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Author(s)	Fujinaga, Taitiro; Okazaki, Satoshi; Yamada, Takeshi
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Flow-Coulometric Determinations of Nanogram Amounts of Bromide and Chloride Ions

Taitiro Fujinaga, Satoshi Okazaki, and Takeshi Yamada*

The determination of nanogram amounts of bromide and chloride ions have been investigated by means of a new type of the flow-coulometry with the silver wire packed column electrode, which assorted the electro-oxidation reaction of silver with the successive chemical reaction between silver cations and halogen anions.
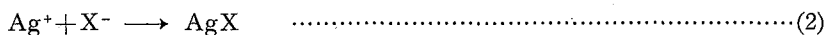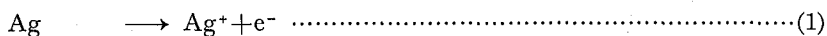
In the present method, bromide ions down to 4 ng were determined absolutely in 0.1 M perchloric acid based on the Faraday's law with the standard deviation of 1.5% and chloride ions down to 70 ng were also determined in 0.2 M perchloric acid and 50% dioxane medium with the standard deviation of 2%.

INTRODUCTION

The determination of halogen ions has mostly been performed by means of the argentmetric titration.[1] Recently, the controlled potential[2] and also the constant current[3] coulometric methods have been developed for the determination of micro-amounts of halogen ions, which have great advantages of the absolute determination based on the Faraday's law and of high sensitivity. The conventional coulometric methods, however, have also such disadvantages that a considerably long electrolysis-time and a relatively large volume of sample solution are indispensable.

The authors have investigated the flow-coulometry with the column electrode,[4,5] which has so large a value of cell factor ($\lambda=1$ sec^{-1}) that the quantitative electrolysis is performed within a couple of seconds and, moreover, very small a volume of sample solution as low as 1 to 50 μl is available.

In the present work, the authors have developed a new type of the flow-coulometry assorted the electro-oxidation reaction of Eq. (1) with the successive chemical reaction given in Eq. (2).

$$\mathrm{Ag} \longrightarrow \mathrm{Ag^+ + e^-} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$\mathrm{Ag^+ + X^- \longrightarrow AgX} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

On the contrary to the previous method in which the metal ions were reduced or oxidized directly at the column electrode, the silver wire packed column electrode has been used in the present method for the indirect flow-coulometric determination of the trace amounts of halogen ions.

The coulometric determination of halogen ions with the silver electrode has first been developed by Lingane and Small,[2] where the milligram amounts of bromide and

* 藤永太一郎, 岡崎　敏, 山田　武 : Department of Chemistry, Faculty of Science, Kyoto University Sakyo-ku, Kyoto.

chloride ions were determined with an accuracy of 0.1%. Takata and others[6,7] reported the application of the flow-coulometry for the detection of the halogenide ion effluents in the liquid chromatography, however, 100% current efficiency were not attained.

In the present method, as low as 4 ng of bromide ions were determined in 0.1 M perchloric acid or nitric acid supporting electrolyte by means of the absolute method based on the Faraday's law. In the case of the chloride ions, however, the absolute method can not be applied in aqueous media owing to the relatively large solubility of silver chloride in water. The situation is greatly improved by the addition of organic solvents; 70 ng of chloride ions were determined in 0.2 M perchloric acid and 50% dioxane medium with the standard deviation of less than 2%.

EXPERIMENTAL

Materials Highly purified silver wire (99.99%) of 0.07 mm in diameter was obtained from Nakarai Chemicals Co. Ltd., and was used without further chemical treatment. The standard solutions of halogen ions were prepared with analytical reagent grade potassium halides and demineralized laboratory distilled water. All other chemicals used were of analytical reagent grade.

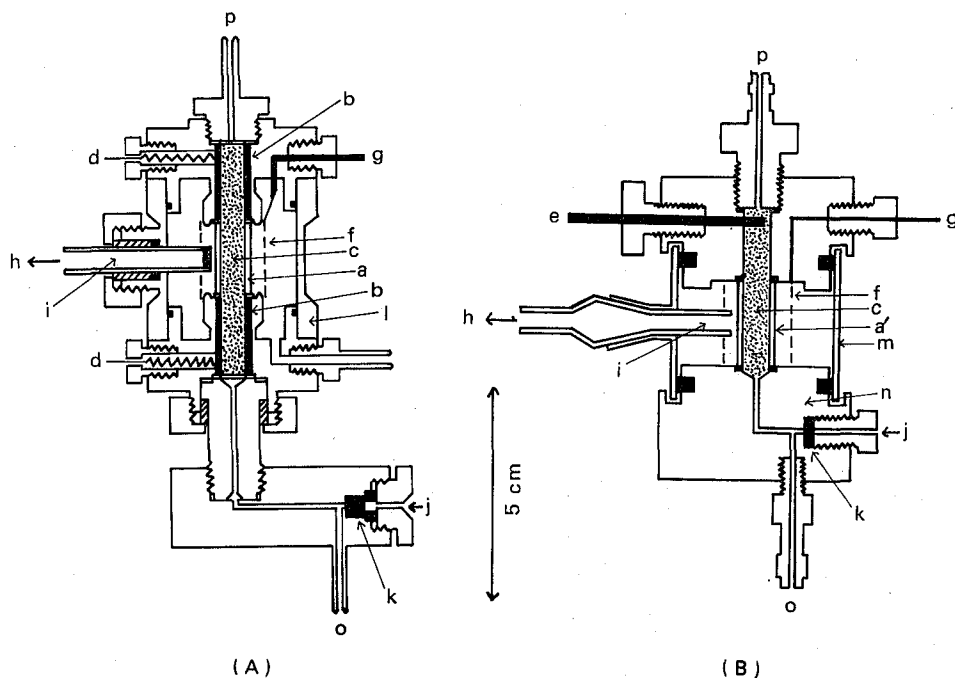**Apparatus** A Yanagimoto potentiostat Model VE-3 was used for both the con-

Fig. 1. Construction of column electrodes.

a, a′: Diaphragm tube of (a) porous glass and (a′) porcelain, b: Glassy carbon tubes, c: Silver wire working electrode, d: Lead to working electrode, e: Glassy carbon rod, f: Platinum net counter electrode, g: Lead to counter electrode, h: to Reference electrode (SCE), i: Salt bridge, j: Sample injection port, k: Silicon rubber stopper, l: Acryl resin body, m: Glass tube, n: Teflon body, o: Inlet, p: Outlet.

trolled potential and the constant current coulometry. A Kyoto Electronics automatic titrator Model AT–05 was used for the potentiometric titration. A Matsushita 2 pen–recorder Model VP–654A was used for recording of electrode potential and electrolysis current. Kusano teflon needle valve Model SML–1 and glass flow-meter Model KG–1 were used for the control and the measurement of flow-rate, respectively. Jintan-Termo 10 μl and 50 μl micro-syringes were used for the injection of the sample solution into the column electrode.

Column Electrode Both column electrodes made by Shibata Mfg. Co. (Fig. 1–A) and by this laboratory with teflon body (Fig. 1–B) were used for aqueous and aqueous–organic solvent medium, respectively.

The construction of the column electrodes is shown in Figs. 1–A and 1–B. The column electrode (A) is divided into two compartments by a diaphragm tube of porous glass (a) which is 6 mm in inner diameter and 20 mm in length. At the top and the bottom of the diaphragm tube, glassy carbon tubes of 5 mm in inner diameter and 20 mm in length (b) are connected in order to make an electrical contact to the electrode materials packed inside the diaphragm tube.

In the inner compartment of the column, a silver wire of 0.07 mm in diameter (c) is compactly packed which plays a part of the working electrode. In the outer compartment, a platinum net (f) is set around the diaphragm tube, which serves for the counter electrode. A saturated calomel reference electrode (h) is connected electrically with a salt bridge of 30% in sodium nitrate and 3% agar (i), whose tip is inserted into the outer compartment almost in contact with the diaphragm tube. A sample injection port (j) with a silicone rubber stopper (k) is jointed just below the column electrode.
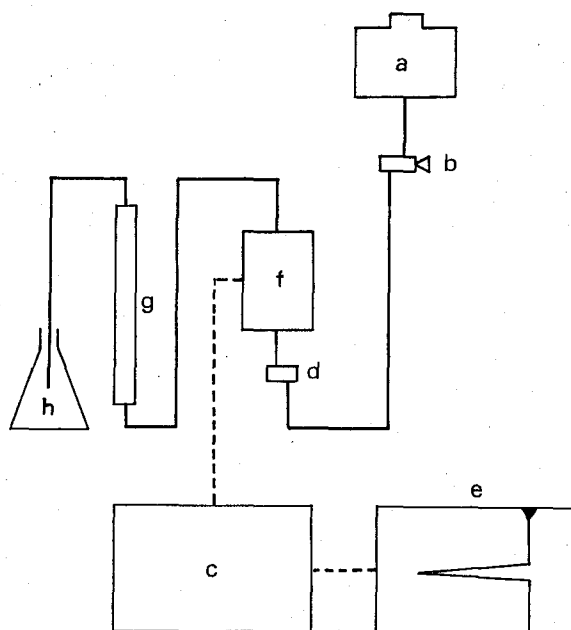

Fig. 2. Schematic diagram of flow-coulometry system.

a: Carrier solution, reservoir b: Teflon needle valve, c: Potentiostat, d: Sample injection port, e: Pen-recorder, f: Column electrode, g: Flow meter. h: Drainger.

Procedure   A schematic diagram for the flow-coulometry system is shown in Fig. 2.   The electrolyte carrier solution stored in an upper reservoir (a), after deaeration, is passed at the constant flow-rate of 2 ml/min through the inner compartment of the column. Then, the potential of the silver working electrode is controlled at the suitable values $vs.$ SCE with a potentiostat (c).   And after the base current reaches to a steady value, the sample solution is injected into the carrier solution from the sample injection port (d) with a 10 μl or a 50 μl micro-syringe.

The electrolysis current flowing through the column is recorded with a pen-recorder (e) after being converted to an ohmic voltage drop between the both ends of the standard resistance (0.1% in accuracy).   The amount of halogen ions in the sample solution is determined absolutely based on the Faraday's law by measuring the total coulombs consumed during the electrolysis.   The calculation of the coulombs is carried out by comparing the weight of the recording paper of the peak in the current-time curve with that of the standard of known coulombs.   This can also be done more conveniently by using electronic digital integrator.

RESULTS AND DISCUSSION

In the case of the coulometric determination of halogen ions with a silver electrode, it goes without saying that the supporting electrolyte composed of such anions as to be reactive with silver cations ought not to be used and the potential of the silver electrode should be kept in an optimum range.   The effect of supporting electrolytes such as perchloric acid, nitric acid and acetate buffer on the coulometric determination of bromide and chloride ions have been investigated by the present method, comparing the result with that obtained by the constant current coulometry and the potentiometric titration methods. The effect of the potential of the silver electrode on the electrolysis efficiency in the flow-coulometry of halide ions have also been investigated.

Determination of Bromide Ions

Supporting Electrolyte   For the comparison with the present method, potentiometric and constant current coulometric titrations were carried out by recording the potential-time curves automatically.   In the potentiometric titration of bromide with silver nitrate, no significant effect of the presence of such anions as perchlorate, nitrate and acetate was observed, provided that the titrant was added at a constant titration velocity.

Table I.   Effect of pH on Peak Current and Half-Peak Width

Sample: 50 μl of 10^{-2} M KBr, Flow-rate: 2 ml/min, Potential: +0.20 V $vs.$ SCE

Supporting electrolyte	pH	Peak current (mA)	Half-peak width (sec)
1 M NaClO$_4$	5.0	3.34	9.7
1 M NaClO$_4$+HClO$_4$	3.9	3.50	9.3
	3.0	3.62	9.3
	2.0	3.76	9.3
0.9 M NaClO$_4$+0.1 M HClO$_4$		4.30	8.8
0.5 M NaClO$_4$+0.5 M HClO$_4$		6.24	6.7
1 M HClO$_4$		7.16	6.6

In the case of a constant current coulometry, however, the dull slope at the vicinity of an end point in the potential-time curves was observed with perchlorate and nitrate at high pH, and the acetate buffer as the supporting electrolyte. The steeper slope was observed in perchlorate and nitrate at low pH. In the flow-coulometric determination, a broad peak, which means relatively long electrolysis-time of about 10 min, was obtained in the acetate buffer and the electrolysis efficiency was not beyond 70%. It is said that acetic acid inhibits the electrode reaction of silver anode owing to the relatively low solubility of silver acetate. A similar peak was exhibited by the injection of 1 M acetate buffer solution instead of the bromide solution into the column. These phenomena were not observed with the perchlorate and nitrate media and the electrolysis-time was as short as 2 min. The influence of pH on the flow-coulometric curves is shown in Table I. The peak current increased significantly with decreasing pH. Therefore, perchloric acid and nitric acid in higher concentration than 0.1 M are recommended for the supporting electrolytes.

Electrode Potential It is most important to select the optimum potential range of the silver electrode for the determination of halogen ions. The theoretical potentials calculated by Lingane and Small.[2] according to the following equations are 0.18 V and 0.26 V $vs.$ SCE for bromide and chloride ions, respectively.

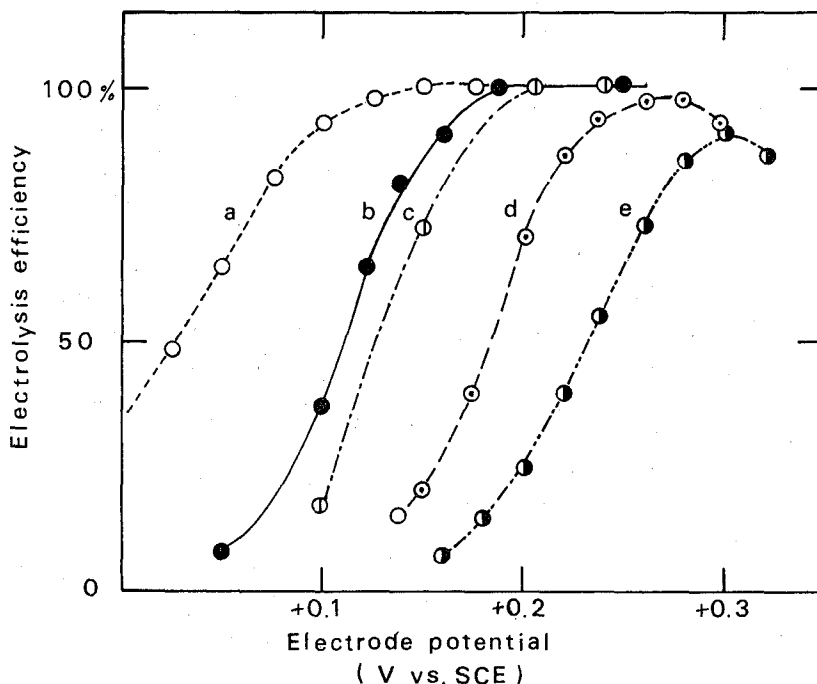$$E=E_0+\frac{RT}{nF}\log[Ag^+] \quad \cdots \cdots (3)$$

Fig. 3. Potential dependence of the electrolysis efficiency of bromide and chloride ions.
Sample: 10 μl of 10^{-2} M KBr and KCl, Carrier: Perchloric acid, Flow-rate: 2 ml/min.
a) KBr in 0.5 M HClO$_4$, b) KBr in 0.1 M HClO$_4$, c) KCl in 2 M HClO$_4$,
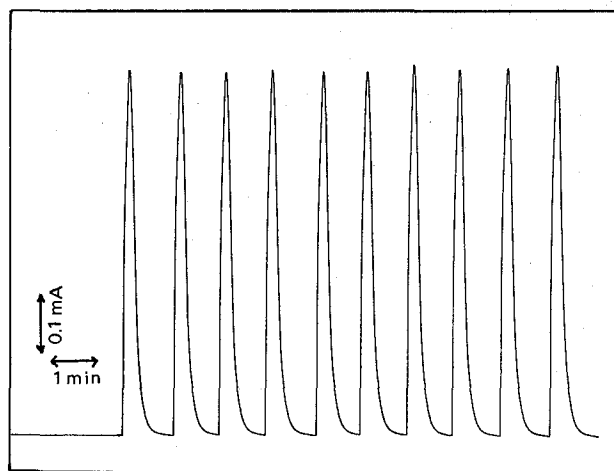d) KCl in 0.5 M HClO$_4$, e) KCl in 0.1 M HClO$_4$.

Fig. 4. Flow-coulometric curves of bromide ions.

Sample: 10 μl of 10^{-2} M KBr, Carrier: 0.1 M HClO$_4$, Potential: +0.18 V vs. SCE.

Table II. Flow-Coulometric Determination of Bromide Ions.

Carrier: 0.1 M HClO$_4$, Flow-rate: 2 ml/min, Potential: +0.18 V vs. SCE

Concentration (mole/l)	Volume (μl)	Amount (ng)	Efficiency (%)	Standard deviation (%)
1.0×10^{-2}	50	39950	103.3±1.4	1.2
	20	15980	103.6±0.8	0.5
	10	7990	100.3±2.1	1.2
	5	3995	101.7±1.3	0.9
	2	1598	100.6±1.5	1.3
1.0×10^{-3}	50	3995	102.7±0.9	0.8
	20	1598	99.0±1.8	1.5
	10	799.0	100.8±0.4	0.4
	5	399.5	100.0±1.9	1.3
	2	159.8	103.4±1.7	1.4
1.0×10^{-4}	50	399.5	102.7±1.7	1.1
	20	159.8	102.2±1.7	1.2
	10	79.90	104.2±0.4	0.4
	5	39.95	104.4±1.3	0.8
1.0×10^{-5}	50	39.95	92.8± 5.8	5.0
	20	15.98	103.0±10.6	6.7
	10	7.990	98.3± 5.8	5.0
	5	3.995	88.6± 5.0	4.8

$$S=[Ag^+][X^-] \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

$$S_{AgCl}=1.8\times10^{-10}, \; S_{AgBr}=5.2\times10^{-13}$$

At the end point, $[Ag^+]=[X^-]$ $\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$

From Eq. (3), (4), and (5), and at 25°C

$$E=0.553+0.0591 \log S^{1/2} \; (V \; vs. \; SCE) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

where, E =potential of silver electrode

E_0 =its standard potential

S =solubility product of silver halide

$[X^-]$=concentration of halogen anions.

Figure 3 shows the efficiency-potential curves of bromide and chloride ions. Although the usable potential range becomes a little narrower in 0.1 M perchloric acid than in 0.5 M, the former concentration is recommended for the determination of bromide owing to its smaller base current. And the electrode potential of 0.18 V $vs.$ SCE is also recommended on account of less interference of chloride ions than that in the potential at more positive potentials.

Sensitivity and Accuracy Figure 4 shows the excellent reproducibility of the flow-coulometric curves of bromide ions. The determination of bromide by the present method is satisfactorily applied between 4 ng and 40 μg and the standard deviation is within 1.5% (Table II).

Determination of Chloride Ions

In Aqueous Solution In 2 M perchloric acid, chloride ions as high a concentration as 10^{-2} M was determined with the electrolysis efficiency of 100% as shown in
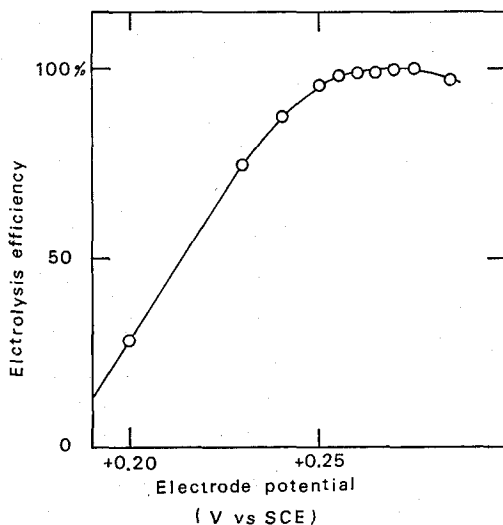

Fig. 5. Potential dependence of the electrolysis efficiency of chloride ions in aqueous-dioxane medium.

Sample: 50 μl of KCl, Carrier: 0.2 M HClO$_4$ in 50 v/v% dioxane, Flow-rate: 1 ml/min.

Table III. Flow-Coulometric Determination of Chloride Ions

Carrier: 0.2 M HClO$_4$ in 50% dioxane, Flow-rate: 1 ml/min, Potential: +0.26 V vs. SCE

Concentration (mole/l)	Volume (μl)	Amount (ng)	Efficiency (%)	Standard deviation (%)
1.0×10^{-2}	50	17730	98.9±0.6	0.4
	20	7091	99.9±1.9	1.4
	10	3545	95.9±1.4	0.8
1.0×10^{-3}	50	1773	97.7±1.7	1.0
	20	709.1	98.2±0.5	0.3
5.0×10^{-4}	50	886.3	95.5±0.7	0.6
	20	354.5	94.8±1.2	0.9
2.0×10^{-4}	50	354.5	94.2±0.3	0.2
	20	141.8	91.0±2.7	1.9
1.0×10^{-4}	50	177.3	92.5±3.5	2.1
	20	70.91	87.1±1.8	1.0

Fig. 3. The efficiency, however, decreased with the decreasing concentration of chloride ions because of the relatively large solubility of silver chloride as seen in Eq. (4).

Effect of Organic Solvents The electrolysis efficiency increased by the addition of organic solvents such as ethanol and dioxane, because of the decrease of the solubility of silver chloride due to the decrease of the dielectric constant of the solution. The aqueous-ethanol and aqueous-dioxane media in various mixing ratio have been investigated and 0.2 M perchloric acid in 50% dioxane medium was found recommendable as the optimum for the determination of chloride ions.

Electrode Potential Figure 5 shows the efficiency-potential curve of chloride ions. The usable potential range develops more than 50 mV with the higher concentration of chloride ions than 10^{-2} M. It decreases, however, with the decreasing concentration of chloride ions and becomes 10 mV with 10^{-4} M. The optimum potential of silver electrode for the determination of chloride ions is +0.26 V vs. SCE.

Sensitivity and Accuracy Table III shows the results obtained with the various concentration and sample-volume of chloride ions. The amounts between 70 ng and 17 μg of chloride ions can be determined with the standard deviation of 2% in this method. However, the current-efficiency tends to decrease with the decrease of concentration of chloride below 10^{-3} M.

REFERENCES

(1) I. M. Kolthoff and N. H. Furman, "Potentiometric Titration" John Wiley & Sons Inc. New York, N.Y., 1926, p. 164.
(2) J. J. Lingane and L. A. Small, $Anal.$ $Chem.$, **21**, 1119 (1949).
(3) J. J. Lingane, $Anal.$ $Chem.$, **26**, 622 (1954).
(4) T. Fujinaga, K. Izutsu, M. Koyama, S. Okazaki, and K. Tsuji, $J.$ $Chem.$ $Soc.$ $Japan$, **84**, 941 (1968).
(5) S. Okazaki, $Rev.$ $Polarog.$ $Japan$, **14**, 164 (1969).
(6) Y. Takata, H. Miyashita, H. Tsuda, and G. Muto, $Japan$ $Analyst$, **15**, 573 (1966).
(7) Y. Takata and G. Muto, $Anal.$ $Chem.$, **45**, 1864 (1973).