

GALVANIC AND POTENTIOMETRIC STRIPPING METHODS IN POLLUTION MONITORING OF CHROMIUM

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ABSTRACT

Galvanic and potentiometric stripping methods are described for the determination of trace amounts of chromium (III) using glassy carbon as working electrode. The developed procedures are useful for the determination of 0 to 50 ppb of chromium (III). The methods are precise and useful in simultaneous determination of hexavalent and trivalent chromium in tap water samples.

Key words: Galvanic stripping method, potentiometric stripping method, pollution monitoring of Cr(III)

INTRODUCTION

The toxicity of chromium is wellknown and a voluminous literature is available for the pollution monitoring by various analytical techniques [1]. Electroanalytical techniques were also developed to determine trace amounts of chromium. The most widely used techniques include single sweep and differential pulse polarographic techniques to determine trivalent and/or hexavalent chromium [2-4]. Stripping voltammetric procedures using solid electrodes are preferred over those involving mercury electrodes in view of the toxicity of the mercury, rapidity of the determination and their capability in enhancing the sensitivity. The determination of chromium by stripping voltammetric techniques falls broadly into three classes of reactions viz by reduction of hexavalent chromium to trivalent chromium and preconcentrating as $\text{Cr}(\text{OH})_3$ [5,6] formation of insoluble mercurous salts [7] and the reduction of trivalent chromium to chromium metal [8,9]. The procedures based on the first two reactions are not reproducible and optical conditions must be found empirically.

Potentiometric stripping analysis [10,11] is a wellknown analytical technique for the determination of heavy metals. Recently, we introduced a novel electroanalytical technique termed galvanic stripping analysis for the determination of cadmium using mercury film coated glassy carbon electrode [12]. This paper describes the usefulness of these techniques in the determination of trace amounts of chromium in tap water samples

EXPERIMENTAL

Reagents

All solutions were prepared using BDH, AR grade chemicals in conductivity water.

Chromium (III) solution, 0.01 M: Dissolve 0.4940 g of chromic potassium sulphate in water and dilute to 100 ml.

Chromium (VI) solution, 0.1 M: Dissolve 1.9421 g of potassium chromate in water and dilute to 100 ml.

Mercury (II) solution, 0.01 M: Dissolve 0.8550 g of mercuric nitrate in water and dilute to 100 ml.

Sodium chloride solution, 5 M: Dissolve 29.22 g sodium chloride in 100 ml of water.

Chloroacetic acid, 1.0 M: Dissolve 23.85 g of monochloroacetic acid in 250 ml of water.

Apparatus

A Wenking Model LB-75 M potentiostat and a Wenking potential scan generator Model VSG 72 were used with a three electrode cell assembly: a normal calomel reference, platinum foil counter and a glassy carbon (Tokai & Co. Japan, 3 mm dia) working electrode. The recordings were made on a Digilog XY-200 Recorder.

Procedure

Galvanic stripping analysis of chromium (III): Transfer a suitable aliquot (up to 40 ml) of the sample solution containing 0-50 ppb of chromium (III) into a 50 ml volumetric flask. Add 5 ml each of buffer and sodium chloride and dilute to volume with double distilled water. Transfer the solution to electrochemical cell. Preconcentrate chromium as Cr metal for 4 minutes by depositing at -1.1 V vs NCE while stirring. At the end of deposition period, switch off the applied potential and record the open circuit potential as a function of time. Prepare a calibration graph for 0-50 ppb of chromium (III) by the same procedure.

Potentiometric stripping analysis of chromium (III): Proceed as in case of galvanic stripping analysis after the addition of 0.5 ml of 10^{-3} M mercury (II).

Simultaneous determination of chromium (III), chromium (IV) and total chromium

Establish the chromium (III) concentration as described earlier by using either galvanic or potentiometric stripping methods. Reduce the chromium (VI) if any to chromium (III) with ferrous sulphate after acidifying the sample to 2 M in HCl. Adjust the pH to 2.5 and determine total chromium by the procedures described above. The difference of chromium contents of second and first determination gives the amount of hexavalent chromium present in the sample.

Determination of chromium in tap water

Proceed as above and establish the chromium concentrations by referring to the calibration graph and also by standard addition technique.

RESULTS AND DISCUSSION

Preliminary studies on the choice of supporting electrolyte indicated that the galvanic and potentiometric stripping signals are maximum in 0.1 M chloroacetate (pH 2.5) buffered medium compared to 0.1 M (pH 5) and 0.1 M ammonia - ammonium chloride (pH 9) buffered media. It was also noticed that galvanic and potentiometric stripping signals are not resolved (i.e. do not exhibit clear-cut breaks in E-t profiles) in 0.5 M sodium chloride medium. However, on the addition of 0.5 M sodium chloride to chloroacetate buffered solution, there is a significant enhancement in the sensitivity, i.e. 5 fold increase (as compared to pure chloroacetate buffer media) as seen from fig. 1.

Effect of pH

The effect of pH on the deposition and subsequent stripping of 25 ppb of chromium by galvanic (curve A) and potentiometric (curve B) methods is shown in fig. 2. It is clear from the figure that the constant and maximum analytical signal is obtained in the pH range 1.5 to 3. Hence, pH 2.0 chloroacetate buffer is used in subsequent experiments.

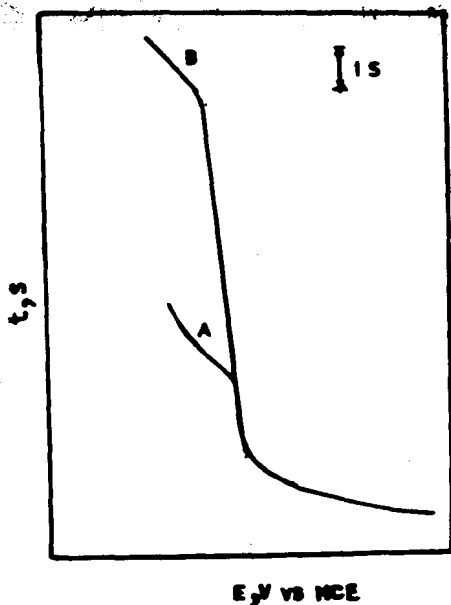


Fig. 1 Effect of addition of sodium chloride on the stripping signal of chromium (III), pH 2.0 chloroacetate solution, concentration of chromium (III) = 50 ppb, deposition potential (E_d) = -1.1 V vs NCE, time of deposition (t_d) = 4 min. curve A = 0.1 M chloroacetate buffer; curve B = 0.1 M chloroacetate buffer + 0.5 M NaCl

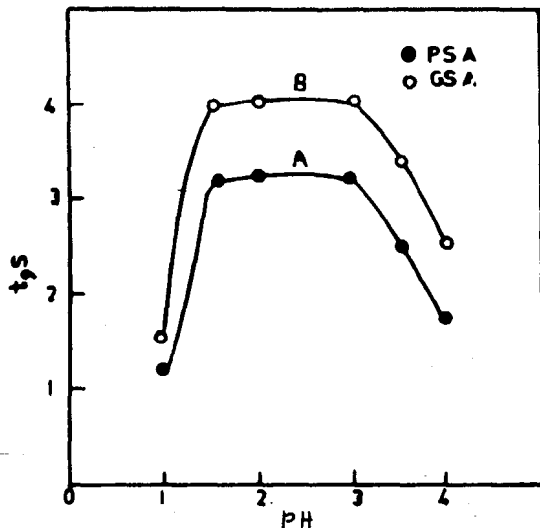


Fig. 2 Effect of pH on the potentiometric and galvanic stripping determination of chromium (III); 0.1 M chloroacetic acid + 0.5 M sodium chloride, E_d = -1.1 V, t_d = 4 min.

Effect of sodium chloride concentration

The effect of addition of varying amounts of sodium chloride in the concentration range 0.1 to 1.0 M to chloroacetate buffer during the determination of 25 ppb of chromium (III) on the galvanic and potentiometric stripping signal was then evaluated. In both the methods, the stripping signal increases with increase in sodium chloride concentration and reaches a constant and maximum value over and above 0.35 M. Hence, 0.5 M sodium chloride is used in subsequent experiments.

Effect of deposition potential (E_d)

In order to ascertain optimum deposition potential, E_d was varied in the range -0.7 to -1.3 V vs NCE with 4 min. of pre-concentrative deposition in 25 ppb chromium (III) solution. As seen from Table I, the stripping signals reach a maximum value at -1.0 V and remain constant on further change upto -1.3 V.

Table-I Effect of deposition potential

Cr (III) = 25 ppb, pH=2, 0.1 M ClCH₂ COOH + 0.5 M NaCl, t_d = 4 min.

Deposition potential E_d (V vs NCE)	Stripping times (s)	
	GSA	PSA
-0.70	0.40	0.36
-0.80	2.00	1.40
-0.90	3.60	3.00
-1.00	4.00	3.20
-1.10	4.00	3.20
-1.30	4.00	3.20

Effect of time of deposition

The effect of deposition time on galvanic and potentiometric stripping signals of 25 ppb of chromium was next investigated by keeping deposition potential constant at -1.1 V. The results obtained are shown in Table II from which it is clear that stripping signal is in proportion to time of deposition only up to 4 minutes.

Table-II: Variation of deposition time

Cr (III) = 25 ppb, pH = 2, 0.1 M ClCH₂ COOH + 0.5 M NaCl, E_d = -1.1 V

S. No.	Time of deposition (min.)	Stripping time (s)	
		GSA	PSA
1	2	2.0	1.6
2	4	4.0	3.2
3	6	4.8	3.8
4	8	5.6	4.5
5	10	6.0	4.8

Variation of chemical oxidant

The effect of addition of varying amounts of mercury during the potentiometric stripping determination of 25 ppb of chromium (III) is shown in fig. 3.

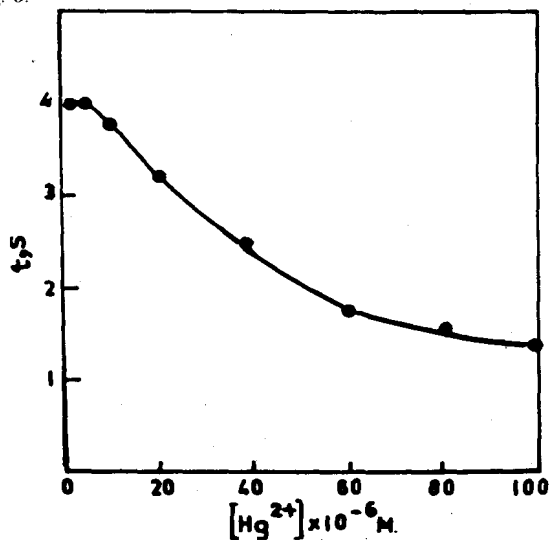


Fig. 3: Effect of chemical oxidant on the galvanic stripping signal; pH 2, chloroacetate buffer (0.1 M) + 0.5 M sodium chloride, E_d = -1.1 V, t_d = 4 min.

As clear from the figure, additions up to 5×10^{-6} M Hg(II) did not have any effect on time required for stripping i.e. galvanic stripping alone is operative. However, on further increase of concentration of mercury (II), the time of stripping decreases. The potentiometric stripping is constant over a very narrow concentration range of mercury (10^{-5} to 2×10^{-5} M). Hence, 10^{-5} M mercury (II) was used in further studies.

Calibration graph and precision

The calibration graphs obtained by the recommended galvanic and potentiometric stripping methods are linear over the range 5 to 50 ppb of chromium (III) and pass through the origin. The coefficient of variation for 5 replicate determinations of 25 ppb of chromium (III) were found to be 1 and 1.5% for galvanic and potentiometric stripping methods respectively.

Estimation of total chromium and chromium (VI)

Total amount of chromium is estimated by reducing hexavalent chromium, to trivalent form after acidification to 2 M in HCl and on addition of 10^{-3} M ferrous sulphate. After addition of slight excess of Fe (II), the acidity of sample is adjusted to pH ~ 2 and then buffered with 0.1 M chloroacetate solution and total chromium content is determined by galvanic and potentiometric stripping methods as described in 'Procedure'. The difference in chromium contents with and without reduction with ferrous ion gives the amount of chromium (VI) present in sample. Table III presents the recoveries obtained by subjecting the synthetic samples of varying ratios of chromium (VI) and chromium (III). From the recoveries, it is clear that galvanic and potentiometric stripping methods are useful in determination of mixtures of chromium (III) and (VI).

Table -III : Analysis of synthetic mixtures of Cr (III) and Cr (VI)

S. No.	Aliquot taken (ml)	Amount added (ppb)		Amount found (ppb)		Recovery (%)	
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	50	5	45	5.0	44.0	100	98.0
2	50	10	20	10.0	19.5	100	97.5
3	50	20	40	19.8	40.0	99	100.0
4	50	30	10	30.0	9.9	100	99.0
5	50	40	5	40.0	5.0	100	100.0

Analysis of tap water samples

Aliquots (≤ 40 ml) of tap water are subjected to analysis for the determination of total and individual amounts of chromium (VI) and (III) by following the procedures described in 'Experimental'. The results obtained are shown in Table IV, from which it is clear that the developed galvanic and potentiometric stripping methods are useful in pollution monitoring of chromium.

Table -IV : Analysis of tap water samples

S. No.	Aliquot taken (ml)	Amount added (ppb)		Amount found (ppb)		Recovery (%)	
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	20	—	—	—	—	—	—
2	40	—	—	—	—	—	—
3	20	5	10	5.0	4.9	100	98
4	30	10	5	10.0	5.0	100	100
5	40	20	5	20.0	5.0	100	100

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