
Cu	0.01 mol/L HEPES[a] pH 7.8	Cu-catechol	HMDE	$6 \cdot 10^{-11}$ mol/L	19
Fe	0.01 mol/L PIPES[b] pH 6.9	Fe-catechol	HMDE	$6 \cdot 10^{-10}$ mol/L	13
Co	0.03 mol/L HEPES[a] pH 7.6	Co-nioxime	HMDE	$6 \cdot 10^{-12}$ mol/L	21
Zn	0.01 mol/L BES[c]	Zn-APDC[d]	HMDE	$3 \cdot 10^{-11}$ mol/L	22
Ni	0.1 mol/L NH_4Cl 0.1 mol/L NH_3	Ni-DMG[e]	HMDE	$1 \cdot 10^{-10}$ mol/L	23
Zr	Acetate buffer pH 4.6	Zr-Solochrome Violet RS	HMDE	$2.3 \cdot 10^{-10}$ mol/L	10
Se	Sodium acetate/ NaOH/HCl pH 4.5	HgSe	HMDE	0.01 ppb	18
La, Ce, Pr		Chelate with cresolphthalexon	HMDE	$2 \cdot 10^{-10}$ mol/L	9

[a] HEPES N-2-hydroxyethyl-piperazine-N'-2-ethanesulphonic acid.

[b] PIPES piperazine-NN'-bis-2-ethanesulphonic acid.

[c] BES NN'-bis- (2 hydroxyethyl)-2-amino-ethanesulphonic acid.

[d] APDC ammonium pyrrolidine dithiocarbamate.

[e] DMG dimethylglyoxime.

face active chelates are electroactive at a similar reduction potential then interference can occur in the stripping of the analyte chelate from the indicator/working electrode. Sometimes it is possible to minimise overlapping of stripping peaks by varying one or more experimental parameters such as ligand concentration, accumulation/deposition potential, pH, scan rate, etc. Secondly, naturally occurring organic molecules can competitively bind the analyte metal ion in the bulk of the solution and/or these molecules can also adsorb on the working electrode, in both cases having an adverse effect on the limit of detection of the voltammetric determination step. These effects can be removed by ultraviolet irradiation of the sample prior to measurement. A suitable instrument is the 705 UV Digester, which allows 12 samples to be treated simultaneously.

Applications

a) Cu, Fe, U and V

These elements can be simultaneously determined by AdSV using an HMDE working electrode after chelation with catechol. Addition of 4×10^{-4} mol/L catechol to sea water at pH 7.0, followed by a 3 minute accumulation of the metal chelates at –0.05 V and their subsequent cathodic stripping using the differential pulse mode, has resulted in the appearance of four well separated peaks at –0.23 V, –0.40 V, –0.56 V and –0.72 V for Cu(II), Fe(III), U(VI) and V(V)[13]. Other metal ions such as Bi(III), Pb(II), In(III), Sb(V), Ni(II) and Zn(II) will also give stripping signals under these conditions but either their peak heights are significantly smaller for a given concentration of the metal ion or selectivity is diminished by overlapping peaks, for example, Sb(V) –0.83 V, Ni(II) –0.86 V. Optimal experimental conditions are different for each metal ion.

The adsorption of the copper catechol chelate is optimised with a catechol concentration of 10^{-3} mol/L at pH 7.8 in the presence of 0.01 mol/L HEPES[19] and using an accumulation potential of –0.05 V. The detection limit using the differential pulse mode of stripping is 6×10^{-11} mol/L after a 3 minute accumulation period. Cu(II) has also been determined by AdSV of its 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol-(5-Br-PADAP) complex.

The determination of Fe by AdSV is optimised using a catechol concentration of 4×10^{-4} mol/L, a pH of 6.9 with 0.01 mol/L PIPES buffer and an accumulation potential of –0.10 V[13]. The detection limit for the determination of Fe in sea water was quoted as 6×10^{-10} mol/L using an accumulation time of 3 minutes. Interference from high Cu and Pb concentrations could be eliminated by addition of EDTA to the solution and natural organic surfactants could be removed by ultraviolet irradiation of the sample. The combined concentrations of Fe(II) and Fe(III) were determined since dissolved Fe(II) was immediately oxidised at the surface of the HMDE during the accumulation period. Fe(III) has also been determined by AdSV using its Solochrome Violet RS chelate with a limit of detection of 0.04 ppb[24] and constant current stripping analysis has achieved a limit of detection of 1 ppb using the same chelate but adsorbed on a carbon fibre electrode[25]. Fe can be determined in electronic grade materials by AdSV of its catechol complex in a PIPES buffer, pH 7.0 to 7.2[1]. The analytical method and sample voltammograms are given in the Co/Ni section.

Uranium can be conveniently determined using a catechol concentration of 2×10^{-3} mol/L, a pH of 6.9, with 0.01 mol/L PIPES and an accumulation potential of –0.10 V. A slightly lower potential can be used in the presence of high concentrations of dissolved iron. The reduction peak of the U(VI) chelate is at –0.56 V and the limit of detection found to be 3×10^{-10} mol/L after a 2.5 minute accumulation period[26]. U(VI) can also be determined by AdSV using its Mordant Blue 9 chelate with a limit of detection of 2×10^{-10} mol/L[27] or as its cupferron chelate[28].

Vanadium has been determined using a catechol concentration of 2×10^{-4} mol/L, a pH of 6.9 using a 0.01 mol/L PIPES buffer and an accumulation potential of −0.10 V. The stripping process is observed at a peak potential of −0.70 V with a limit of detection of 3×10^{-10} mol/L using a 2 minute accumulation period. This detection limit can be lowered to 10^{-10} mol/L using a 15 minute accumulation period. The V(V) chelate stripping peak is preceeded by that of U(VI) and followed by that of Sb(V). The peak current corresponding to the Sb(V) chelate is relatively low and that of the U(VI) chelate was found not to interfere at concentrations commonly found in sea water (e.g., 1.3×10^{-8} mol/L). The interference of natural organic surfactants in sea water was removed by ultraviolet irradiation.

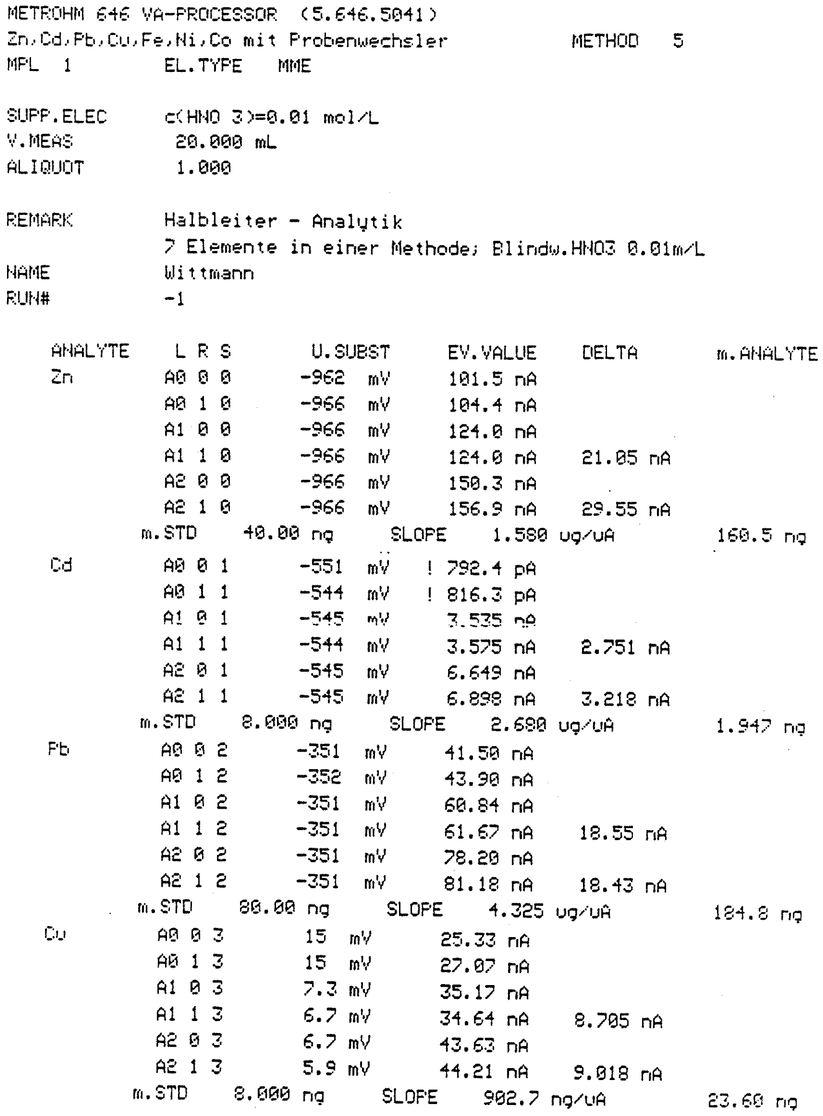
On the basis of the adsorptive characteristics of the V(V) complex with 5-Br-PADAP, a 1.5th and 2.5th order derivative AdSV technique has been developed with a limit of detection of 2.5×10^{-11} mol/L. This method can be used to determine vanadium in tap water samples[46].

b) Co and Ni

Co and Ni can be determined in electronic grade materials by AdSV of their dimethylglyoxime chelates. In these same materials, Cd, Cu, Pb and Zn are determined by ASV (differential pulse mode) and Fe by AdSV of its catechol chelate[1]. The total method for these 7 metals uses the Metrohm 646 VA Processor with the 647 VA Stand and, depending on the degree of automation required, the VA Sample Changer and Multi-Dosimats. The analytical method involves placing one drop of HF on the silicon chip followed by evaporation by warming leaving a white powdery residue. This is dissolved in a drop of conc. HNO_3 and rinsed into the polarographic vessel with ultra pure water (<0.1 µS/cm, 20 °C). A blank is prepared using the same reagents. The first voltammetric step is to simultaneously determine Zn(II), Pb(II), Cd(II) and Cu(II) at pH 5 using ASV in the differential pulse mode of operation. In the second step Fe(III) is determined in PIPES buffer pH 7.0 to 7.2, using AdSV (differential pulse mode of operation) of the Fe(III) catechol chelate. Finally Co(II) and Ni(II) are determined as their dimethylglyoxime chelates in NH_3/NH_4Cl buffer, pH 9.1. In this latter determination, duplicate determination of both Co and Ni is carried out with two standard additions used per element. Fig. 1 shows a typical result block and Fig. 2 shows the voltammograms corresponding to Fe, Ni and Co in the sample. Triethanolamine is used in the preparation of the dimethylglyoxime solution and this increases the sensitivity of the Co determination. At the same time, it suppresses possible interferences due to a relatively large Zn content. The Ni peak is found to be somewhat attenuated.

Co and Ni have been determined in sea water at picomolar and nanomolar concentrations respectively[21]. Cyclohexane-1,2-dione dioxime (nioxime) chelates of Co(II) and Ni(II) were concentrated by adsorption from 10 mL of sample onto a HMDE followed by cathodic stripping using the differential pulse mode. Optimum conditions were ligand concentration 10^{-4} mol/L, HEPES buffer concentration of 0.03 mol/L, solution pH 7.6 and an accumulation potential of −0.6 V. Replicate analyses of sea water reference materials yielded excellent agreement with certified values. Analytical precision for Co and Ni at coastal and open ocean concentrations were approximately ±5% relative standard deviation. Detection limits for Co and Ni were reported to be 6×10^{-12} mol/L and 0.45×10^{-9} mol/L respectively after a 15 minute accumulation period. As an alternative to nioxime, dimethylglyoxime has been used for the determination of Co and Ni in Mediterranean sea water samples[29] and Co in estuarine water samples[30]. The chelating ligand 2,2' dipyridyl has been used for the AdSV determination of Ni in Japanese rivers[31].

The determination of traces of Ni in NIST (formerly NBS) fly ash has been automated using a medium exchange flow system and a chemically modified carbon paste electrode containing dimethylglyoxime[32].



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METROHM 646 VA-PROCESSOR  (5.646.5041)
Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler          METHOD   5
MPL  1          EL.TYPE   MME

SUPP.ELEC       c(HNO 3)=0.01 mol/L
V.MEAS           20.000 mL
ALIQUOT          1.000

REMARK          Halbleiter - Analytik
                7 Elemente in einer Methode; Blindw.HNO3 0.01m/L
NAME            Wittmann
RUN#            -1

    ANALYTE      L R S        U.SUBST      EV.VALUE     DELTA        m.ANALYTE
    Zn          A0 0 0       -962  mV     101.5 nA
                A0 1 0       -966  mV     104.4 nA
                A1 0 0       -966  mV     124.0 nA
                A1 1 0       -966  mV     124.0 nA    21.05 nA
                A2 0 0       -966  mV     150.3 nA
                A2 1 0       -966  mV     156.9 nA    29.55 nA
           m.STD     40.00 ng      SLOPE     1.580 ug/uA             160.5 ng
    Cd          A0 0 1       -551  mV   ! 792.4 pA
                A0 1 1       -544  mV   ! 816.3 pA
                A1 0 1       -545  mV     3.535 nA
                A1 1 1       -544  mV     3.575 nA    2.751 nA
                A2 0 1       -545  mV     6.649 nA
                A2 1 1       -545  mV     6.898 nA    3.218 nA
           m.STD     8.000 ng      SLOPE     2.680 ug/uA             1.947 ng
    Pb          A0 0 2       -351  mV     41.50 nA
                A0 1 2       -352  mV     43.90 nA
                A1 0 2       -351  mV     60.84 nA
                A1 1 2       -351  mV     61.67 nA    18.55 nA
                A2 0 2       -351  mV     78.20 nA
                A2 1 2       -351  mV     81.18 nA    18.43 nA
           m.STD     80.00 ng      SLOPE     4.325 ug/uA             184.8 ng
    Cu          A0 0 3        15   mV     25.33 nA
                A0 1 3        15   mV     27.07 nA
                A1 0 3        7.3  mV     35.17 nA
                A1 1 3        6.7  mV     34.64 nA    8.705 nA
                A2 0 3        6.7  mV     43.63 nA
                A2 1 3        5.9  mV     44.21 nA    9.018 nA
           m.STD     8.000 ng      SLOPE     902.7 ng/uA             23.60 ng
```

Fig. 1a Result block printed out by 646 VA Processor

```
Fe          A0 0 4       -451   mV      16.42 nA
            A0 1 4       -454   mV      16.51 nA
            A1 0 4       -451   mV      24.87 nA
            A1 1 4       -452   mV      24.71 nA     8.325 nA
            A2 0 4       -445   mV      32.59 nA
            A2 1 4       -446   mV      33.53 nA     8.275 nA
          m.STD     50.00 ng      SLOPE     6.023 ug/uA          99.24 ng
Ni          A0 0 5       -948   mV      105.3 nA
            A0 1 5       -948   mV      109.5 nA
            A1 0 5       -948   mV      114.9 nA
            A1 1 5       -948   mV      137.3 nA     18.67 nA
            A2 0 5       -947   mV      136.3 nA
            A2 1 5       -947   mV      159.7 nA     21.94 nA
          m.STD     100.0 ng      SLOPE     4.923 ug/uA          526.3 ng
Co          A0 0 6       -1.089 V       3.047 nA
            A0 1 6       -1.089 V       3.464 nA
            A1 0 6       -1.087 V       6.766 nA
            A1 1 6       -1.087 V       8.159 nA     4.207 nA
            A2 0 6       -1.086 V       11.32 nA
            A2 1 6       -1.085 V       13.43 nA     4.916 nA
          m.STD     4.000 ng      SLOPE     876.8 ng/uA          2.751 ng

rho(Zn)     =     8.029          ug/L
rho(Ni)     =     -----          ug/L
rho(Co)     =     -----          ug/L
rho(Cd)     =   ! 97.36    E- 3  ug/L
rho(Fe)     =     -----          ug/L
rho(Pb)     =     9.242          ug/L
rho(Cu)     =     1.180          ug/L
rho(Cd)     =     -----          ug/L
rho(Pb)     =     -----          ug/L
rho(Fe)     =     4.962          ug/L
rho(Zn)     =     -----          ug/L
rho(Ni)     =     26.31          ug/L
rho(Co)     =     .1375          ug/L

SMPL.V,m          20.0000 mL         IDENT Test mit Probenw.
DATE   87-01-09   TIME    12:37
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Fig. 1b Result block printed out by 646 VA Processor (continued)

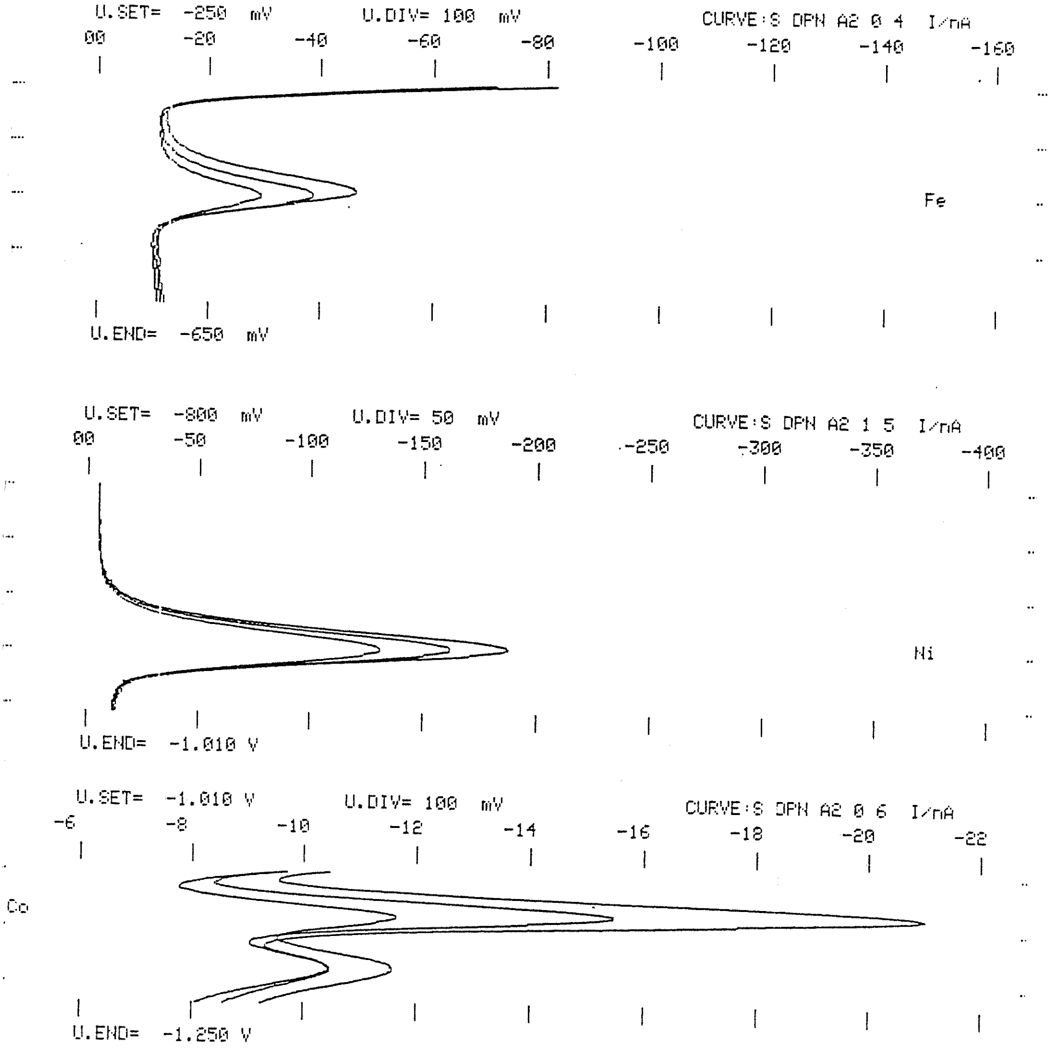

Fig. 2 Voltammograms for Fe, Ni and Co

c) Zr

In the case of Zr, accumulation is achieved through adsorption of a Zr-Solochrome Violet RS chelate onto a HMDE. Optimal experimental conditions were found to be chelating agent concentration 1.5×10^{-6} mol/L in acetate buffer pH 4.6, accumulation potential –0.3 V for 10 minutes and stripping of the chelate using the linear scan mode. The detection limit was found to be 2.3×10^{-10} mol/L[10].

d) Zn

Zn can be determined by AdSV using adsorption of its chelate with APDC on the HMDE from a background electrolyte of 0.01 mol/L NN'-bis-(2 hydroxyethyl)-2 aminoethanesulphonic acid (BES). For a 10 minute accumulation period, a detection limit of 3×10^{-11} mol/L was reported[22]. The Zn content of a NIST (formerly NBS) spinach sample has also been measured by AdSV using the chelating ligand 2,5-dimercapto-1,3,4-thiadiazole (DMTD)[15]. The certificate for spinach lists three major constituents, namely K, Ca and Mg, and 13 trace metal constituents of which Al (870 µg/g), Fe (550 µg/g) and Mn (165 µg/g) are present in the largest amounts. Ten separate determinations for Zn were carried out (sample sizes ranging between 195 and 291 mg) and yielded an average value of 49.10 ± 0.01 µg/g. This compared well with the certified value of 50 ± 2 µg/g.

e) Mo

Mo has been determined by differential pulse AdSV in a pH 2 phosphate buffer utilising the adsorption of 12-molybdophosphoric acid at the HMDE[12]. Using a 1 minute accumulation time, calibration graphs were linear up to 7×10^{-7} mol/L Mo and a detection limit of $< 10^{-9}$ mol/L can be expected. For this method of Mo determination the Metrohm 646 VA Processor was used in conjunction with the 647 VA Stand which incorporates the Multi-Mode Electrode and has the facility of easy, rapid and reproducible production of a HMDE in the voltammetric cell. Fig. 3 shows the differential pulse AdSV for different Mo(VI) concentrations and Fig. 4 the differential pulse AdSV for 5.6×10^{-9} mol/L Mo(VI) in phosphate buffer pH 2.0 for different accumulation times.

AdSV has recently been applied to the determination of Mo(VI) in water and soil using 0.048 mol/L oxalic acid and 6×10^{-5} mol/L Toluidine Blue (pH 1.8) supporting electrolyte. Mo(V), the reduction product of Mo(VI) in the sample solution, can form a ternary complex which can be adsorbed on the SMDE at –0.1 V (vs. Ag/AgCl).

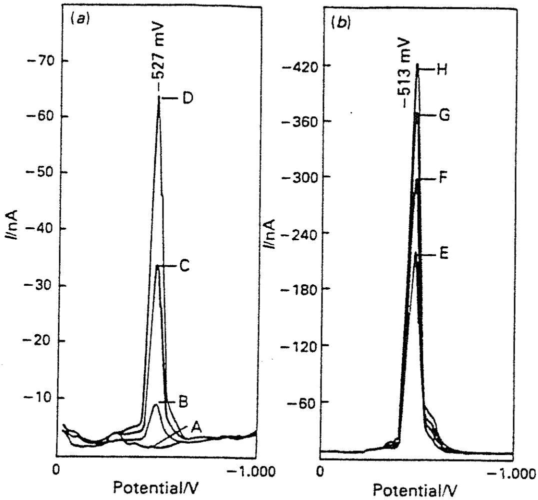

Fig. 3 Differential-pulse adsorptive stripping voltammograms for different Mo(VI) concentrations. Accumulation potential: –100 mV. Accumulation time: 1 min. Mo concentration: A 0; B 1.1×10^{-7}; C 2.2×10^{-7}; D 3.3×10^{-7}; E 4.0×10^{-7}; F 5.1×10^{-7}; G 6.2×10^{-7} and H 7.4×10^{-7} mol/L.

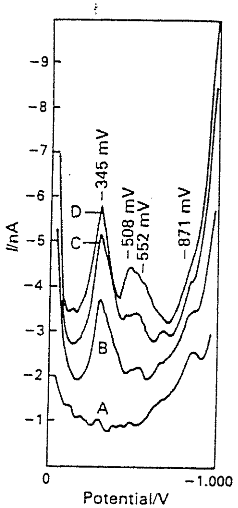

Fig. 4 Differential-pulse adsorptive stripping voltammograms for Mo (5.6×10^{-9} mol/L) in phosphate buffer, pH 2.0. Accumulation time: A 0; B 2; C 4 and D 6 min.

Permission to reproduce Figs. 3 and 4 from Reference 12 has been granted by the Royal Society of Chemistry, UK.

f) Al

As with Zr, Al can be similarly determined using AdSV of its Solochrome Violet RS chelate[16]. Optimal experimental conditions were found to be an accumulation potential of –0.45 V and a ligand concentration of 10^{-6} mol/L; the linear scan stripping mode gave a detection limit of 0.15 ppb (5.5×10^{-9} mol/L) using a 10 minute accumulation period. Most cations were found not to interfere in this determination of Al and the Fe(III) interference could be eliminated by addition of ascorbic acid. The method was applied to snow samples in the vicinity of a smelter.

g) Se

Se(IV) can be determined by CSV after the formation of a piazselenol with 3,3'diaminobenzidine[18]. The Se was then accumulated as HgSe at the HMDE held at –0.45 V. Differential pulse CSV gave a detection limit of 0.01 ppb. For the determination of Se(IV) in natural waters, interferences can be avoided by extraction of the piazselenol into toluene followed by back extraction into 0.5 mol/L HCl. The accuracy of the method was checked by analyses of a standard reference material and applied to the determination of Se(IV) in sea water samples at concentrations of the order of 20 ng/L with a concentration factor of 10 during the extraction procedure. Stara et al[34] have used the same ligand to give a working method with a linear calibration curve in the range 3.10^{-9} to 3.10^{-8} mol/L. Wang et al[35] have found a limit of detection of 4×10^{-10} mol/L for Se(IV) using AdSV of its complex with phenylenediamine.

h) Pt

AdSV has recently been applied to the determination of Pt in blood[36], for use in estimation of natural Pt levels, for monitoring patients treated with Pt containing cytotoxic drugs and for monitoring occupational exposure to these drugs and other Pt containing compounds. Blood samples were dry ashed in a muffle furnace and Pt determined by adsorption of the Pt-formazone complex which results in catalytic hydrogen evolution following reduction of available protons[37]. This effect has also been observed in the AdSV of the antibiotic Cephalothin at the SMDE[38]. The detection limit for a 100 µL sample of blood is 0.017 ppb, the recovery 94% and the relative standard deviation 7% at a Pt level of 1 ppb. The results were verified by inductively coupled plasma mass spectrometry (ICP-MS) with blood prepared by wet ashing and using Au as an internal standard (Table 2).

Table 2 Determination of blood Pt levels by ICP-MS after wet ashing and AdSV after dry ashing

Sample	Pt concentration in ppb	
	ICP-MS	AdSV
A	1.71 ± 0.04	1.66 ± 0.11
B	0.61 ± 0.03	0.58 ± 0.03
C	0.47 ± 0.01	0.51 ± 0.05
D	0.85 ± 0.02	0.74 ± 0.06
E	2.33 ± 0.03	2.24 ± 0.16

i) Ge

Ge(IV) has been adsorbed on a SMDE in the form of a catechol chelate followed by differential pulse voltammetric determination at –0.61 V (vs. Ag/AgCl)[39]. Optimum solution conditions were 3.2 mmol/L catechol, 0.7 mol/L acetate buffer (pH 4.5) and 0.1 mol/L sodium perchlorate. As(III) and Sn(II) interfered with the determination. Ge was determined in Al-Ge alloys as shown in Table 3.

Table 3 Determination of Ge in Al-Ge alloys by AdSV

Sample	Sample taken mg	Ge found mg	Conc.[b] %	Rel. standard deviation %
Alloy I (12.4%)[a]	22.0	2.65 ± 0.12	12.1 ± 0.5	2.2
	25.3	3.07 ± 0.05	12.2 ± 0.3	
	20.7	2.60 ± 0.10	12.5 ± 0.5	
		Mean	= 12.3 (n = 9)	
Alloy II (23%)[a]	10.3	2.59 ± 0.10	25.1 ± 0.9	1.8
	12.9	3.18 ± 0.13	24.7 ± 1.0	
	11.2	2.74 ± 0.12	24.4 ± 1.0	
		Mean	= 24.7 (n = 9)	

[a] certified values.

[b] 95% confidence limit.

An AdSV technique has been developed by Schleich et al.[40] based on the accumulation of Ge(IV)-diol complexes. Pyrogallol gave rise to a limit of detection of 0.1 ng/mL with a standard deviation of ±13%. The method was applied to Ge(IV) determination in ginseng and garlic.

j) Cd

Chiang et al[15] have studied various sulphur-containing ligands for the AdSV of Cd and Zn and concluded that 2,5-dimercapto-1,3,4-thiadiazole (DMTD) was the preferred ligand. They have developed a method for the direct determination of these metals in biological samples using benzyltrimethylammonium methoxide as the digesting solvent.

k) Pd

Preconcentration in the case of Pd has been achieved by adsorption of the dimethylglyoxime chelate on a HMDE in a stirred acetate buffer solution (pH 5.15) containing 2×10^{-4} mol/L ligand at an accumulation potential of –0.20 V. For a 10 min preconcentration time, the limit of detection is 20 ng/L (2.1×10^{-10} mol/L)[41].

l) Cr

Torrance et al[42] have developed an analytical method for the direct determination of soluble Cr at concentrations <2 µg/L in simulated PWR (Pressurized Water Reactor) coolant by differential pulse AdSV. The method is based on measurement of the current associated with reduction of a Cr(III)-DTPA chelate (DTPA = diethylenetriaminepentaacetic acid). No interference was observed from other transition metal ions expected to be present in PWR coolant.

The use of the Cr(III) complex with 5-Br-PADAP gives rise to an AdSV method with a limit of detection of 9×10^{-10} mol/L and is applicable for the determination of total Cr in millet and rice[43].

m) Sn

Sn can be complexed with tropolone prior to AdSV[44] and results in a method of superior detection limit and selectivity to conventional ASV. The limit of detection was 2.3×10^{-10} mol/L (28 ng/L) and the method was free from interference by Pb, Cd, In and Tl, which seriously interfere with conventional ASV methods.

n) As

As has been measured in oyster tissue[45] by AdSV after digestion of the sample with benzyltrimethylammonium methoxide and chelation with 2,5-dimercapto-1,3,4-thiadiazole (DMTD). An attempt was also made to extend the method to simultaneous determination of As, Se and Ni in oyster tissue and this results in some distortion of both peak potential and peak shape.

o) Ti

Ti(IV) forms a complex with 4-(2-pyridylazo) resorcinol (PAR) in weakly acidic solutions and this[47] has been used to develop an AdSV method with a detection limit of 0.1 ng/g.

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