

ELECTROLYTIC CHROMATOGRAPHY AND COULOMETRIC DETECTION WITH THE COLUMN ELECTRODE

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ABSTRACT

A very rapid electrolytic analysis termed 'electrolytic chromatography', using a column electrode with glassy carbon grains, has been developed. The column electrode has been used not only for coulometric detection, but also for separation of metals, elimination of interfering elements, unification of oxidation state, and concentration of an element.

Some analytical applications of electrolytic chromatography are introduced especially with radioactive nuclides. Down to 1.0 μ l of a 10^{-2} M or 1000 ml of a 10^{-8} M solution can be analysed with satisfactory accuracy.

INTRODUCTION

There have been proposed many separation methods based on a heterogeneous phase formation, such as adsorption, ion-exchange, solvent extraction, etc. Recently advances have been made in the use of most of these methods, to transfer them from batchwise procedures into chromatographic procedures. In the present paper, the author reports on a new method of multi-stage separation using electrolytic deposition and dissolution.

The new 'electrolytic chromatography'¹ utilizes the principle of controlled potential electrolysis and it produces a separated and localized deposition of metals followed by stepwise dissolution. For the detection and determination of metal ions in the eluate, d.c. and a.c. amperometric, spectrophotometric, radiometric and coulometric methods were employed as necessary. The d.c. amperometric method seemed practical and versatile for use with most metals but lacked sensitivity. The a.c. amperometric method proved more sensitive than the d.c. amperometric method if the potential was selected exactly and maintained at the peak of the wave. The spectrophotometric method was also satisfactory for the detection of metal ions such as bismuth, copper and lead by using xylenol orange as the universal colour developer and by the proper selection of the wavelength. The use of radioactivity was extremely effective in the detection of trace amounts if the active isotope was available. The method of coulometric detection was the most successful in the sense that it is relatively sensitive and also versatile to most of the metals examined.

The total set-up is shown in *Figure 1*. As seen from the figure, the carrier solution which contains the supporting electrolyte and is deaerated if

necessary flows continuously through the chromatograph column and the detector column. The sample solution usually less than 0.1 ml is injected into the system ahead of the chromatograph column. As the potential of the chromatograph cell is properly controlled, the metal ions in the sample are graded while flowing through the column and are conveyed into the detector

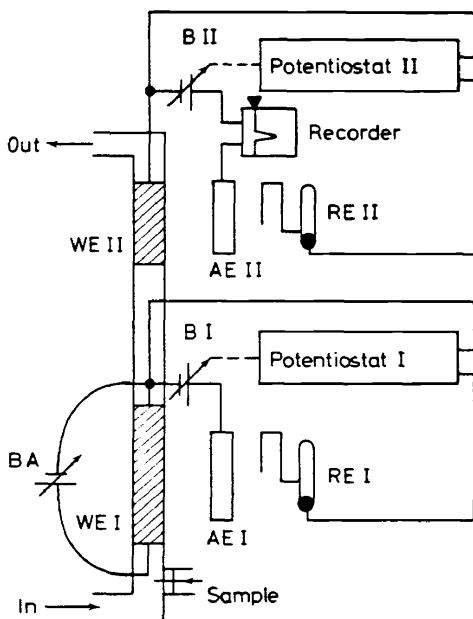


Figure 1. Schematic apparatus of electrolytic chromatograph with coulometric detector.

cell one after another. The detector column, controlled at a proper potential, measures the amount of each ion coulometrically and the results are recorded as a current/time curve or a coulombs/time curve. Other methods of detection are also possible; however, unless otherwise mentioned, coulometric detection is applied as shown in *Figure 1*.

PRINCIPLE

Rapidity of column electrolysis

Electrolysis is a heterogeneous reaction at a solid/solution interface and therefore a relatively slow process; in the usual electrolytic analysis, it takes from ten minutes to several hours to obtain a quantitative result.

As the rate of electrolysis is mainly controlled by diffusion, the decrease of concentration of the metal ions in solution and therefore that of the current are represented by the following equations²

$$-dC/dt = \lambda C \quad (1)$$

and

$$-di/dt = \lambda i \quad (2)$$

Therefore a current i at a time t is given by the following equation

$$i = i_0 e^{-\lambda t} \quad (3)$$

If now the time τ of quantitative electrolysis is defined as the time when the ratio of i/i_0 reaches 10^{-3} , then

$$\tau = 6.9/\lambda \quad (4)$$

In conventional electrolysis, more than 20 minutes are needed to obtain a quantitative deposit; the value of λ never exceeds 0.005 sec^{-1} . In this equation, λ is represented by the following formula²,

$$\lambda = DA/\delta V \quad (5)$$

where D [$\text{cm}^2 \cdot \text{sec}^{-1}$] is the diffusion coefficient of the metal ions; A [cm^2], the surface area of the working electrode; δ [cm], the thickness of the diffusion layer; and V [cm^3], the volume of the electrolytic solution.

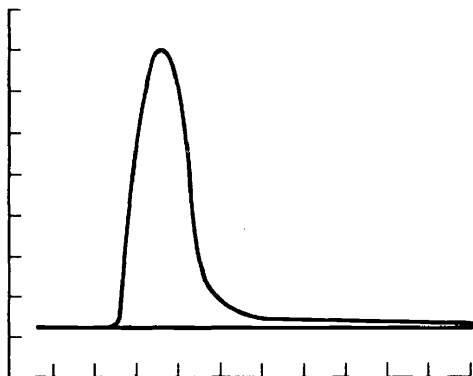


Figure 2. Current/time curve in the reduction of lead ions at the column electrode. $5 \mu\text{l}$ of $1.0 \times 10^{-2} \text{ M Pb}^{2+}$ solution was injected into the carrier stream. Vertical axis: 0.4 mA/div. ; horizontal axis: 2 sec/div.

According to equation 5, the value of λ increases with increasing D and A , and with decreases of δ and V . Many efforts³⁻⁵ have been made to carry out electrolysis where the λ value is large; for instance Bard⁴ designed a cell of extremely small volume with a platinum gauze electrode agitated with ultrasonic waves, and obtained the λ value of $0.1 \text{ [sec}^{-1}\text{]}$. The author designed a column cell with silver or carbon grain as electrode material¹, by which the specific surface area was markedly increased and the λ value of $1.0 \text{ [sec}^{-1}\text{]}$ or more was realized. A similar cell was reported later by Blaedel and others^{6,7}.

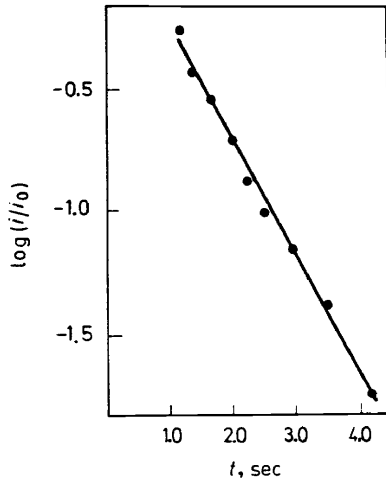


Figure 3. Analysis of current/time curve. Data taken from Figure 2.

Chromatographic consideration

Blaedel⁸ discussed the distribution coefficient at the mercury electrode using the Nernst equation. In electrolytic deposition at the mercury electrode, the equation is expressed as

$$M^n + ne \rightleftharpoons M(\text{Hg})$$

$$E = E_a^0 + (RT/nF) \ln [M^{n+}]/[M] \quad (6)$$

Therefore the distribution coefficient K_D is

$$K_D = [M]/[M^{n+}] = 10^{(n/0.059)(E_a^0 - E)} \text{ at } 25^\circ\text{C} \quad (7)$$

This equation indicates that the distribution coefficient is sharply dependent upon the potential; $K_D = 1$ when $E = E^0$ and $K_D = 10$ when $E = E^0 - 0.059/n$ volt. Accordingly, if the column electrode is maintained at a constant potential, metal ions whose standard potential is more positive than the column potential deposit quantitatively and show a large retention volume. On the other hand metal ions whose standard potential is more negative than the column potential pass through the column and are eluted together at zero retention volume. This means that in the constant potential column all the metal ions are separated into two groups.

In order to improve the situation, the authors^{11, 12} tried to use (1) a multi-stage column electrode having stepwise electrode potentials and (2) a long column electrode having a gradient electrode potential. Relevant details are presented here.

ELECTROLYTIC CHROMATOGRAPHY AT THE GRADIENT POTENTIAL ELECTRODE

(1) Coulometric determination of lead and copper^{9, 10}

In order to determine the most suitable conditions, many experiments were

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carried out by changing the dimensions of the column, the materials of the electrode, the potential of the electrode, the composition of the carrier solution and the flowrate.

Instruments used

In the separation and determination of lead and copper, a chromatographic cell and a coulometric detector cell shown in *Figure 4* were used; the column

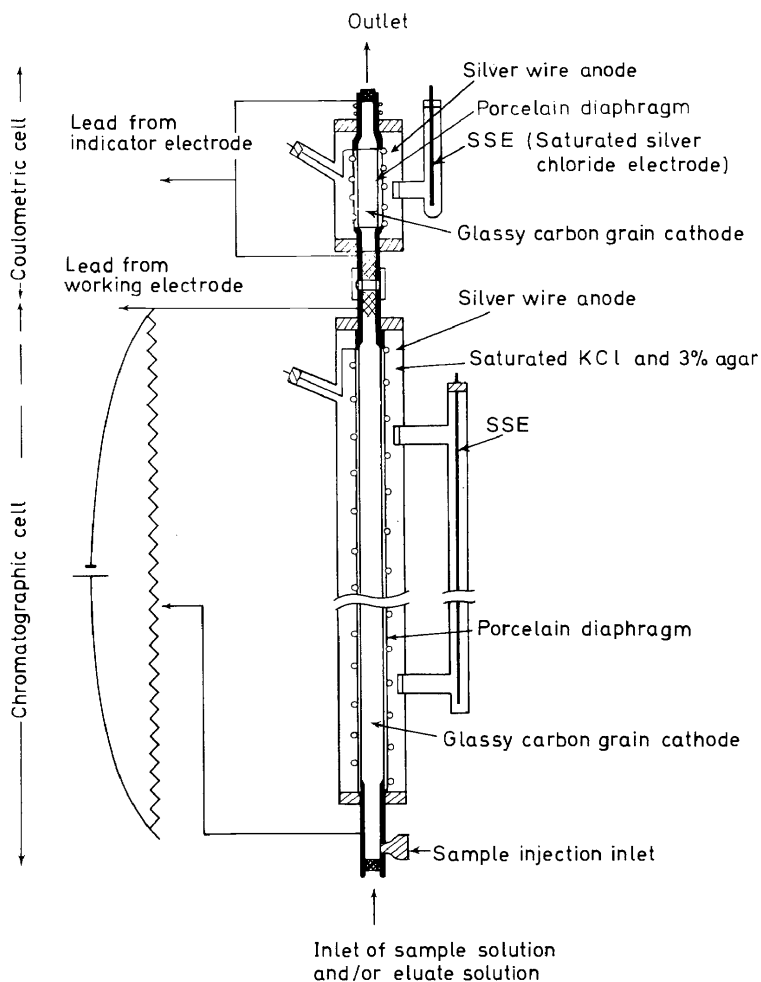


Figure 4. Chromatographic column cell and detector column cell.

cathodes of both cells were filled with 60 to 100 mesh glassy carbon grains prepared by the Tokai Denkyoku Mfg Co. Electrolysis was carried out between the column cathode composed of glassy carbon grains packed in a porous glass tube, and silver wire wound around the outside of the glass tube,

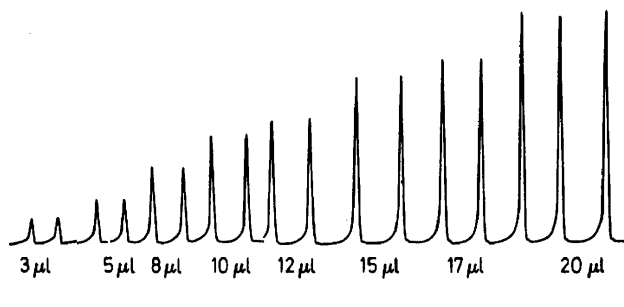


Figure 5. Coulometric recordings of lead ions (1.0×10^{-2} M): from left to right: 3 μ l (two), 5 μ l (two), 8 μ l (two), 10 μ l (two), 12 μ l (two), 15 μ l (two), 17 μ l (two), 20 μ l (three).

which in turn was inserted into an outer plastic tube containing saturated potassium chloride as an anolyte.

Two potentiostats model VE-101 made by Yanagimoto Mfg Co. were used for the control of the cathode potentials of the outlet part of the chromatograph cell and of the coulometric cell. The current/time curve was recorded

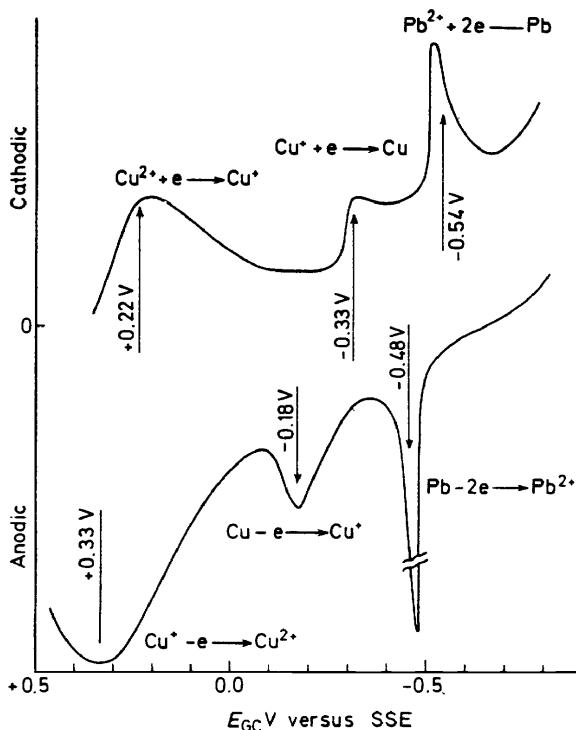


Figure 6. Cyclic polarogram at the glassy carbon electrode. Solution: 1.0×10^{-3} M Pb^{2+} and Cu^{2+} in 0.5 M HCl.

by a potentiometer recorder connected in parallel with a standard resistance in the circuit. The number of coulombs was calculated from the area under the current/time curve; an integrated circuit was also mounted ahead of the recorder, which gave the coulomb/time curve directly.

Procedure

A carrier solution of 0.5 M hydrochloric acid, deaerated by bubbling nitrogen gas, was passed through the column at the rate of 1.0 ml/min. Then -0.70 V against the saturated silver chloride-potassium chloride electrode (SSE) was applied to the outlet part of the chromatograph cathode using the potentiostat. Next the voltage drop of 0.30 V was applied along the column, resulting in the potential of the inlet part of the cathode being maintained at -0.40 V versus SSE.

A fraction of 0.001 to 0.10 ml of the sample solutions of 1.0×10^{-2} M lead and copper was introduced using a microsyringe as customary in gas chromatography. The cupric ions in the solution were deposited at the inlet of the column but the lead ions passed through it and were deposited close to the outlet.

After several minutes the cathode potential (E_2) of the outlet was raised to -0.4 V, resulting in the increase of the potential (E_1) of the inlet to -0.1 V. By this procedure lead was dissolved and conveyed into the coulometric cell, in which the cathode potential had been set at -0.7 V versus SSE, and copper was moved and redeposited at the outlet. After completion of the dissolution of lead, which could be seen on the coulometric recorder, again the cathode potentials were transferred to $E_1 = E_2 = +0.40$ V. By this procedure copper was transferred into the coulometric cell and the current recorded.

Discussion

Determinations were made with the solutions of 1.0×10^{-2} M lead and cupric ions in various ratios; the size of the sample solutions was 0.001 ml to 0.1 ml. The results obtained were satisfactory with the accuracy of ± 3 per cent with 0.01 ml samples and ± 5 per cent with 0.001 ml samples.

In the experiment the appropriate potentials to be applied to the column cathode were first examined by cyclic voltammetry using the glassy carbon as the indicator electrode (see *Figure 6*). From the curves it can be predicted that the lead ions would deposit at -0.7 V versus SSE and the deposited lead would dissolve at -0.4 V, while the cupric ions would deposit at -0.4 V and the copper at $+0.0$ V forming cuprous ions and at $+0.4$ V, cupric ions. It is important to apply a potential gradient along the column cathode in the course of deposition, otherwise deposited metals would form alloys or intermetallic compounds which cannot always be separated in the course of elution even though the potential of the column electrode would be controlled most carefully. The rate of decrease of the potential and/or the potential gradient also plays an important role and must be programmed automatically for separation under more severe conditions. In the determination of a very dilute solution, a preliminary concentration with a larger sample is necessary; for a solution of 10^{-7} M of lead ions, for example, some 100 ml of sample are needed and preliminary concentration with a preliminary column must be carried out.

(2) Radiometric determination of ThB, ThC and ThC''^{13, 14}

Electrolytic chromatography is especially suitable for rapid separation and can be operated under remote control, so that its application for the separation of unstable radioactive nuclides seems to be promising.

This section deals with the quantitative aspects of the separation of ThB, ThC and ThC'' as tracers of lead, bismuth and thallium respectively.

Reagent and apparatus

A carrier-free solution of a mixture of ThB, ThC and ThC'' in radioactive decay equilibrium was prepared from 'radio thorium' from the Radiochemical Centre, Amersham according to the usual method¹⁶.

A single channel pulse height analyser equipped with a 1.5×2 in. NaI well typed crystal was used for the radioactivity measurements.

Experimental

The potential of the chromatograph column electrode was so controlled as to distribute between $E_1 = -0.40$ V versus SSE at the inlet and $E_2 = -0.70$ V at the outlet. A deaerated solution of 0.5 M hydrochloric acid was passed at 1 ml/min. From the injection inlet, 0.20 ml of the sample solution (containing ThB, ThC and ThC'' with or without 1×10^{-2} M Pb^{2+} or Bi^{3+} as carrier) was introduced using a microsyringe.

By this procedure, ThC and bismuth ions were deposited at the inlet, ThB and lead ions at the outlet, and ThC'' came out immediately without deposition on the electrode at the potential. The solution coming out was divided into fractions of 1 ml each using a fraction collector all the time after the sample introduction.

After ten minutes, the electrode potentials were changed to $E_1 = 0.00$ V and $E_2 = -0.40$ V. Then ThB with lead ions eluted out. Finally the electrode potentials were adjusted to $E_1 = E_2 = 0.00$ V. Then ThC with bismuth was dissolved and transported to the fraction collector.

It can be seen from the decay scheme of radio thorium shown in *Figure 7* that ThB (half-life $\tau = 10.6$ h), ThC ($\tau = 60.5$ min) and ThC'' ($\tau = 3.1$ min) are the measurable nuclides when existing in equilibrium. *Figure 8* demonstrates the chromatograms of radioactivities obtained with the fractions collected by the procedure described. Decay curves for the three peaks are presented in *Figure 9*. As can be seen from the figures, the activities of the first chromatographic peak were eluted out with a very short retention time and showed the half-life of 3.3 minutes which agreed well with that of ThC''. The activities of the second peak were eluted out when E_2 was changed to -0.40 V and the half-life was measured to be 10.6 hours which is the same as the listed value for ThB. The activities of the third peak resulted when E_2 became 0.00 V and the half-life of 60 minutes was obtained, in good agreement with the listed value of 60.5 minutes with regard to ThC. The total recovery of the activities injected was 101.4 per cent which indicates that the quantitative elution is possible with the glassy carbon grain electrode.

Figure 10 shows the elution curves of a carrier-free mixture of ThB, ThC and ThC'' under the same experimental conditions; the concentrations of ThB, ThC and ThC'' are approximately 10^{-11} , 10^{-12} and 10^{-13} M, respectively.

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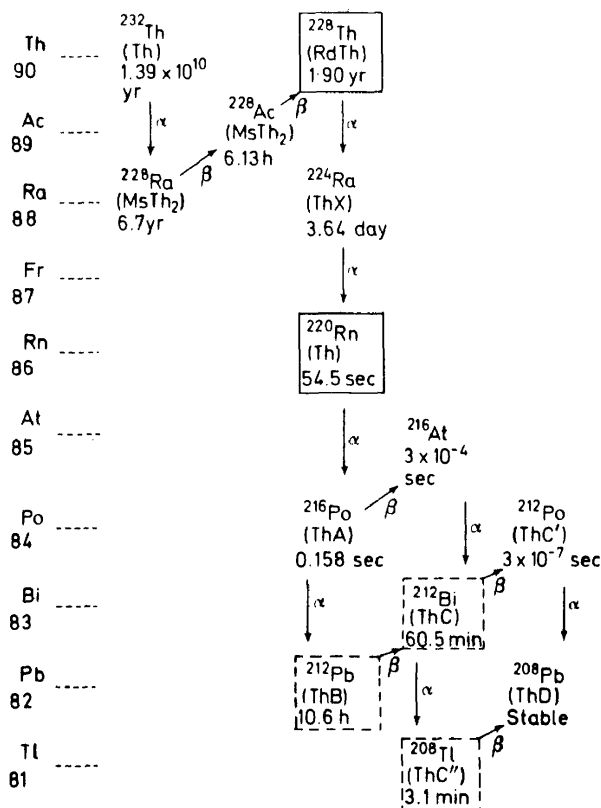


Figure 7. Decay scheme of Th series.

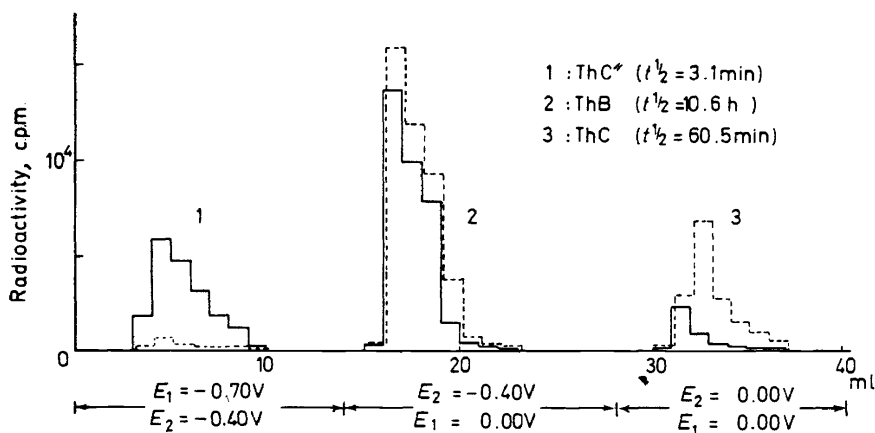


Figure 8. Elution chromatogram of radioactivities in the presence of their stable isotopes. Sample: 20 μ l solution containing 2.0×10^{-7} mole Pb^{2+} (ThB), Bi^{3+} (ThC) and (ThC'). Carrier solution: 0.5 M HCl, flowrate 1.0 ml/min. Straight line: histogram not corrected for decay. Dotted line: histogram corrected for decay.

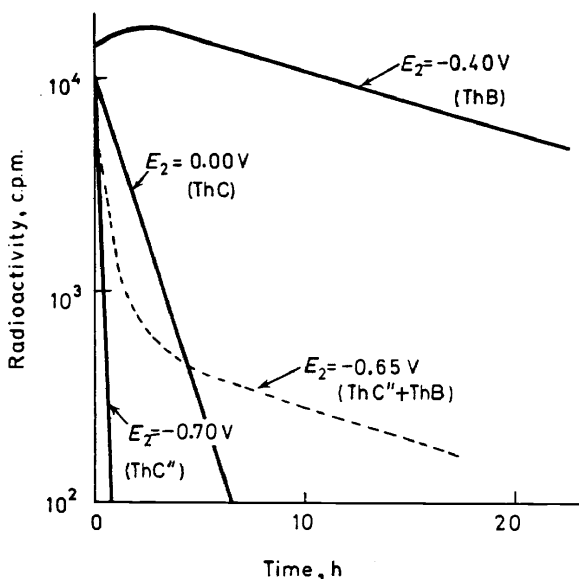


Figure 9. Decay curves of separated components.

The results are summarized in *Table 1*. ThB and ThC in the sample were quantitatively deposited even from the extremely dilute solution and were eluted out anodically without leaving any activities due to absorption. When the sample solution was passed through the column in an open circuit, all of the radioactivities came out of the column as shown in *Table 1*.

For the quantitative deposition of lead and ThB, the potential E_2 should be controlled at a negative potential of more than -0.70 V. When the potential was maintained at -0.65 V, about five per cent of the lead ions eluted without being deposited. The electrode potential of -0.70 V was

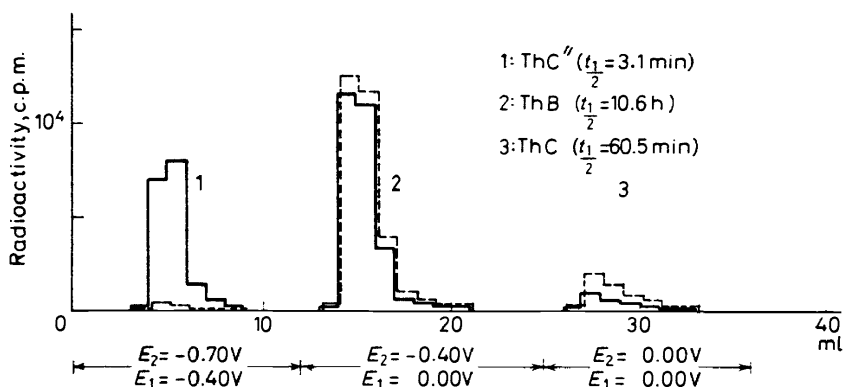


Figure 10. Elution chromatogram of carrier-free radioactivities. Sample: $20 \mu\text{l}$ solution containing about 10^{-16} mole ThB, 10^{-17} mole ThC and 10^{-18} mole ThC''. Other conditions same as *Figure 8*.

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Table I. Recoveries of radioactivities

Exp. No.	RI taken (c.p.m.)	RI found (c.p.m.)			Total	Recoveries (%)
		ThC''	ThB	ThC		
1*	19532	(No applied voltage)			19183	98.3
2†	18400				18097	98.0
3*	46750	17763	26690	2221	46675	99.9
4†	58336	19075	34896	5238	59209	101.4

* Carrier free: ThC'' $\approx 10^{-16}$ mole, ThB $\approx 10^{-14}$ mole, ThC $\approx 10^{-13}$ mole.

† With carrier: ThC'' $\approx 10^{-16}$ mole, ThB + Pb²⁺ = 2×10^{-7} mole, ThC + Bi³⁺ = 2×10^{-7} mole.
All activities are corrected for decay.

also found sufficient for the quantitative deposition of carrier-free ThB. The fact that the 10^{-11} M Pb²⁺ (ThB) solution is quantitatively electrolysed at the same potential as the 10^{-2} M Pb²⁺ solution cannot be explained by the Nernst equation; underpotential of lead ions in an extremely dilute solution may be responsible for the phenomenon, but further investigation must be carried out to solve this problem. ThC'', which is a daughter of ThC and is an isotope of thallium, was eluted out and isolated from other species without being deposited; it would be the first time that ThC'' was successfully isolated, because its half-life is too short (3.1 min) for effective isolation by the conventional electrolytic method.

ELECTROLYTIC CHROMATOGRAPHY AT THE UNIFORM POTENTIAL ELECTRODE

(1) Elucidation of the reaction mechanism at the glassy carbon electrode¹⁵

For the purpose of preparing a desirable sample solution, a uniform potential column electrode has been extensively used in this laboratory; the cell acts as a pretreatment apparatus to remove interfering elements in some cases and in other cases as a smoothing apparatus to make the oxidation state of the sample uniform before it enters the detector column. This two-step flow coulometric system is especially effective when the reaction products are unstable or oxidizable in air. A sample solution in amounts as small as 10 μ l could be analysed and the unstable product of 10^{-2} to 30 seconds in half-life could be measured.

As a preliminary test, the electrolytic reduction of cupric ions was investigated. In the study various kinds of coulomb/potential curves were examined and are shown in the *Figure 11*. (1) The quantity of electricity Q_{II} was measured at a definite potential E_{II} with a definite amount of cupric ions (8×10^{-7} mole) without using the preparatory column I. The measurements of Q_{II} were made at various potentials E_{II} and the Coulomb/potential (Q_{II}/E_{II}) curve similar to the polarographic current/potential curve was obtained, which can be seen as Curve 1 in *Figure 11*. The Q_{II}/E_{II} curve shows two waves. Both correspond to one electron reduction, and therefore the first wave is the reduction to the cuprous state and the second wave, to the metal.

(2) The quantity of electricity Q_{II} was measured at constant potential (+0.50 V versus SSE) of the coulometric detector but the potential E_1 of the

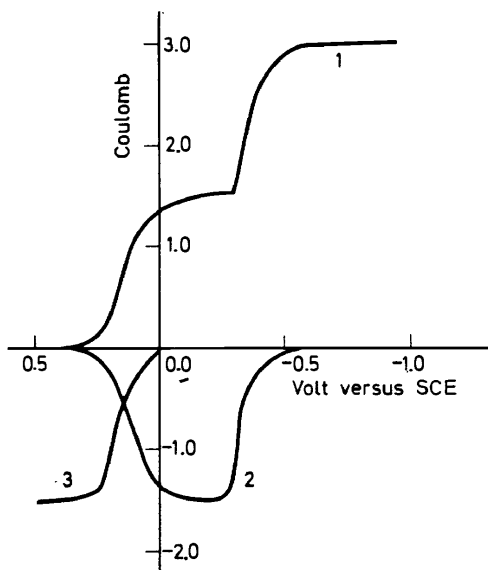


Figure 11. Coulomb/potential curves of cupric ions in hydrochloric acid solution: Curve 1: Q_{II}/E_{II} curve without first cell; Curve 2: $Q_{II} (+0.5 \text{ V})/E_I$ curve; Curve 3: Q_{II}/E_{II} curve at $E_I = -0.15 \text{ V}$.

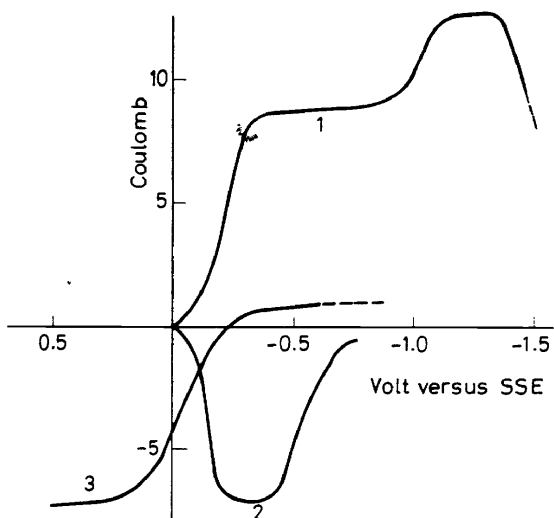


Figure 12. Coulomb/potential curves of uranyl ions in hydrochloric acid solution: Curve 1: Q_{II}/E_{II} curve without first cell; Curve 2: $Q_{II} (+0.3 \text{ V})/E_I$ curve; Curve 3: Q_{II}/E_{II} curve at $E_I = -0.65 \text{ V}$.

preparatory column I was kept at a definite value. The measurements of Q_{II} were made at various potentials E_I and the coulomb/potential $Q_{II} (+0.5 \text{ V})/E_I$ curve was plotted, which is shown as Curve 2 in the figure. This curve clearly demonstrates that the cupric ions are reduced in column I with the potential ranging from $+0.3 \text{ V}$ to -0.4 V to form cuprous ions, which are then oxidized to cupric state in column II showing the oxidation current of Curve 2. At a more positive potential than $+0.3 \text{ V}$, cupric ions are not reduced and at more negative potential than -0.4 V , all cupric ions are reduced further to the metallic state; therefore in both regions no current due to cuprous ions flows at column II.

(3) The quantity of electricity Q_{II} was measured at a definite potential E_{II} as in case (1). However, the potential E_I of column I was kept constant at -0.15 V versus SSE. The measurements of Q_{II} were made at various potentials E_{II} and the Q_{II}/E_{II} curve of the anodic side was plotted: this is shown as Curve 3.

In order to elucidate the reaction mechanism of uranyl ions in chloride media, a similar investigation was carried out with a series of carrier solutions of varying acidity. One of the results is shown in *Figure 12*.

Curve 1 in this figure is the Q_{II}/E_{II} curve obtained with the uranyl ions (8.4×10^{-7} mole UO_2^{2+} in 0.1 M KCl) without applying potential to column I. Curve 2 is the $Q_{II} (+0.3 \text{ V})/E_I$ curve, which was obtained by the measurement of Q_{II} at $E_{II} = +0.3 \text{ V}$ at various potentials E_I of the column I. Curve 3 is the Q_{II}/E_{II} curve obtained with the column I of the electrode potential E_I kept at -0.65 V .

It can be seen from the curves that the UO_2^{2+} or U(vi) is reduced quantitatively to U(v) at the half-wave potential $E_{\frac{1}{2}}$ of around -0.2 V versus SSE and is further reduced probably to U(IV) at $E_{\frac{1}{2}}$ of ca. -1.0 V . However, the latter reduction proceeds too slowly to be quantitative. The fact that the first step reduction product U(v) is oxidized at $E_{\frac{1}{2}} = -0.05 \text{ V}$ (Curve 3) means the redox reaction of $\text{U(v)} \rightleftharpoons \text{U(vi)}$ proceeds fairly reversibly. However, the second reduction product U(IV) is not oxidized because it is hydrolysed very rapidly; this could be confirmed by the experiments using a lower flowrate. The U(IV) is also unstable at a potential higher than -0.5 V , where the disproportionation reaction becomes appreciable; it was observed that the U(IV) was stabilized in acidic solutions.

The comparison of the coulometric results at the two step column electrode with the polarographic observations at the dropping mercury electrode is very interesting; it will, however, be discussed elsewhere.

(2) Determination of plutonium in the presence of uranium, iron and chromium¹⁵

The aim of this study is to analyse for plutonium in the presence of other metals in a shielded room as a protection from its strong activity.

Plutonium is well known to have many oxidation states such as Pu(vi)O_2^{2+} , Pu(v)O_2^+ , Pu(IV) , Pu(III) in aqueous solution and it is pretty difficult to prepare a solution of uniform ionic state by a simple chemical procedure.

In the present study, two step column electrolysis was applied; the first cell was used to remove interfering elements and at the same time to smooth the oxidation state of plutonium, and the second cell to measure the amount of plutonium coulometrically.

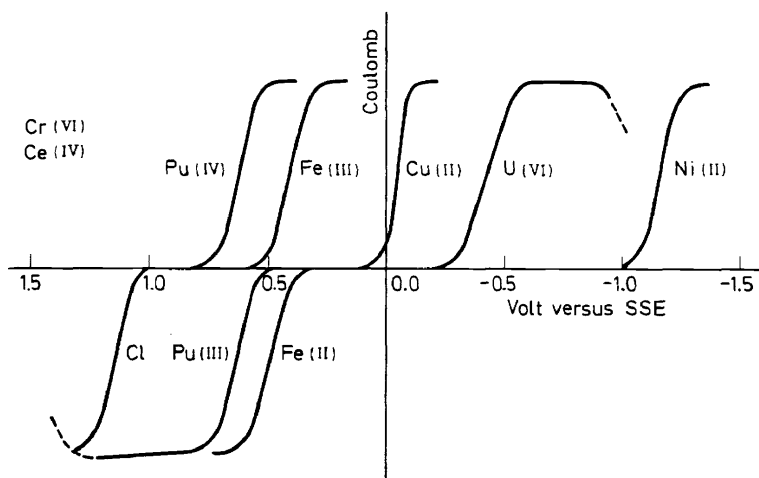


Figure 13. Coulomb/potential curves of plutonium and other metal ions.

Figure 13 shows coulomb/potential curves of plutonium and some other elements in 0.5 M H_2SO_4 at the glassy carbon column electrode. From the figure it becomes clear that plutonium(III) is quantitatively oxidized at +0.75 V but chloride is not oxidized, and quantitative reduction of plutonium proceeds at +0.45 V, whereas ferric iron is not reduced; this was proved experimentally as is shown in Table 2.

As for the results, the following procedure is recommended for the semi-automatic analysis of plutonium; 0.5 M H_2SO_4 solution is continuously

Table 2. Determination of plutonium in the presence of iron

E_{II}	Electricity consumed	
	Calculated	Found
V vs. SSE +0.500	Coulomb 2.017×10^{-3}	Coulomb 1.27×10^{-3} 1.39 2.41
+0.475	2.017×10^{-3}	1.89×10^{-3} 1.81 1.97
+0.450	2.017×10^{-3}	2.20×10^{-3} 2.21 2.23
+0.425	2.017×10^{-3}	2.24×10^{-3} 2.31 2.30

Sample: 2.09×10^{-8} mole Pu, 2.00×10^{-8} mole Fe. Carrier solution: 0.5 M H_2SO_4 . Flowrate: 5 ml/min $E_1 = +0.75$ V vs. SSE.

ELECTROLYTIC CHROMATOGRAPHY AND COULOMETRIC DETECTION

allowed to flow through the two column cell as carrier and the potential of the first cell is controlled at +0.75 V and that of the second cell at +0.45 V using two independent potentiostats. The sample solution is introduced into the carrier stream. As the sample includes both Pu(III) and Pu(IV), the current recorder of the first column measures the quantity of Pu(III) due to the reaction $\text{Pu(III)} - e = \text{Pu(IV)}$. The current recorder of the second column measures the quantity of Pu(IV) based on the reaction $\text{Pu(IV)} + e = \text{Pu(III)}$, hence it represents the sum of Pu(III) and Pu(IV) in the sample.

If the sample contains ferrous iron or other reducible substances, the first recorder will also measure them in addition to Pu(III). However, the second recorder measures only Pu(VI) and not other ions because they are hardly reduced at +0.45 V; Ce(IV) and Cr(VI) are reduced at the first column ($E_1 = +0.75$ V) and Fe(III), Ce(III), Cr(III), Cu(II), Ni(II), U(VI) and Cl(-I) are neither reduced nor oxidized at the second column ($E_{II} = -0.45$ V). Hence few ions interfere with the determination of plutonium.

Table 3. Determination of plutonium

Pu taken	Electricity consumed		Pu found
	Calculated	Found	
($\times 10^{-8}$ mole)	(coulomb)	(coulomb)	(%)
20.9	2.017×10^{-2}	2.04×10^{-2}	101.1
		2.07	102.6
		2.06	102.1
		2.01	99.7
10.5	1.009×10^{-2}	1.05×10^{-2}	104.1
		1.03	102.1
		1.04	103.1
1.05	1.009×10^{-3}	1.07×10^{-3}	106.1
		1.04	103.1
		1.05	104.1
		1.03	102.1
0.21	2.017×10^{-4}	2.20×10^{-4}	109.1
		2.07	102.6
		2.02	100.2
		2.15	106.6
		2.05	101.6
0.042	4.03×10^{-5}	3.97×10^{-5}	98.7
		3.94	97.7
		4.07	99.3
		3.93	97.6
		3.92	97.2

Carrier solution: 0.5 M H_2SO_4 . Flowrate: 5 ml/min. $E_1 = +0.35$ V vs. SSE. $E_{II} = +0.75$ V vs. SSE.

Various amounts of plutonium (mixture of III and IV) were analysed and the results are summarized in Table 3. The effect of the presence of various ions is shown in Table 4.

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Table 4. Determination of plutonium in the presence of various ions

Pu <i>taken</i>	Pu <i>found</i>	
($\times 10^{-8}$ mole)	($\times 10^{-8}$ mole)	(%)
4.18	4.12	101.2
	4.07	99.9
	4.19	102.7
Other ions present		
Ce: 6.42 ($\times 10^{-8}$ mole)		
Cr: 16.0		
Cu: 4.01		
Ni: 8.00		
U: 3.98		
Cl: 8.00		

Carrier solution: 0.5 M H₂SO₄, Flowrate: 5 ml/min, $E_I = +0.75$ V, $E_{II} = +0.10$ V.

In conclusion, the proposed analytical method is accurate within ± 3 per cent with 0.05 ml of 4×10^{-3} M Pu(III and IV) solutions and is sensitive down to 0.02 ml of 2×10^{-5} M Pu. The determination is automatically performed except for the introduction of samples.

The determination of the ratio of plutonium to uranium is often important because the mixed oxides or carbides are used as nuclear fuels. A coulometric procedure similar to that described above was developed as follows: a 100 mg of the mixed oxides sample was dissolved with 5 ml of 10 M HNO₃ and three drops of 1 M HCl, and evaporated nearly to dryness. The addition of HNO₃ and HCl and the evaporation were repeated three times followed by the dissolution with 25 ml of 0.5 M H₂SO₄. 10 μ l of the aliquot was taken as the sample and injected into the carrier stream of deaerated 0.5 M H₂SO₄. For the determination of plutonium, the potential E_I of the first column was kept +0.10 V versus SSE and the quantity of electricity Q_{II} consumed at the second column was measured at the potential E_{II} of +0.75 V. For the determination of uranium, E_I was kept at +0.10 V and Q_{II} was measured at -0.60 V. Therefore the electrode reactions of

Table 5. Determination of plutonium in the plutonium-uranium samples

Pu/Pu + U <i>taken</i>	Pu <i>found</i>	U <i>found</i>	Pu/Pu + U <i>found</i>
(%)	(mg)	(mg)	(%)
25.0	21.83	65.53	24.97
	30.44	90.68	25.13
	22.13	66.15	25.06
30.0	33.25	82.20	28.80
	32.80	84.04	28.07
	32.76	80.01	29.02
33.0	24.27	49.83	32.75
	23.00	47.00	32.89

$\text{Pu}^{3+} - e = \text{Pu}^{4+}$ and $\text{U}^{6+} + 2e = \text{U}^{4+}$ were used respectively for the determinations. The results of the determination by the proposed procedure are summarized in *Table 5*.

(3) Coulometric process analysis of very dilute lead ions¹⁷

In the studies described above, a very small amount (less than 0.1 ml) of relatively concentrated solution ($10^{-5} \sim 10^{-2}$ M) was supplied as sample for analysis. With very dilute solutions of less than 10^{-6} M, preliminary concentration with the column electrode is extremely effective. The method was automated and applied to the determination of traces of lead ions in water. The instrumentation and the procedure were as follows. Sample water and supporting electrolyte (0.2 M HCl) solution were mixed at the ratio of 1:1; dissolved oxygen was next removed by bubbling nitrogen gas, and the mixture introduced to the two column cell in the same arrangement as shown in *Figure 1*. The potential of the first and second cells was kept at -0.6 V versus SSE and the electrolytic current of the second cell was recorded. At this potential all lead ions deposit at the first column electrode and no current flows in the recorder of the second cell. After a definite time (e.g. 30 minutes) had passed, the potential of the first cell was changed to -0.40 V for a further definite time (e.g. one minute). Under this voltage drop all the lead deposited in the first cell dissolved again and was conveyed to the second cell, where the lead ions were electrolytically reduced once more. The recorder of the second cell recorded the quantity of electricity passed, which was proportional to the amount of lead supplied for the period. By a simple switching of the potential with a definite time interval, 10^{-6} to 10^{-8} M lead solution is analysed without any interference of other ions and the result is recorded automatically on a chart. The details will be reported elsewhere.

CONCLUSION

The author has discussed rapid electrolysis using a column electrode packed with glassy carbon grains. The column electrode is used not only as a coulometric detector but also for the separation of metals, the elimination of interfering ions, the smoothing of the oxidation state and the concentration of the dilute solutions. In order to separate metals whose deposition potentials are nearly equal, the column electrode of gradient potential has been proposed. By the use of two or more column cells in series in the carrier stream, automated fractional determination of metals has been performed with satisfactory results. The method has been applied to the remote controlled determination of radioactive nuclides in a shielded room.

As the rate of electrolysis is controlled not only by the equilibrium potential but also by the rate of the change of the potential, it is hoped that the superimposing of an alternating voltage on the d.c. potential would provide a better separation of metals in this electrolytic chromatography.

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REFERENCES

- ¹ T. Fujinaga, T. Nagai, C. Takagi and S. Okazaki, *Nippon Kagaku Zasshi*, **84**, 941 (9, 1963). (In Japanese with English abstract.)
- ² J. J. Lingane, *Analyt. Chim. Acta.* **2**, 591 (1948).
- ³ E. L. Eckfeldt, *Analyt. Chem.* **31**, 1453 (1959).
- ⁴ A. J. Bard, *Analyt. Chem.* **35**, 1125 (1963).
- ⁵ G. Johanson, *Talanta.* **12**, 163 (1965).
- ⁶ W. J. Blaedel and J. H. Strohl, *Analyt. Chem.* **36**, 1245 (1964).
- ⁷ W. J. Blaedel and J. H. Strohl, *Analyt. Chem.* **36**, 445 (1964).
- ⁸ W. J. Blaedel and J. H. Strohl, *Analyt. Chem.* **37**, 64 (1965).
- ⁹ T. Fujinaga, C. Takagi and S. Okazaki, *Kogyo Kagaku Zasshi*, **69**, 1798 (1964). (In Japanese with English abstract.)
- ¹⁰ T. Fujinaga, K. Izutsu and S. Okazaki, *Review of Polarography, Japan*, **14**, 164 (1967).
- ¹¹ S. Okazaki, *Review of Polarography, Japan*, **15**, 154 (1968).
- ¹² T. Fujinaga, *Japan Analyst*, **17**, 651 (1968). (In Japanese.)
- ¹³ T. Fujinaga, K. Izutsu, M. Koyama, S. Okazaki and K. Tsuji, *Nippon Kagaku Zasshi*, **89**, 673 (1968). (In Japanese with English abstract.)
- ¹⁴ T. Fujinaga, M. Koyama, K. Izutsu, S. Okazaki and K. Tsuji, *Proceedings of the 9th Japan Conference on Radioisotopes, A/C 7*, **83** (1969).
- ¹⁵ T. Fujinaga, K. Motojima, T. Yamamoto and S. Kihara, in preparation.
- ¹⁶ M. Ishibashi, T. Fujinaga and Y. Kusaka, *Nippon Kagaku Zasshi*, **75**, 13 (1954). (In Japanese.)
- ¹⁷ T. Fujinaga, S. Okazaki and K. Aoki, in preparation.