Chemistry for Sustainable Development **14** (2006) 23–27

Inversion Voltammetry for Mercury Detection in Lithium-Containing Solutions and Carbon Sorbents

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(Received February 15, 2005; in revised form October 31, 2005)

Abstract

Inversion voltammetry method applying glass carbon electrode was developed for the case specific mercury control. Mercury concentration was measured in the lithium-containing solvents and in modified carbon adsorbents (MCA). In MCA mercury content was measured after weighted sample burning and mercury stripping by the H_2O_2 containing 1 M HCl solution. Diapason of mercury concentration measurement was 0.2–3.5 mg/l, s_r = 4–9 %.

INTRODUCTION

Nowadays environmental problems attract a lot of research attention due to the growing amount of liquid and solid wastes containing toxic substances and heavy metals. These problems become rather serious at chemical plants using mercury and its compounds, since metallic mercury is very toxic for all life forms. All existing plants producing alkali metals and their salts, lithium in particular, use a lot of process mercury, and therefore should include technologies, neutralizing solid and liquid mercury containing wastes. These technologies require precise analytical methods for the mercury content control. Inversion voltammetry method (IVA) may serve as an express and inexpensive method for mercury control in the processes of lithium production (alkali solutions, lithium hydroxide solutions, wastewater). Usually IVA is widely used for analysing chloride, nitrate, and mixed thiocyanate-perchlorate mercury-containing solutions [1–3] with graphite and carbon electrodes [4, 5]. However, lithium process solutions contain a lot of salts, which cause the smearing of mercury peaks in the registered volt-ampere curves and thus distortion of analysis results. Mercury detection in MCA, used at acid wastewater purification from mercury, also meets several complications [6, 7].

In the present study we focus on developing the IVA based method for detecting mercury in lithium-containing solutions and carbon adsorbents.

EXPERIMENTAL

IVA method was applied for measuring mercury content in the lithium production wastewater (pH 3–4, 8.5–10) containing 0.2–3.5 mg/l of mercury, and in carbon adsorbents with a mercury content of 0.002–0.009 mass %.

In the study we used Hg^{2+} solutions (10, 1, 0.01 mg/l) prepared by diluting standard solution GSO No. 7343–96 acidified with HNO_3. IVA measurements were performed in a three-electrode cell with potentiostate PI-50-1 with programmer PR08 and two-coordinate potentiometer LKD4-003. Chlorine silver electrode was used as the reference one. Platinum electrode was the auxiliary electrode. Glass carbon electrode with a working surface of 13.7 mm^2 was used as the indicating one (Fig. 1).

Preliminary experiments were done under the following conditions:

a) 0.1 M HCl solution: accumulation potential $E_a = -0.6$ V, regeneration potential $E_r = +0.5$ V, set-up time τ_s = 30 s, regeneration time τ_r = 2 min, $C_{Cd} = 10^{-6}$ mol/l;

b) 0.02 M KSCN solution: $E_a = -0.7$ V, $E_r = +0.8$ V, τ_s = 30 s, τ_r = 1 min, accumulation time τ_a = 5 min, $C_{Cd} = 10^{-6}$ mol/l;

c) 0.1 M $HClO_4$ solution: $E_a = -1.0$ V, $E_r = +1.8$ V, τ_s = 30 s, τ_r = 2 min, τ_a = 5 min, $C_{Cd} = 10^{-6}$ mol/l.

We have also studied base electrolyte effect (HNO_3 solution 1 : 1, 0.1 M HCl, 0.1 M HCl + H_2O_2) on the mercury analysis sensitivity. Anode Hg dissolving current force was found to be linear with respect to Hg content as $HgNO_3$ in the HNO_3 medium in a range of 1–3 mg/l. According to experimental results we have chosen base electrolyte 0.1 M HCl + H_2O_2 in order to expand measurable mercury content range to that of 0.2–3.5 mg/l. Hydrogen peroxide (2.5 ml of 29 % H_2O_2 per 50 ml of HCl) was added to oxidize metallic mercury in the lithium-containing solutions. We also added 1–2 ml of cadmium chloride solution (containing 0.2 mg/l Cd^{2+}) into the analysed 50 ml sample to increase the sensitivity towards mercury signal [1].

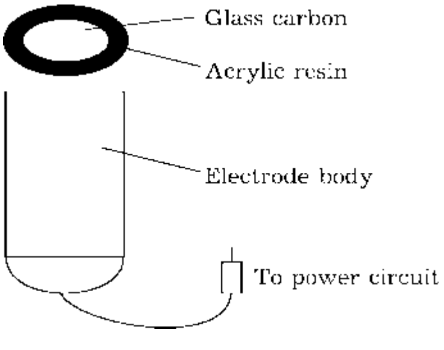

Fig. 1. Measuring electrode presented schematically.

Measurements were done under the following conditions: medium – 0.1 M HCl solution (with H_2O_2 and Cd^{2+} addition), $E_a = -0.6$ V, $E_r = +0.5$ V, τ_a was varied from 200 to 500 s, τ_s = 20 s, τ_r = 120 s, scan rate was 0.2 cm/s at potential ranging from –0.1 to 0.8 V. Before each measurement we mechanically renewed the electrode working surface with an abrasive (alumina, grains 14 μm in size), and registered the volt-ampere plot of the "blank" 0.1 M HCl solution.

Results reproducibility was set by the steady state hydrodynamic regime at the mixing of analysed solution during accumulation stage (for the purpose we used magnetic stirrer operated with a rate of 100 min^{-1}). Measurement duration was 3–8 min in total.

RESULTS AND DISCUSSION

Figures 2 and 3 show typical mercury peaks on the volt-ampere curves and also peak height *versus* accumulation time. While mercury precipitated on the glass carbon electrode is dissolving, maximum current force is linear with respect to mercury content in the range of 0.2–3.5 mg/l. Calibration plot for Hg^{2+}, calculated regarding the height of the volt-ampere peaks, is given in Fig. 4. Mercury analysis results are listed in Table 1.

Samples preparation

Lithium-containing solutions. Preliminary experiments have shown mercury to stay as Hg^0 (87 %) and Hg^{2+} (23 %) in the 4 M LiOH solutions. Conventional IVA mercury analysis in such solution is not possible (even after the complete Hg^0 oxidation) due to the mercury peak smearing. Therefore, samples were preliminarily prepared for analysis. Sample aliquot (100 ml) by HCl to pH 4–6 was neutralized. Then 0.5 ml of 2 % $KMnO_4$ solution and 0.5 ml of concentrated H_2SO_4 were added, and thus prepared mixture was heated at 80 °C for 20 min to convert Hg^0 into Hg^{2+}. After that 1 ml of 10 % $SnCl_2$ solution was added. After solution lost its colour, and thus all Hg^{2+} was reduced to Hg^0, whole sample was accurately transferred into the Polezhaev vessel [8]. Then

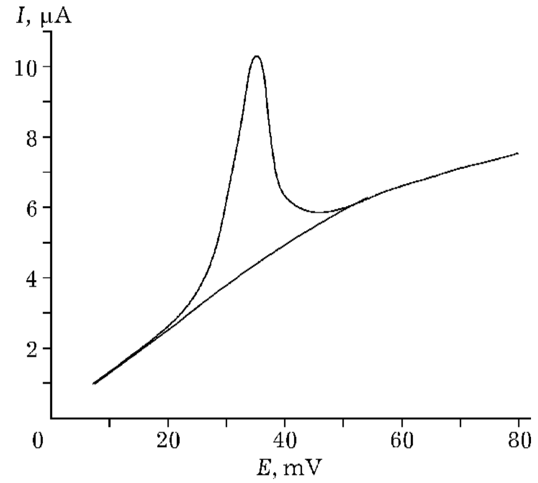

Fig. 2. Typical mercury peak on a volt-ampere curve.

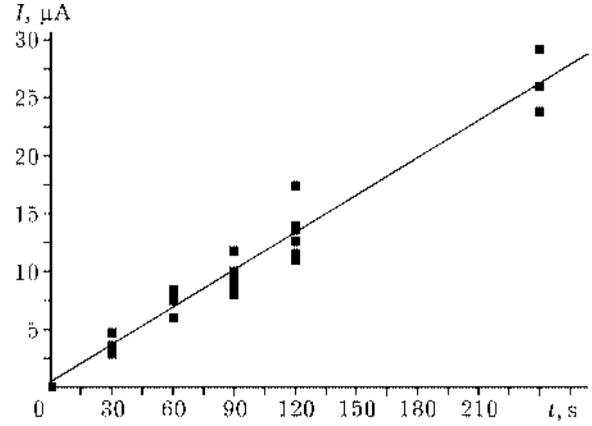

Fig. 3. Mercury peak height *versus* accumulation time.

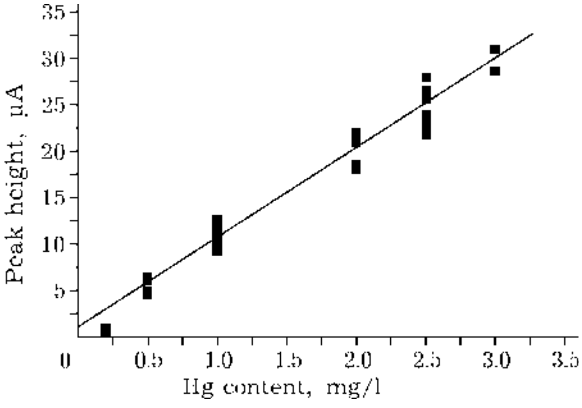

Fig. 4. Calibration plot for determining mercury content in solution 0.1 M HCl + H_2O_2.

TABLE 1

Measured Hg^{2+} content in model solutions (1 M HCl + H_2O_2)

Exp. No.	Hg content, mg/l		Number of measurements	s_r, %
	Introduced	Detected		
1	0.50	0.48 ± 0.04	2	9
2	1.00	0.93 ± 0.08	6	9
3	2.00	1.96 ± 0.08	5	4
4	2.50	2.46 ± 0.10	6	4
5	3.00	2.95 ± 0.18	2	6
6	4.00	3.80 ± 0.23	5	6

TABLE 2

Mercury content analysis in lithium-containing solutions

IVA data	AAS data	s_r, %
0.015 ± 0.003	0.020 ± 0.005	20
0.018 ± 0.002	0.020 ± 0.005	9
0.20 ± 0.02	0.19 ± 0.05	6

for 30 min it was bubbled with preliminary cleaned air with a flow rate of 0.4 m/s. Thus mercury was stripped away and absorbed in another Polezhaev vessel by 10 ml of solution 0.1 M HCl + 0.5 ml 29 % H_2O_2. After that IVA method was used to determine Hg^{2+} concentration in the 0.1 M HCl solution. Analysis results were well reproduced in the mercury content range of 0.2–3.5 mg/l. Three independent measurements were done to obtain reliable results.

For the IVA analysis accuracy estimation, IVA data were compared with the atomic absorption spectroscopy (AAS) data, obtained for the same samples (Table 2). Apparently, IVA results obtained for mercury content range 0.2–3.5 mg/l well agree with the AAS data, error being 9–20 rel. %.

Carbon adsorbents. MCA samples weighting 0.2–5 g were put into nickel holders then inserted into a quartz tube reactor, where samples were heated to 600 °C. Afterwards mercury was stripped away by the clean airflow (10 l/min) for 30 min into absorbing solution, where its content was determined. Mercury content in the MCA samples was ranging from 0.002 to 0.009 mass %. Experimental set-up for thermal mercury stripping is schematically shown in Fig. 5.

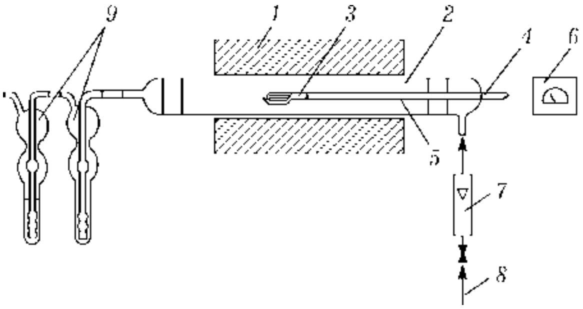

Fig. 5. Set-up for mercury thermal stripping: *1* – tube furnace, *2* – reactor (glass, quartz), *2* – analysed sample holder, *4* – thermocouple, *5* – thermocouple jacket, *6* – voltmeter, *7* – rotameter, *8* – compressed air supply, *9* – absorbing vessels.

TABLE 3

Mercury stripping degree *versus* time (sample mass 0.3 g, mercury mass 0.3 mg, T = 400 °C, air flow rate 5 l/min)

Time, min	Hg mass, mg	Stripping degree, rel. %
10	0.093 ± 0.007	31
20	0.18 ± 0.01	60
50	0.27 ± 0.02	89
70	0.29 ± 0.02	97
90	0.30 ± 0.02	100
110	0.30 ± 0.02	100
130	0.30 ± 0.02	100
150	0.30 ± 0.02	100

TABLE 4

Mercury analysis results. Mercury stripping conditions (model sample): air flow rate 4 l/min, T = 600 °C, stripping time 30 min

Exp. No.	Introduced, mg/l	C_{Hg}, mg/l	Detected, mg
1	0.14	2.8 ± 0.2	0.14 ± 0.01
2	0.14	2.8 ± 0.2	0.14 ± 0.01
3	0.10	0.20 ± 0.01	0.10 ± 0.01
4	0.44	8.8 ± 0.5	0.44 ± 0.03

In order to study mercury stripping process, we prepared a model sample of MCA of given mercury content. Mercury was introduced as $Hg(NO_3)_2$ by impregnation followed by drying at the ambient temperature. Mercury content in thus prepared sample was 0.1 mass %. Mercury stripping was done at 400 and 600 °C (Tables 3 and 4 for the results obtained). Obviously, mercury stripping degree depends on the process temperature and duration. Using these conditions we analysed MCA samples after they were used for adsorbing mercury from the process wastewater (mercury concentration 0.15 mg/l, pH 3–4). The worked out adsorbent was dried, parted layer by layer (along the adsorption column), and mercury content was then determined in each layer (stripping parameters: 30 min, 600 °C). Basing on these data we obtained mercury content distribution along the adsorption column (Fig. 6). Apparently, top layers contain the maximum amount of mercury.

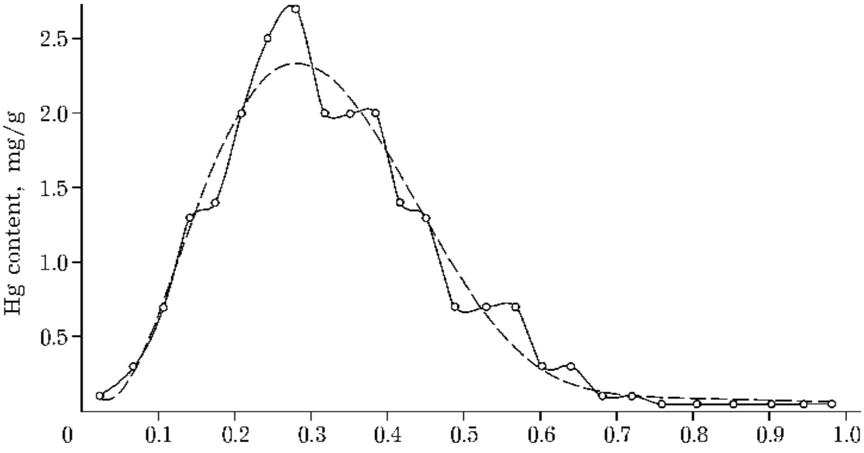

Fig. 6. Distribution of mercury content along the adsorption column *versus* height of layer.

CONCLUSIONS

1. Inversion voltammetry method for determining mercury content in the waste lithium-containing solutions has been developed. Reliably determined mercury concentration range is 0.2–3.5 mg/l, s_r = 4–9 %.

2. It has been shown that it is possible to apply IVA for mercury detection in the worked out carbon adsorbents after mercury is thermally stripped away into absorbing solution containing 0.1 M HCl with H_2O_2, mercury concentration ranging from 0.002 to 0.009 mass %.

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