Studies on the Coulometric Determination of Uraninm (VI) and Thallium (I) by Controlled Potential Electrolysis

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In recent years, coulometric analysis has been developed and widely used as a technique for the determination of substances in solution by measuring the quantity of electricity required for the completion of a reaction in an electrolysis cell. Of two coulometric techniques, i. e., coulometric titration with a constant current and coulometric analysis with a controlled potential of a working electrode, the latter is more interesting to the author, because by this method both electrolytic separation and quantitative determination of chemical species can be achieved simultaneously. Especially, the use of a mercury cathode as the working electrode[1] has an advantage that the optimum control potentials can easily be determinable from polarographic data.

In our laboratory, we took up the coulometry of uranium as one of the interesting themes of researches when we had an opportunity in studying various kinds of analytical methods for uranium in accordance with the request by Japan Atomic Fuel Corporation. The coulometric determination of uranium (VI) by using a mercury cathode at a controlled potential was studied by G. L. Booman, W. B. Holbrook and J. E. Rein[2]. It was found to be very useful for the analysis of uranium in a highly enriched nuclear element which underwent fission to an appreciable extent. But the instrument used by them[3] was complicated and expensive. Therefore, a simple counter millicoulometer has been coustructed in our laboratory, a ready-made potentiostat (electrical instrument for automatic controlled potential electrolysis) being tried for electrolysis. By these instruments, the author studied the fundam ental conditions of coulometry for uranium and tried the successive determinations of uranium and thallium in mixed solutions.

Coulometer

There are many kinds of coulometers capable of measuring the quantity of electricity (coulombs) required for electrolysis. A hydrogen-oxygen coulometer is not suitable for measuring a very small quantity of electricity in microanalysis. Comparing many coulometers of other types[4] including a titration coulometers, an electromechanical integrater, and various types of electronic coulometers, the author adopted a counter millicoulometer utilizing a blocking oscillator because of its

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simplicity in construction and high sensibility for measuring the quantity of electricity in very small orders. This coulometer was introduced by M. Masui and H. Sayo[5] and is considered to be an improved type of a coulometer described previously by K. W. Krammer and R. B. Fischer[6]. The present author constructed a coulometer the circuit of which is shown in Fig. 1. It was examined in several points affecting its efficiency.

Fig. 1 Coulometer
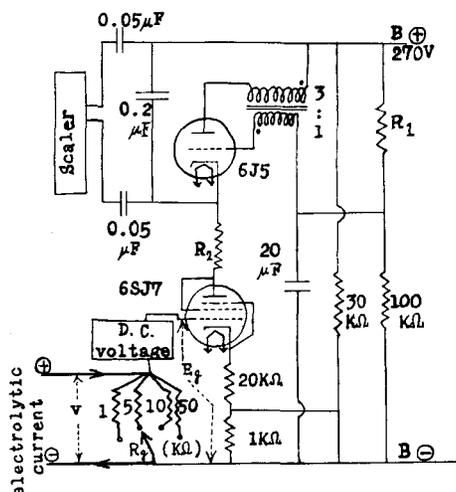
With this coulometer, the quantity of electricity was measured by the following principle. The total resistance in an oscillator circuit containing a 6SJ7-GT tube was made to change automatically with the change in electric pressure by the current flowing through a resistance in the grid circuit. The oscillation frequencies were changed in proportional to the current. So the oscillation counts summed up by a scaler indicated the total quantity of electricity flowing through the resistance in the grid circuit.

For supplying electric power to this coulometer, the alternating current source was first connected to an iron resonance transformer to stabilize its voltage. Moreover, vacuum tube electric pressure stabilizer was used to supply the B electric pressure of the coulometer.

In order to examine the linearity and sensitivity of this coulometer, the resistance R_1 and R_2 in Fig. 1 were varied. The results are shown in Fig. 2.

From these results, it was found that frequency (f : counts per minute) for a definite electric pressure (v) in the grid circuit was altered by choosing an appropriate resistance value for R_1 and that the sensitivity (a: change in frequency for unit change of electric pressure) depended mainly on the value fo resistance R_2. Furthermore, the responce and the accuracy of this coulometer was examined by regularly changing the electric pressure supplied from the potentiometer drum of a polarographic instrument. In this case, total counts summed up by the coulometer was compared with the theoretical values calculated as follows.

If the frequency (f) of the coulometer changes linearly to the electric pressure (v) in the grid circuit, namely $f = av + f_0$ (a and f_0 are constant characteristic of a

Fig. 2 Relation between f and E
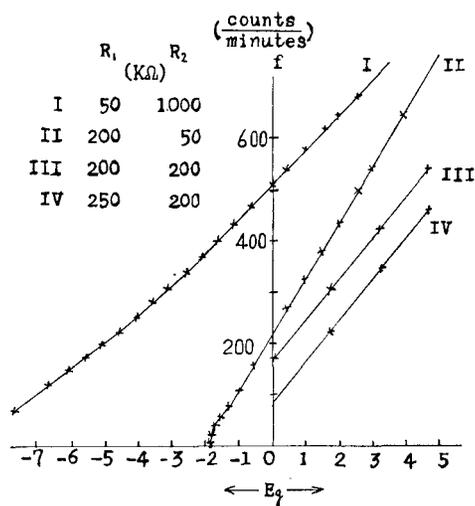
coulometer), the total counts (S) for a certain period of time (t) are expressed by the following equation.

$$S = \int_0^t f dt$$
$$= \int_0^t (av + f_o) dt \qquad \text{(Eq. 1)}$$

In this equation, if v increases from zero in proportion with t, namely v=bt (b is the rate of change in v),

$$S = \int_0^t (abt + f_o) dt$$
$$= avt^2/2 + f_o t$$
$$= (av_t/2 + f_o) t \qquad \text{(Eq. 2)}$$

In Eq. 2, v_t is an electric pressure in the grid circuit at time t. Table 1 shows results obtained from experiments with various v_t and b, both R_1 and R_2 in the coulometer being at 200kΩ. As shown in Table 1, values determined by this coulometer agreed excellently with those calculated theoretically from Eq. 2.

Table 1

Span voltage	0→2	0→2	0→5	0→4.5	4.5→0
b (volt/minute)	0.1905	0.376	0.476	0.478	0.478
Experimental counts	2415	1224	5022	4492	4483
Theoretical counts	2421	1226	5026	4484	4484

Electric circuit for electrolysis

The block diagram of the electric circuit for our controlled potential coulometry is shown in Fig. 3.

A Shimazu AEA-I type potentiostat was used to control the cathode potential at a constant value during the electrolysis. In this instrument, the e. m. f. between a mercury cathode and a saturated-calomel electrode was connected in series-opposition to a potentiometer slide wire. The off-balance d. c. voltage (error signal)

Fig. 3 Electrical circuit for electrolysis
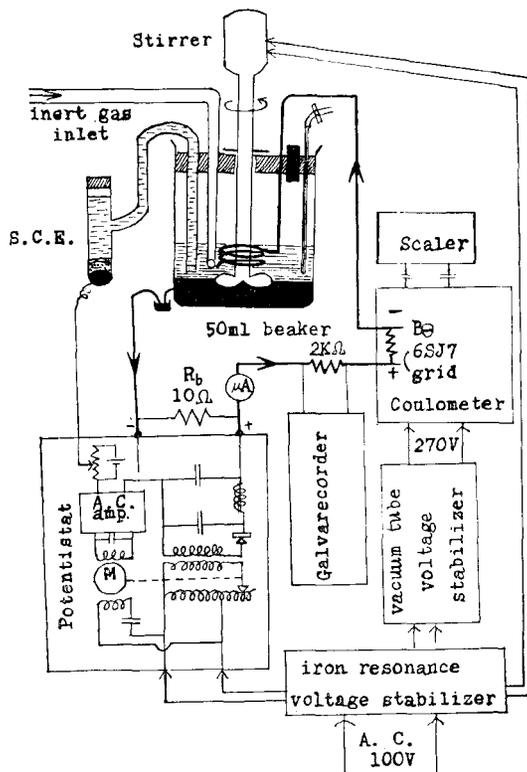
was fed back to a converter-amplifier and was amplified up to a power level. By this power, a balancing motor was driven to change the total input voltage applied to the electric cell until the potential of the working electrode (cathode) returned to the value set on the potentiometer.

The use of a 10 ohm bleeder resistor (R_b) across the output was found to very effective in keeping the RC time constant small and aided in preventing hunting when a high resistance was connected with the cell circuit. The electric current flowing through the electrolysis cell circuit was recorded automatically by a Yanagimoto GR-103 type galvarecorder whose input voltage was supplied across a 2 kΩ resistance inserted in this circuit. This current was integrated by means of the coulometer described above. The scaler part of a radioactivity counter in our laboratory was used as a scaler for the coulometer in our experiments.

Electrolysis cell assembly

A 50 ml beaker of borosilicate glass was used for the electrolysis cell. A piece of platinum wire was sealed into the side of the beaker at its bottom to make electric contact with cathode mercury and the negative terminal of the potentiostat. The anode was a helical platinum wire immersed in a solution as shown in Fig. 3. In order to vigorously agitate the mercury solution interface, the propeller blades of a glass stirrer were partially immersed in mercury. The side arm of a saturated-calomel electrode was filled with saturated potassium chloride solution.

The tip of this salt bridge was closed by a sintered glass disk and placed near the mercury surface.

A gas delivery tube was used for removing dissolved air from the solution by means of an inert gas. As this inert gas, the author tried to use commercially available propane in a high pressure container. It was found from our experiments by use of a polarographic method that by passing this commercial propane gas through the solution for about five minutes the polarographic oxygen wave disappeared completely and no appreciable effect was seen for the wave height of the polarographic uranyl wave as compared with the experiment using hydrogen gas to remove dissolved air.

In addition to the inlets of above mentioned equipments, a rubber stopper for the glass cell had an inlet for the sample solution and a hole for inserting the capillary glass tube of a dropping mercury electrode which was used for checking the changes of dissolved species in the solution by the polarographic method.

Electrolytic solution

As the present author used a platinum anode immersed directly in the electrolytic solution of 1 mol/l sulfuric acid rather than a seperate anode used by Booman et al. [2], an anodic depolarizer [7] had to be used to prevent the generation of oxygen at the anode. The author adopted hydrazine as a depolarizer and a 1 mol/l sulfuric acid solution almost saturated with hydrazine as a supporting electrolyte in our experiments. It was found from our experiments that hydrazine was very effective for settling the background current of the supporting electrolyte and did not reduce uranyl ions in the sample solution because the polarographic wave height of uranyl ion was not affected by adding hydrazine in the solution.

During the electrolysis, the following reactions took place at the platinum anode and the mercury cathode, respectively.
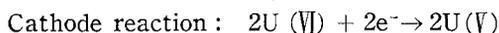
$$\text{Anode reaction}: \quad N_2H_5^+ \rightarrow N_2 + 5H^+ + 4e^-$$
$$\text{Cathode reaction}: \quad 2U\,(Ⅵ) + 2e^- \rightarrow 2U\,(Ⅴ)$$
$$\text{Disproportionation in the solution}:$$
$$2U\,(Ⅴ) \rightarrow U\,(Ⅵ) + U\,(Ⅳ)$$
$$\text{Total reaction by a controlled potential}$$
$$\text{mercury cathode}: \quad U\,(Ⅵ) + 2e^- \rightarrow U\,(Ⅳ)$$
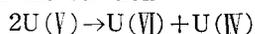
General procedure for analysis

The aforementioned supporting electrolyte through which hydrogen was passed in advance to remove dissolved air, was taken (10 ml) in the electrolysis cell and was subjected to electrolysis at a controlled cathode potential, while commercial propane gas was passed vigorously and the solution was stirred by means of a glass propeller, until a constant background current was obtained. Then 1 or 2 ml of the sample solution from which dissolved air was removed in advance was pipetted in the cell. The electrolysis was allowed to proceed at a controlled cathode potential until the electrolysis current recorded by the galvarecorder decreased nearly to the same value as observed with the supporting electrolyte alone (background current). The time spent for the electrolysis was measured by a stop watch. The time (t) required for making the electrolysis complete as well as the form of the current curve obtained by the galvarecorder depended mainly on the following factors: the

concentration of the sample solution, the rate of stirring and the outer resistance of the electrolysis circuit. The general form of the current curve is shown in Fig. 4.

Fig. 4 Current curves during electrolysis
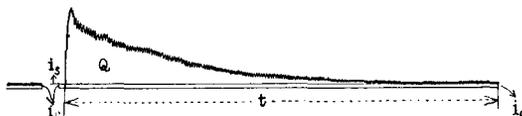
The net charg (Q) in coulombs required for the electrolysis of the sample solution was calculated from the following relation.

S : total counts read by the scaler of the coulometer

R_g: the resistance used in the grid circuit of the coulometer (Fig. 1) (expressed in ohms)

i : the current flowing through the electrolytic circuit (i $=i_s + i_c$)

i_s : the net current for the electrolysis of the sample ($i_s = i - i_c$)

i_c : the background current (assumed as constant)

a : the characteristic of the coulometer (counts per minute/volt)

Since $v=R_g i$, from Eq. 1

$$S = \int_0^t (aR_g i + f_o)dt$$
$$= \int_0^t aR_g (i_s + i_c)dt + \int_0^t f_o dt$$
$$= \int_0^t aR_g i_s dt + (aR_g i_c + f_o) t$$
$$= aR_g Q/60 + f_o t \qquad \text{because } Q = \int_0^t i_s dt \times 60$$

In this equation, f_c is the frequency observed by the coulometer at the background current (expressed in counts per minute). The electrolysis time (t) is expressed in minutes.

From this equation

$$Q = 60 (S - f_o t)/aR_g \qquad \text{(Eq. 3)}$$

The controlled cathode potential was determined from the half-wave potential of the polarogram obtained by the same electrolyte solution of the analysis. For the electrolysis of uranyl ions whose half-wave potential was found to be -0.18 volt against the standard calomel electrode, the cathode potential was controlled at -0.3 volt vs. S. C. E.. For the electrolysis of thallous ions (half-wave potential: -0.475 volt vs. S. C. E.), the controlled potential was fixed at -0.5 volt. vs. S. C. E..

In several preliminary experiments for our method, the polarograms of solutions in the electrolysis cell were recorded at the beginning and the end of electrolysis in order to know the chemical species in the electrolytic solution and to ascertain the completion of the electrolysis.

By the procedure mentioned above, the coulometric determination of the sample could be carried out several times on the same supporting electrolyte once pipetted in the cell if the electrolysis of the preceding sample was complete.

Experimentals and Results

Many standard sample solutions containing various amounts of uranyl ions were analyzed by this method. Though the cathode potential was controlled at —0.3 volt vs. S.C.E., some hunting was observed on the meter of the potentiostat: the electrolytic current curves showed jagged forms in the courses of exponential decreases.

The net charge in coulombs required for the electrolysis of the uranyl ions in these experiments were calculated from Eq. 3 and are shown in Table 2 along with the theoretical values calculated on the basis of Faraday's law of electrolysis. As the reaction is regarded as two electron reduction (as referred to the cathode reaction),

$$\text{Theoretical value} = 2 \times 96520 \times m/238.08$$

(m: grams of uranium in the sample)

Table. 2

uranium in the sample (micrograms)	net coulombs required for the electrolysis		electrolysis times (minutes)
	"theoretical"	"experimental"	
20	0.0162	0.0161	60
		0.0218	28
40	0.0324	0.0326	40
		0.0281	45
		0.0315	42
		0.0396	42
		0.0311	21
		0.0341	20
80	0.06488	0.0632	55
		0.0660	45
90	0.07299	0.0728	45
		0.0758	40
		0.0747	40
		0.0773	28
		0.0704	26
		0.0755	25
200	0.1622	0.151	28
		0.158	50
		0.148	40
		0.155	60
		0.167	76
		0.166	100
400	0.3244	0.338	40
		0.352	40
		0.323	93
500	0.4055	0.399	50
846	0.6861	0.7014	85
1692	1.372	1.345	105

Fig. 5

Uranium (micrograms)
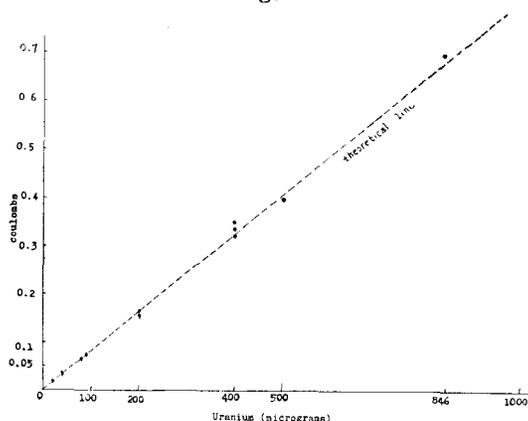
As shown in Table 2 and Fig. 5, fairly good agreements with the theoretical values were obtained in these experiments, although the relative deviations were greater for smaller amounts of uranyl ions in sample solutions.

The author tested also the coulometric determinations of thallous ions. Furthermore, the successive determination of uranyl and thallous ions was attempted for the mixed solutions of these ions. In this experiment, the solution was electrolyzed at -0.1 volt vs. S. C. E. first and then the cathode potential was controlled at -0.3 volt and -0.5 volt vs. S. C. E. successively. In this way, both uranyl and thallous ions were coulometrically determined successively without interfering each other. An example of the electrolytic current curves in these experiments is shown in Fig. 6.

Fig. 6   Current curves for the electrolysis of the mixed solution of uranyl and thallous ions at different controlled cathode potentials
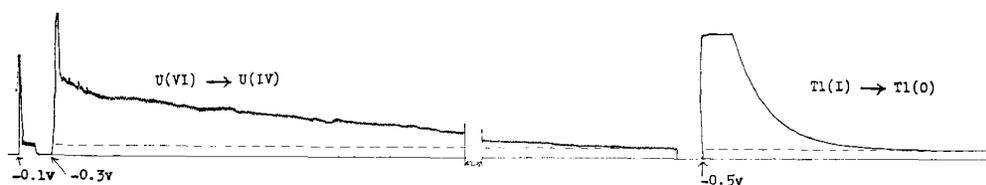
The results are shown in Table 3, in which the net charge in coulombs required for the electrolysis of each kind of ions is compared with the theoretical values calculated from Faraday's law. In these electrolytic reactions, thallous ions were reduced to the metallic state by one electron reduction.

Table 3

Uranium in the sample ($\times 10^{-7}$mol)	Net coulombs for uranium		Thallium in the sample ($\times 10^{-7}$mol)	Net coulombs for thallium	
	"theor."	"exper."		"theor."	"exper."
—	—	—	3.9	0.0376	0.0381
					0.0370
10.5	0.2016	0.1982	10.6	0.1013	0.092
		0.1902			0.116
1.0	0.019	0.023	0.8	0.0075	0.0098
		0.022			0.011

In the electrolysis of thallous ions, the electrolytic current decreased smoothly in contrast to the jagged form for the electrolysis of the solutions of uranyl ions. It was presumed that this smooth curves were due to the fact that, because thallium metal resulting from thallous ions was amalgamated by the cathode mercury, fairly uniform diffusion layers were formed on the cathode surface and hence the cathode potential could be controlled at a fixed voltage smoothly by the potentiostat. In contrast to this, because uranous ions formed by the reduction of uranyl ions did not combine with the cathode mercury, these ions diffused back to the solution from the cathode surface and accordingly the cathode potential was liable to hunt near the controlled value by our potentiostat.

From the consideration on the results of the experiments, it is concluded that the coulometric determination of uranyl ions can be made in principle by the method outlined above and that a more faithful potentiostat and the improvement of the analytical condition will increase the precision of this method.

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