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A novel graphite electrode for mercury-free adsorptive stripping analysis

Kh. Brainina, L. Kalnischevskaia, N. Malakhova, P. Rach, C. Berndt

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Introduction

Stripping voltammetry on stationary electrodes is a well established electrochemical ultratrace analytical technique for the determination of toxic elements such as Cd, Pb, Ni, Co, etc. in the lowest µg/L (ppb) range. Its merits are especially the very high sensitivity and the possibility to perform multielement determinations. A disadvantage of this already classical trace determination technique is the use of mercury as electrode material in the form of hanging drops or as thin films on conductors such as carbon materials.

A novel carbon electrode which can be manufactured on an industrial base in different geometrical shapes allows now to analyse a number of elements without the use of mercury. The new type of graphite electrode is commercially available from Metrohm under the name ‹Ultra Trace Graphite Electrode›.

A new electrochemical conditioning procedure controlled by the Metrohm 693 VA Processor optimizes the electrode behaviour.

The determinations are based on adsorption and subsequent stripping of the metal complexes. With some applications there is no need to deareate the electro-

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lyte. The mercury-free applications which have been developped until now for the use in real samples are the determination of Cr, W and Se.

Experimental section

Electrodes Working:
Impregnated graphite: ‹Ultra Trace Graphite electrode›, Metrohm 6.1204.10
The electrode has to be conditioned electrochemically before the determinations.

Reference: Ag/AgCl/KCl (3mol/L) Metrohm 6.0728.020 + 6.1245.100

Auxiliary: Glassy Carbon Metrohm 6.1247.000 + 6.1241.020

Instruments
693 VA Processor (Metrohm)
694 VA Stand (Metrohm)
705 UV Digester (Metrohm)

Instrument parameters

	Cr determination	*W determination*
Type	CAdSV	AAdSV
Method	DCT	DP 50mV
Electrolysis	60 to 300 s	10 to 180 s
Initial voltage	0.35 V	−0.5 V
Final voltage	−0.05 V	−0.05 V
Sweep rate	40 mV/s	20 mV/s
Peak potential	60 mV ± 30 mV	−230 mV ± 10 mV

CAdSV: Cathodic Adsorptive Stripping Voltammetry
AAdSV: Anodic Adsorptive Stripping Voltammetry.

Chemicals
Reagents of the highest purity available and also high purity water have been used.

Sample preparations
Organic matrices in water samples have to be destroyed through UV Photolysis under the following conditions:

pH of the sample between	1...2
Duration of pretreatment	2 hours
Temperature	90 °C
Added H_2O_2 volume	100 µL per 10 mL sample

		I	II	III	IV	V	VI	VII	VIII			
I	1	H										He
II	2	Li	Be	B	C	N	O	F				Ne
III	3	Na	Mg	Al	Si	P	S	Cl				Ar
IV	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	
	5	Cu	Zn	Ga	Ge	As	Se	Br				Kr
V	6	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	
	7	Ag	Cd	In	Sn	Sb	Te	I				Xe
VI	8	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	
	9	Au	Hg	Tl	Pb	Bi	Po	At				Rn
VII	10	Fr	Ra	Ac	Ku							

	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Elements that can be determined without mercury application.
Elements that can be determined with mercury application only.
Elements that can be determined either with or without mercury.

Table 1: Elements that can be determined by Stripping Voltammetry.

Determination of Chromium traces

Chromium (VI) undergoes a redox reaction with 1,5-diphenylcarbazide forming a chromium(III) complex. This Cr(III)-diphenylcarbazonate complex is adsorbed on the graphite electrode. It can be stripped from the graphite surface.

In the range of 1 to 25 ppb the DC stripping current is proportional to the chromium (VI) concentration. The working range of the determination is 1 to 250 µg/L.

$$2Cr^{6+} + 3DPCI = 2Cr^{3+} + 3\ DPCO + 6H^{+}$$
$$Cr^{3+} + DPCO = [CrDPCO]^{+} + 2H^{+}$$

Organic compounds present in the samples (e.g. natural waters) cause strong interferences. Therefore, they have to be removed e.g. by UV digestion.

Chromium should be determined immediately after sampling and filtering through cellulose nitrate membrane filter of 0.45 µm

Matrix	Preparation	Sample size, ml	Final results	RSD %
0.15 M H_2SO_4	–	20	Added: 1.00 µg/L Found: 1.06 µg/L	10.3
0.15 M H_2SO_4	-	20	Added: 1.00 µg/L Found: 0.91 µg/L	9.0
Artificial sea water	–	20	Added: 1.00 µg/L Found: 1.13 µg/L	5.3
Sea water (Canary Islands)	–	20	Added: 1.00 µg/L Found: 0.82 µg/L	2.4
Sewage water (A)	UV + H_2O_2	0.02	5,59 mg/L	8.9
Sewage water (B)	UV + H_2O_2	0.5	146.3 µg/L	3.8

Table 2: Results of Cr^{6+} determinations

Matrix	Preparation	Sample size ml	Final results	RSD %
0.9 M H_2SO_4	–	20	Added: 2.50 µg/L Found: 2.30 µg/L	8.0
0.9 M H_2SO_4	-	10	Added: 8.00 µg/L Found: 7.74 µg/L	4.1
Artificial sea water	UV	10	Added: 5.00 µg/L Found: 5.28 µg/L	6.5
Sea water (Canary Islands)	UV	10	<0.1 µg/L	
Sewage water (A)	UV	2	3.3 µg/L	18.6
Sewage water (B)	UV	2	<0.1 µg/L	

Table 3: Results of W^{6+} determinations

pore size. In case the samples cannot be directly analyzed, an addition of HNO_3 to reach pH = 2 is recommended.

If Cr(III) is present in the samples it has to be oxidized by Ammonium Persulphate solution prior to the determination.

The chromium content is determined by the standard addition method.

Determination of Tungsten traces

W(V) is concentrated on the surface of the graphite electrode by means of the electrochemical reduction of W(VI). W(V) forms a sparingly soluble complex with e.g. antipyrine and thiocyanate ions. The analytical signal is the anodic oxidation current of the compound concentrated on the graphite electrode. Determinations are possible in the range of 0.2 to 50 µg/L (ppb).

Organic compounds present in the samples interfere with the determination. Therefore, they have to be removed by UV digestion. Interferences of Fe(III) up to a concentration of 100 mg/L is being eliminated by reduction to Fe(II) with ascorbic acid. When the amount of Cu(II) in the samples exceeds the amount of W(VI) 200 times Cu-ions have to be bound by thiourea.[2]

The following scheme can be used to visiualize the electrochemical conentration of W(VI):

$$WO_2^{2+} + e^- = WO_2^+$$
$$WO_2^+ + 3\ SCN^- + nR + 2H^+ = WO(SCN)_3R_n + H_2O$$

R: Pyramidone or Antipyrine.

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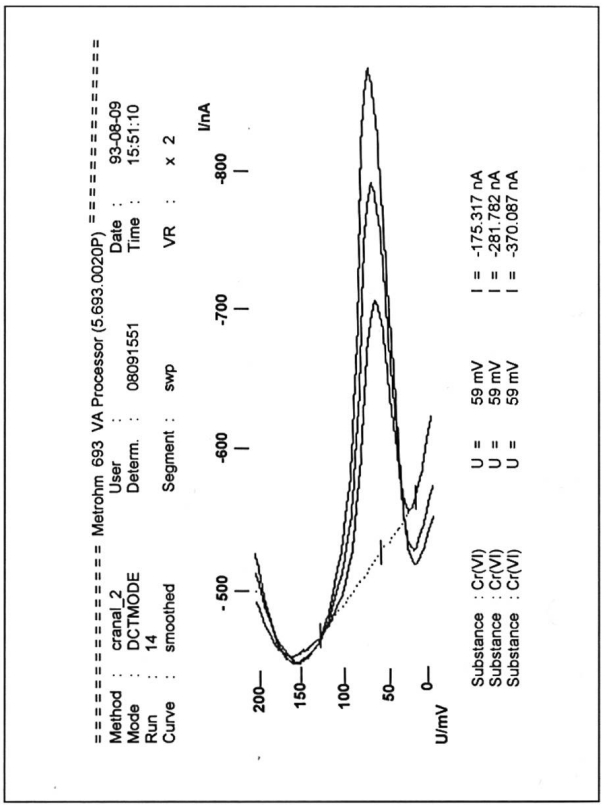

Fig. 1: Curves of Cr determination ρ (Cr) = 1 µg/L of model water by CAdSV (2 standard additions).

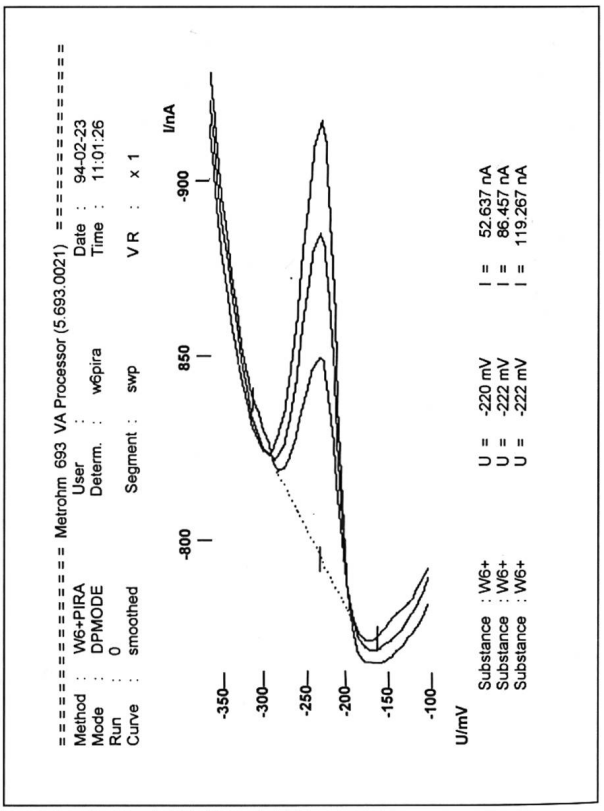

Fig. 2: Curves of W determination ρ (W)= 1 µg/L of model water by CAdSV (2 standard additions).