

Title	Fundamental Studies on Inorganic Coulopotentiography : Determination of Trace Impurities of Lead in Reagent Grade Potassium Chloride
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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1978), 55(6): 473-481
Issue Date	1978-03-15
URL	http://hdl.handle.net/2433/76759
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Fundamental Studies on Inorganic Coulopotentiography

—Determination of Trace Impurities of Lead in Reagent Grade Potassium Chloride—

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Received October 11, 1977

The fundamental aspect of inorganic coulopotentiography was investigated under various analytical conditions changing the composition of base electrolyte, pH, ionic strength, flow-rate and potential scanning rate.

Optimum operating conditions for the determination of trace amounts of lead ion were confirmed. Lead ion at 0.1 ppm level was directly determined by this method with the relative standard deviation of 2.9%. The detection limit of this method was about 0.02 ppm. From 1.7 to 3.8 ppm of lead contaminants were determined in potassium chloride of analytical reagent grade.

INTRODUCTION

One of the recent progress in electroanalytical methodologies owes to the development of rapid electrolysis. The authors have developed such methods as electrolytic chromatography,¹⁾ flow-coulometry,²⁾ and coulopotentiography^{3,4)} based on the rapid electrolysis with glassy carbon column electrode.

In the present paper, the fundamental aspect of inorganic coulopotentiography was investigated under various analytical conditions changing the composition of base electrolyte, pH, ionic strength, flow-rate, and potential scanning rate.

Potassium chloride which is commonly used as the supporting electrolyte is always contaminated by small amounts of lead impurities, which bring about the lower limit of detection in electroanalysis. The trace impurities of lead at ppm level in reagent grade potassium chloride were directly analyzed by this method.

EXPERIMENTAL

Reagents JIS primary standard sodium chloride was used as the supporting electrolyte for the trace analysis of lead. The standard solutions of metal ions were prepared from analytical reagent grade chemicals and were standardized by conventional methods. All other chemicals were of analytical reagent grade.

Apparatus and Procedures The glassy carbon column electrode was designed in our laboratory and made by Shibata Chemical Instrument Co. Ltd.²⁾ A schematic diagram of coulopotentiograph was shown in the previous paper.⁴⁾

The procedure was as follows; the sample solution, after deaerated with nitrogen

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gass, was fed through the column electrode constantly at about 4 ml/min. Then the potential of the column electrode was controlled by a potentiostat against a silver silver chloride reference electrode (SSE) and the electrode was preconditioned at +0.4 V vs. SSE for 10 minutes. After the base current assumed a steady value at the initial potential, the column potential was swepted linearly at 4000 sec/V with Nikko-Keisoku Potential Sweeper SPC-200. The electrolysis current flowing through the column electrode was recorded against the column potential by Matsushita X-Y Recorder Model VP-6431A. The limiting current was measured from the current-potential curve by means of the same manner in polarography. The concentration of the depolarizer was calculated directly from a differential equation of Faraday's law as given in Eq. (1).

$$I_l = 1.608 n \cdot C \cdot V_f \quad (1)$$

where I_l is the limiting current (A), n is the number of electron involved in one molal reduction, C is the concentration of the depolarizer (M) and V_f is flow-rate (ml/min).

The current-potential profile for the reversible electro-deposition of metal ion is given by Eqs. (2) and (3) at 25°C.

$$E = E_{1/2} + \frac{0.0592}{n} \log [I_l - I] \quad (2)$$

$$E_{1/2} = E'_0 + \frac{0.0592}{n} \log \frac{C_M}{2} \quad (3)$$

where $E_{1/2}$ and C_M are the half-wave potential and the concentration of the depolarizer, respectively.

RESULTS AND DISCUSSION

1. Background Current of the Glassy Carbon Column Electrode

Figure 1 shows the base current-potential curves in acidic carrier solutions. Acetic acid - potassium chloride base electrolyte solution was recommended because of its smallest base current. In case of perchloric and nitric acid carriers, large

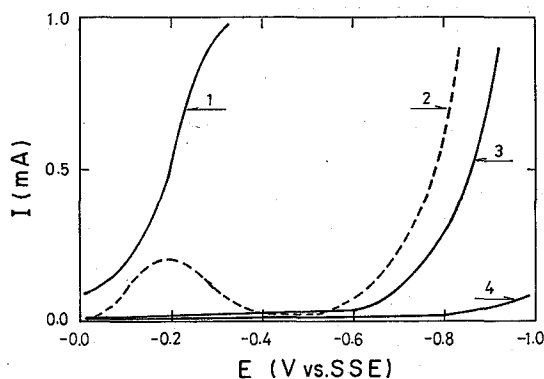


Fig. 1. Residual current of the glassy carbon column electrode in acidic carrier solution. 1) 1 N-HNO₃, 2) 1 N-HClO₄, 3) 1 N-HCl and 4) 0.1 N-CH₃COOH + 1 M-KCl, flow-rate: 2.0 ml/min, scan-rate: 4000 sec/V.

humps were observed in the vicinity of -0.2 V *vs.* SSE, which seemed to be due to the electro-reduction of oxidized carbon surface. Nitric acid higher than 0.5 M was not of use owing to its vigorous catalytic hydrogen wave.

2. Coulopotentiography of Lead and Bismuth Ions

2.1 Reduction Behavior of Lead and Bismuth Ions in Acidic Potassium Chloride Base Solutions

The coulopotentiographic behavior of lead and bismuth ions is summarized in Table I. Lead ion was reduced reversibly and gave the good reproducible waves in acidic chloride base solutions. The reversibility of the reduction wave of bismuth were dependent upon the composition of the carrier solutions, *i.e.* particularly on pH and the chloride ion concentration. Although the wave in 1 M-HCl carrier was enough defined for analytical measurement, the reduction process was still irreversible.

Table I. Coulopotentiographic Behavior of Lead and Bismuth Ions

Supporting Electrolyte	Pb ²⁺		Bi ³⁺	
	E _{1/2} (V <i>vs.</i> SSE)	log-plot slope (mV)	E _{1/2} (V <i>vs.</i> SSE)	log-plot slope (mV)
0.1 N-AcOH+1 M-KCl	-0.536 ± 0.002	30 ± 2	-0.18 ± 0.01	83 ± 10
0.1 N-HCl+0.9 M-KCl	-0.534 ± 0.002	31 ± 2	-0.17 ± 0.01	39 ± 10
0.5 N-HCl+0.5 M-KCl	-0.543 ± 0.002	30 ± 2	-0.18 ± 0.01	35 ± 5
1 N-HCl	-0.542 ± 0.001	25 ± 1	-0.18 ± 0.01	27 ± 5

Concentration of Pb²⁺ and Bi³⁺: 10^{-4} M, flow-rate: 2.0 ml/min, scan-rate: 4000 sec/V.

2.2 Effect of Ionic Strength

Figure 2 shows the effect of ionic strength on the coulopotentiogram of lead ion in acetic acid - KCl base solution. Lead ion gave the reversible waves with the ionic strength higher than 0.5. The half-wave potential shifted to more and more

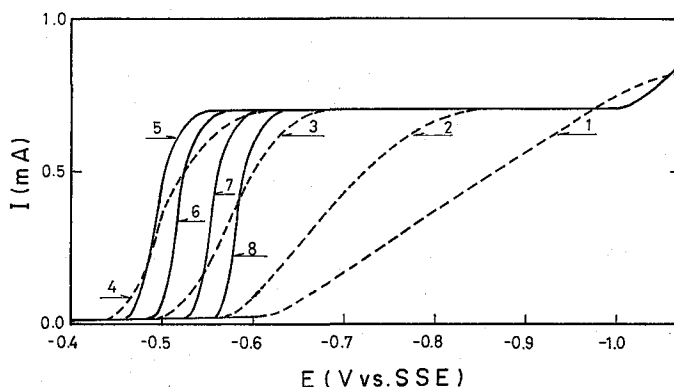


Fig. 2. Effect of ionic strength on the coulopotentiogram of lead ion. 10^{-4} M Pb²⁺ in 1 M-CH₃COOH+KCl, concentration of KCl: 1) 0.001 M, 2) 0.01 M, 3) 0.05 M, 4) 0.1 M, 5) 0.5 M, 6) 1.0 M, 7) 2.0 M and 8) 3.0 M, flow-rate: 2.0 ml/min, scan-rate: 4000 sec/V.

Table II. Effect of Supporting Electrolyte on the Reduction of Bismuth Ion

Supporting Electrolyte	$E_{1/2}$ (V vs. SSE)	log-plot slope (mV)	Electrolysis Efficiency (%)
1 M KCl	-0.180	83.3	99.9
2 M KCl	-0.213	48.5	100.8
3 M KCl	-0.236	49.7	100.7
1 M KBr	-0.217	45.4	98.9
2 M KBr	-0.226	40.3	99.9

10^{-4} M-Bi³⁺ in 0.1 M-CH₃COOH, flow-rate: 2.0 ml/min, scan-rate: 4000 sec/V.

negative potential and the wave shape was getting distorted with decreasing ionic strength on account of the increasing impedance of the solution. The half-wave potential moved again to negative direction when the chloride concentration increased more than 0.5 M, due to the complexing effect. This effect was observed more notably in the case of bismuth waves as shown in Table II.

2.3 Effect of Flow-Rate

From Eq. (1), the limiting current of the coulopotentiogram is expected to increase linearly with increasing flow-rate of the carrier solution. A good agreement between the calculated (solid line) and observed (dots) values was obtained as shown in Fig. 3. In contrast, no significant effect of flow-rate on the residual current was observed. Consequently, the relatively high flow-rate of 4 ml/min was adopted for the analysis of the dilute sample.

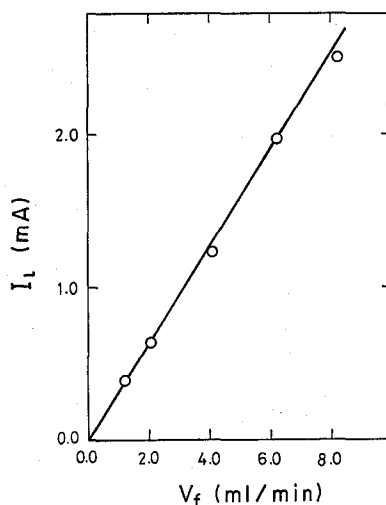


Fig. 3. Relation between limiting current and flow-rate. 10^{-4} M Pb²⁺ in 0.1 N-HCl+0.9 M KCl, scan-rate: 4000 sec/V.

2.4 Effect of Potential Scanning Rate

Figures 4 and 5 show the effects of potential scan-rate on the coulopotentiograms of lead and bismuth ions, respectively. The half-wave potential of lead ion was inclined to shift slightly toward the negative potential with increasing scan-rate.

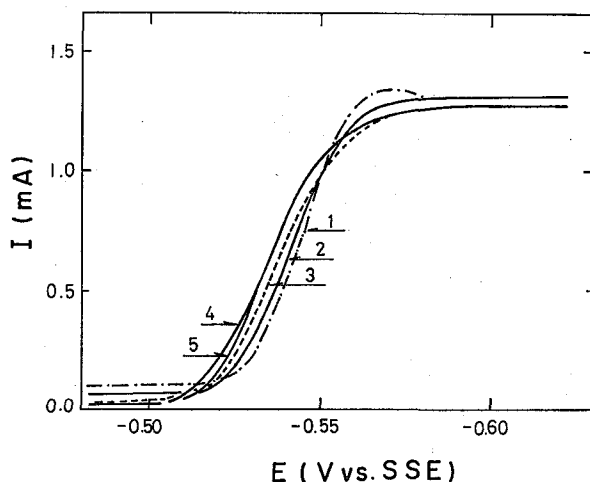


Fig. 4. Effect of scan-rate on the coulopotentiogram of lead ion. $10^{-4} M Pb^{2+}$ in $0.1 N-HCl+0.9 M KCl$, flow-rate: $4.0 ml/min$, scan-rate: 1) 400, 2) 800, 3) 2000, 4) 4000 and 5) 8000 sec/V .

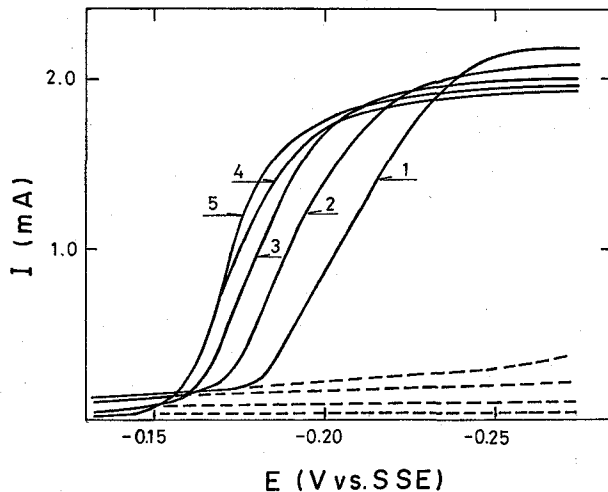


Fig. 5. Effect of scan rate on the coulopotentiogram of bismuth ion. $10^{-4} M Bi^{3+}$ in $1 N-HCl$, flow-rate: $4.0 ml/min$, scan-rate: 1) 400, 2) 800, 3) 2000, 4) 4000 and 5) 8000 sec/V . solid lines: reduction waves of bismuth ion, dotted lines: residual current.

In case of bismuth wave, which was not reversible enough, the effect was more remarkable. The residual current increased extremely with the faster scan-rate than $800 sec/V$, so that the moderate scan-rate slower than $200 sec/V$ was desirable for the dilute sample.

3. Determination of Lead Contaminants in Analytical Reagent Grade Potassium Chloride

3.1 Relationships between the Limiting Current and the Half-Wave Poten-

tial and the Concentration of Lead Ion

Figure 6 shows the calibration curve for lead ion in 0.1 *M*-CH₃COOH+0.7 *M*-NaCl base solution. For this, sodium chloride supporting electrolyte was used instead of potassium chloride, because no lead contaminant was detected in its blank solution.

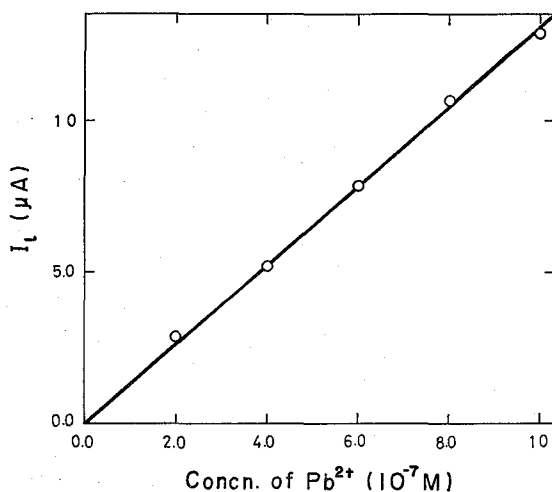


Fig. 6. Calibration curve for lead ion. Pb²⁺ in 0.1 *M*-CH₃COOH+0.7 *M*-NaCl, flow-rate: 4.0 ml/min, scan-rate: 8000 sec/V.

Table III. Reproducibility of Coulopotentiographic Data

Concentration (<i>M</i>)	<i>E</i> _{1/2} (V vs. SSE)	<i>I</i> _l		Electrolysis efficiency (%)
		Calcd.* (μA)	Obsd. (μA)	
4.0 × 10 ⁻⁷	-0.610	5.16	5.10	98.8
	-0.610	5.16	5.00	96.9
	-0.618	5.16	4.88	94.6
	-0.613	5.16	5.60	107.7
Mean**	-0.613 (0.62%)			99.5 (5.0%)
6.0 × 10 ⁻⁷	-0.600	7.80	7.48	95.9
	-0.604	7.80	7.80	100.0
	-0.606	7.80	7.90	101.3
	-0.614	7.80	8.00	102.6
Mean**	-0.613 (0.97%)			100.0 (2.9%)
8.0 × 10 ⁻⁷	-0.604	10.37	10.64	102.6
	-0.590	10.37	10.60	102.2
	-0.615	10.37	10.40	100.7
	-0.603	10.37	10.42	100.7
Mean**	-0.603 (1.7%)			101.6 (0.84%)

Pb²⁺ in 0.1 *M*-CH₃COOH+0.7 *M*-NaCl, flow-rate: 4.0 ml/min, scan-rate: 8000 sec/V.

* calculated from Eq. (1), ** with the relative standard deviation in parentheses.

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A good accordance between the theoretical (solid line) and observed (dots) values was obtained in the concentration range from $10^{-7} M$ (20 ppb) to $10^{-6} M$ (200 ppb). The electrolysis efficiency was 100.0% with the relative standard deviation of 2.9% for 0.124 ppm lead ion as shown in Table III. The detection limit of lead ion was about 20 ppb.

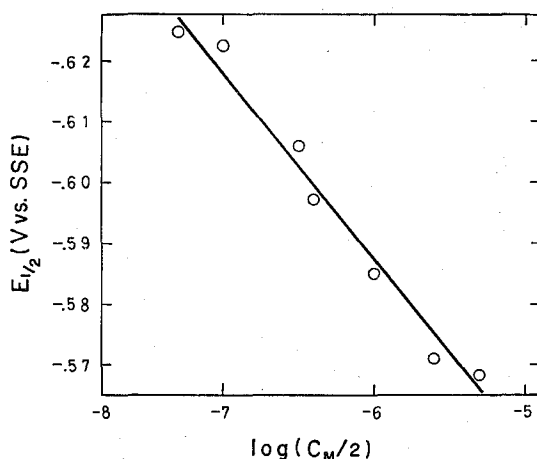


Fig. 7. Concentration dependence of the half-wave potentials of lead ion. Conditions are the same as those in Fig. 6.

Figure 7 shows the negative shift of the half-wave potential of lead ion with its decreasing concentration with the slope of 30 mV as expected from Eq. (3).

3.2 Analytical Results

The results of the analysis of lead in potassium chloride are listed in Table IV. Each sample was taken from 7 reagent bottles of potassium chloride of the same grade. The sample solutions were prepared by dissolving 7.500 grs of KCl and 0.6 ml of CH_3COOH with double distilled water into a 100 ml volumetric flask. From 1.7 to 3.8 ppm of lead were found with the relative standard deviation between 1.7% and 6.7%.

CONCLUSION

The optimum analytical conditions for the determination of trace lead ion are concluded as follows; carrier solution is $0.1 M\text{-CH}_3\text{COOH} + 0.7 M\text{-NaCl}$, flow-rate is 4.0 ml/min and potential scan-rate is 4000 sec/V. And the corresponding results are $E_{1/2} = -0.613 \text{ V vs. SSE}$ with the relative standard deviation of 0.97% and the electrolysis efficiency is 100.0% with the relative standard deviation of 2.9% for 0.124 ppm lead ion. Potassium chloride of analytical reagent grade is always contaminated by lead at ppm level.

The electro-deposition behavior of the other metal ions in acidic and alkaline carrier solutions and their analytical applications are being studied and will be presented elsewhere.

Table IV. Determination of Lead in Potassium Chloride

Sample No.	Lot No.	Pb in KCl	
		Found (ppm)	Mean* (ppm)
1	M6R3019	3.81	3.75 (1.8%)
		3.76	
		3.68	
2	M6R3019	3.79	3.74 (1.7%)
		3.71	
		3.71	
3	M6R3019	3.85	3.79 (1.6%)
		3.78	
		3.73	
4	M7A4930	2.61	2.49 (5.2%)
		2.51	
		2.35	
5	LDE0369	1.92	1.78 (6.7%)
		1.72	
		1.71	
6	LDE0369	1.77	1.71 (4.1%)
		1.65	
		1.70	
7	LDE0369	1.67	1.66 (1.9%)
		1.62	
		1.68	

Amounts of KCl taken: 7.50 g/100 ml, base electrolyte: 0.1 M- $\text{CH}_3\text{COOH} + 0.7 \text{ M-NaCl}$, flow-rate: 4.0 ml/min, scan-rate: 4000 sec/V.

* with the relative standard deviation in parentheses.

ACKNOWLEDGMENT

This work is supported by the Grant in Aid for Scientific Research from the Ministry of Education (project number 111211).

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