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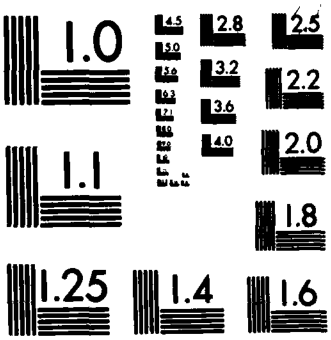
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ATOMIC ENERGY
OF CANADA LIMITED

L'ÉNERGIE ATOMIQUE
DU CANADA LIMITÉE

AUTOMATED CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM

Détermination de l'uranium par coulométrie automatisée à potentiel contrôlé

C.H. KNIGHT, D.E. CLEGG, E.D. WRIGHT and R.M. CASSIDY

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Chalk River, Ontario

June 1982 juin

ATOMIC ENERGY OF CANADA LIMITED

AUTOMATED CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM

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General Chemistry Branch

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L'ENERGIE ATOMIQUE DU CANADA, LIMITEE

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Résumé

Un coulomètre à potentiel contrôlé a été automatisé dans notre laboratoire pour la détermination routinière de l'uranium en solution. Ce système automatisé conçu à Chalk River contrôle le dégazage, la pré-réduction et la réduction de l'échantillon. Le résultat final est affiché sur l'écran de lecture numérique du coulomètre. Les modes manuels et automatisés de fonctionnement sont comparés pour montrer la précision et l'exactitude du système automatisé. Les résultats sont également indiqués pour le titrage coulométrique d'échantillons typiques d'alliages d'uranium et d'aluminium.

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ABSTRACT

A controlled-potential coulometer has been automated in our laboratory for routine determination of uranium in solution. The CRNL-designed automated system controls degassing, prereduction, and reduction of the sample. The final result is displayed on a digital coulometer readout. Manual and automated modes of operation are compared to show the precision and accuracy of the automated system. Results are also shown for the coulometric titration of typical uranium-aluminum alloy samples.

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AUTOMATED CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM

by

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1. INTRODUCTION

Controlled-potential coulometry (CPC) is an analytical technique commonly used in the nuclear industry for determination of electroactive metals (1). At Chalk River Nuclear Laboratories this technique has been used routinely for the analysis of unirradiated nuclear fuels for uranium and plutonium and could also be applied to the analysis of irradiated fuels if the appropriate separations from interfering elements are performed. CPC analysis involves the accurate measurement of the amount of electricity required in an electrolysis during which the potential of a working electrode is held at a constant value (2, 3). Under the proper experimental conditions the total amount of electricity required for complete reduction is a measure of the amount of reducible species present. Therefore, based on Faraday's Law (4), which states that the extent of the electrolysis reaction is directly proportional to the charge, Q, that results from the electrolysis current, it is possible to calculate the amount of the electroactive material present.

The main advantages of CPC analysis are that it is accurate and precise, selective for certain materials, and can be calibrated both physically and chemically.

The coulometric procedure for the determination of milligram amounts of uranium is based on the direct electrolytic reduction of uranium (VI) in sulfuric acid at a mercury cathode. The reduction is carried out under conditions where the total amount of electricity required is used as a direct measure of uranium (VI) present in the sample. Interferences from oxidants such as Cr (VI), Ce (IV), Fe (III), Pu (VI) and Pu (IV) are prevented by prereduction at +0.080 V versus a S.C.E. (saturated calomel electrode). Ions that reduce at potentials more negative than -0.325 V, such as Zn (II) and Ni (II), can be present in relatively large quantities (1). The sulphate content can vary from 0.5 - 2.5 M without affecting the results, and although nitric acid is normally removed from the samples (by fuming), it can be tolerated in concentrations up to 5 M as long as sufficient sulphamic acid is added to destroy any nitrite present. Most fission products do not interfere, except Mo, which must be separated (5). Oxygen interference is avoided by continuous degassing with argon.

Without an automated system the analyst must monitor sample degassing, prereduction, and reduction. In the prereduction and reduction steps the analyst's attention is required almost continually. For an average sample the analysis time required is ∿ 45 min, which includes a degassing of 20 min, prereduction of ≃ 5 min and sample reduction of 15-20 min. An automated system allows the analyst to leave the instrument unattended from the time the sample is loaded until the time the final results are displayed on the digital coulometer unit.

This report describes the modifications made to automate a CPC system and the use of the system to analyze for uranium.

2. EXPERIMENTAL

2.1 Apparatus

The controlled-potential coulometric system was a Princeton Applied Research model 380. A Hewlett Packard model 7101B strip chart recorder was used to continuously monitor the cell current.

2.2 Apparatus Modifications

The electronic modifications to the coulometer system were mounted as a separate unit, and are schematically represented in Figure 1. After a sample has been introduced into the coulometer cell, the automated procedure is initiated by pushing the START button on the front panel of the unit which energizes a delay timer which controls the time of sample degassing. After 15 minutes a relay is energized, and a prereduction potential is applied to the cell.

The coulometer converts the cell current output to voltage which drives the voltage-to-frequency (V/F) converter. This V/F output is compared to a reference oscillator in a frequency comparator consisting of two 74192 BCD counters. When the V/F output drops below a reference level (TRIP POINT) an output pulse from the reference counter resets the digital coulometer and triggers the potentiostat to the preset reduction potential; the reference oscillator is adjustable from 3.5 to 12.0 Hz via a front panel helipot control (TRIP POINT). When the V/F output again drops below the reference level, the sequence control logic disconnects the potential applied to the cell and sounds an audible alarm indicating the end of the sequence.

Before another sample is analyzed the digital coulometer must be reset, the potentiostat must be returned to the prereduction potential, and the automatic control system must be reset by pushing the RESET button on the front of the unit.

2.3 Reagents and Materials

All the reagents were of analytical reagent grade unless otherwise stated. Deionized distilled water was used and the mercury used in the coulometer cell was triple-distilled grade.

Saturated sulphamic acid was prepared by the dissolution of ≈15 g of NH_2HSO_3 in 100 mL of water. The 23.10 mg/g uranium standard was prepared from NBS-960 uranium-metal ingot. Typical samples for analysis were sections of an unirradiated uranium-aluminum fuel alloy.

2.4 Sample Preparation

A section of the uranium-aluminum alloy was cut, degreased, and accurately weighed. This sample was dissolved in 6 M HNO_3 solution which was 0.05 M in $Hg(NO_3)_2$ (6). Once the sample was completely dissolved it was diluted with water, cooled and accurately weighed. An aliquot of this solution containing 4-6 mg of uranium was accurately weighed into a beaker. One millilitre of concentrated H_2SO_4 was added to the aliquot and it was heated until heavy SO_3 fumes appeared. After cooling and rinsing into the beaker with 0.5 M H_2SO_4 it was fumed once again; after cooling, the rinsing and fuming steps were repeated once more. It was cooled and quantitatively transferred to the coulometer cell using 0.5 M H_2SO_4. The coulometer cell contained 7 mL of mercury and the total sample volume in the cell was brought to 8 mL with 0.5 M H_2SO_4. Five drops of saturated sulphamic acid were added and the cell was coupled to the coulometer system.

2.5 Sample Analysis

After the coulometer electronics system, cell stirrer motor, and the Ar degassing system were turned on and stabilized, the prereduction potential was set to +0.080 V and the reduction potential to -0.325 V on the galvanostat-potentiostat. The digital coulometer readout and the modified electronics system were reset, and the trip-point helipot was set to the appropriate level (see Figure 2). The start button was activated and the analysis proceeded automatically until the alarm sounded indicating the completion of the analysis.

2.6 Blank Determination

A blank value, obtained daily for the system, was determined on 8 mL of 2 M H_2SO_4 to which 5 drops of saturated sulphamic acid had been added. Sample degassing, prereduction and reduction were carried out as they were for uranium samples.

The blank was determined by the manual mode of operation because the cell current dropped rapidly below the endpoint value; in the automatic mode the coulometer shuts off as soon as this value is reached and the blank value obtained at this point would not account for background current that would accumulate over the length of time required for an actual sample.

2.7 Calculations

Calculation of the results is based on Faraday's Law (4) where

$$Q = nFW/M \tag{1}$$

where W = the weight of uranium in grams

Q = the total coulombs of electricity required to completely reduce the sample

F = 96,487 coulombs/equivalent = 1 Faraday

n = 2 (for uranium, 2 electrons are involved in the reaction)

M = the gram molecular weight of the uranium in the sample.

Taking the blank B into account and rearranging equation (1), the amount of U in the aliquot is given by

$$W = \frac{(Q - B)M}{nF}$$

Results are normally reported in mg of U per gram of sample solution.

3. RESULTS AND DISCUSSION

The automated coulometer system monitors all of the functions that the analyst would normally be required to perform. The functions controlled by the automated system are shown as points A, B, C, and D in Figure 3. The analysis begins as the sample is degassed (A → B on Figure 3). Then at B on Figure 3, the prereduction potential is applied and immediately the cell input current rises sharply due to reduction of impurities. The current decreases until it reaches a trip value (less than 2-10 μA, C on Figure 3), as determined by the setting on the reference oscillator helipot (see Figure 2). At point C the system automatically resets the digital coulometer to zero and switches the applied potential to the value required for sample reduction. The cell input current again rises very sharply, normally to a value greater than 100 μA, and then decreases as the reduction of U (VI) to U (IV) proceeds. When the endpoint is reached (D on Figure 3), as determined by the setting of the reference oscillator helipot, the applied potential to the cell is turned off.

If a sample is analyzed manually (i.e. without the automatic system) the analyst must monitor the cell input currents on a strip chart recorder and when the current value is less than the desired endpoint level (normally 10 μA) manually switch the cell to the required potential. Because the cell input current fluctuations are quite large (±1-2 μA), mainly because of the effects of stirring, manual endpoint selection is somewhat subject to the analyst's discretion. The automatic system compares a time averaged output of the voltage/frequency converter (which is proportional to cell current) to the reference oscillator setting, and thus consistently selects the endpoint without the introduction of operator bias.

As a comparison of the methods of endpoint selection, and to ensure that no bias was being introduced by the automatic system, a series of coulometric determinations was performed on a NBS-960 natural uranium standard. This standard had been gravimetrically prepared here to contain 23.10 mg of uranium per gram of solution; the standard was stored in sealed glass ampoules. The endpoint selected for this comparison was less than 10 μA manually, and in the automatic mode it corresponded to a reference oscillator helipot setting of 8.0 (see Figure 2). The results (Table 1) show that the precisions of both methods were comparable, and the accuracies were well within the limits normally accepted for coulometric uranium analysis (1). The results in Table 1 were not obtained consecutively but rather randomly over a two month period. Thus parameters such as cell stirring, room temperature, acid concentrations, and cell contaminants were more variable than would be expected during a set of consecutive analyses, and reflect realistic day-to-day operating precision.

Results of duplicate runs of a series of uranium-aluminum alloy samples with the automatic system are shown in Table 2. These results show the excellent agreement obtainable on consecutive determinations on routine samples.

The automated system is now in routine use at the Chalk River Nuclear Laboratories for quantitative uranium determination in unirradiated fuels. The system has proven to be a valuable timesaver and leaves the analyst free to perform other duties during the analysis. It can be used readily in a glove box or hot cell where simplicity of operation is of utmost importance. The system could be used in the electrolysis of any electroactive species requiring a two step reduction.

TABLE 1

A Comparison of Coulometric Results Obtained on a Laboratory-Prepared 23.10 mg/g Uranium Standard by the Manual and Automatic Modes of Operation

RESULT #	MANUAL OPERATION (mg U/g)	AUTOMATIC OPERATION (mg U/g)
1	23.01	23.16
2	23.01	23.13
3	23.08	23.02
4	23.21	23.07
5	22.95	23.20
6	23.03	23.21
7	23.13	22.96
8	23.10	23.14
9	23.14	23.08
10	22.99	23.09
AVERAGE	23.07	23.11
RELATIVE STANDARD DEVIATION	0.35%	0.34%

TABLE 2

Results of Duplicate Automated Coulometric Uranium Determinations on Uranium-Aluminum Alloy Samples (expressed as wt. % uranium)

SAMPLE #	RUN #1	RUN #2
81-21	20.26	20.29
81-22	20.92	20.96
81-23	20.62	20.66
81-24	20.89	20.84
81-25	21.02	20.91
81-26	20.68	20.64
81-27	20.29	20.36
81-28	21.22	21.27
81-29	20.74	20.74
81-30	20.48	20.46

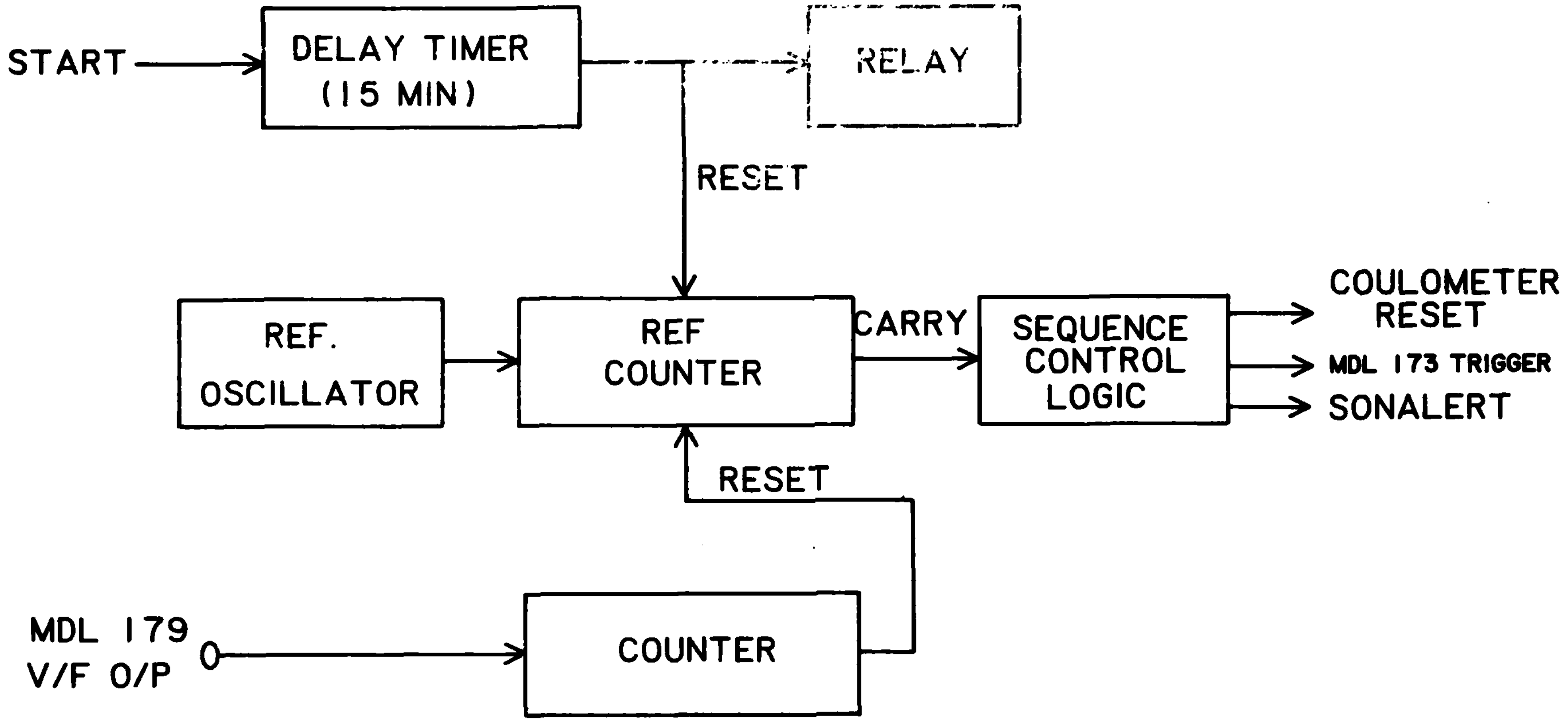

FIGURE 1: SCHEMATIC DIAGRAM OF COULOMETER MODIFICATIONS

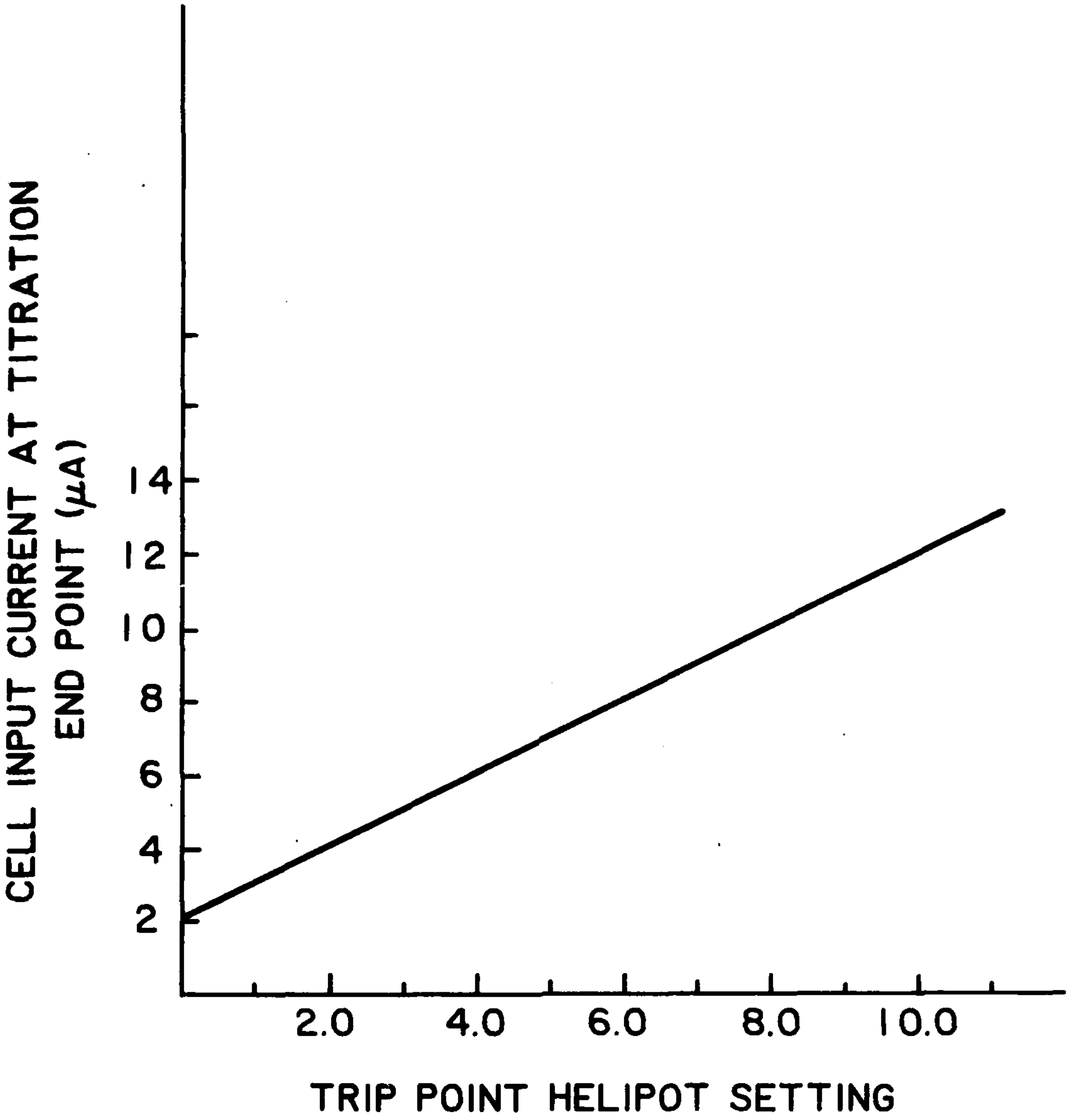

FIGURE 2: TRIP POINT CONTROL HELIPOT SETTING VS. CELL INPU CURRENT SHUT OFF FOR THE AUTOMATIC MODE OF OPERATION.

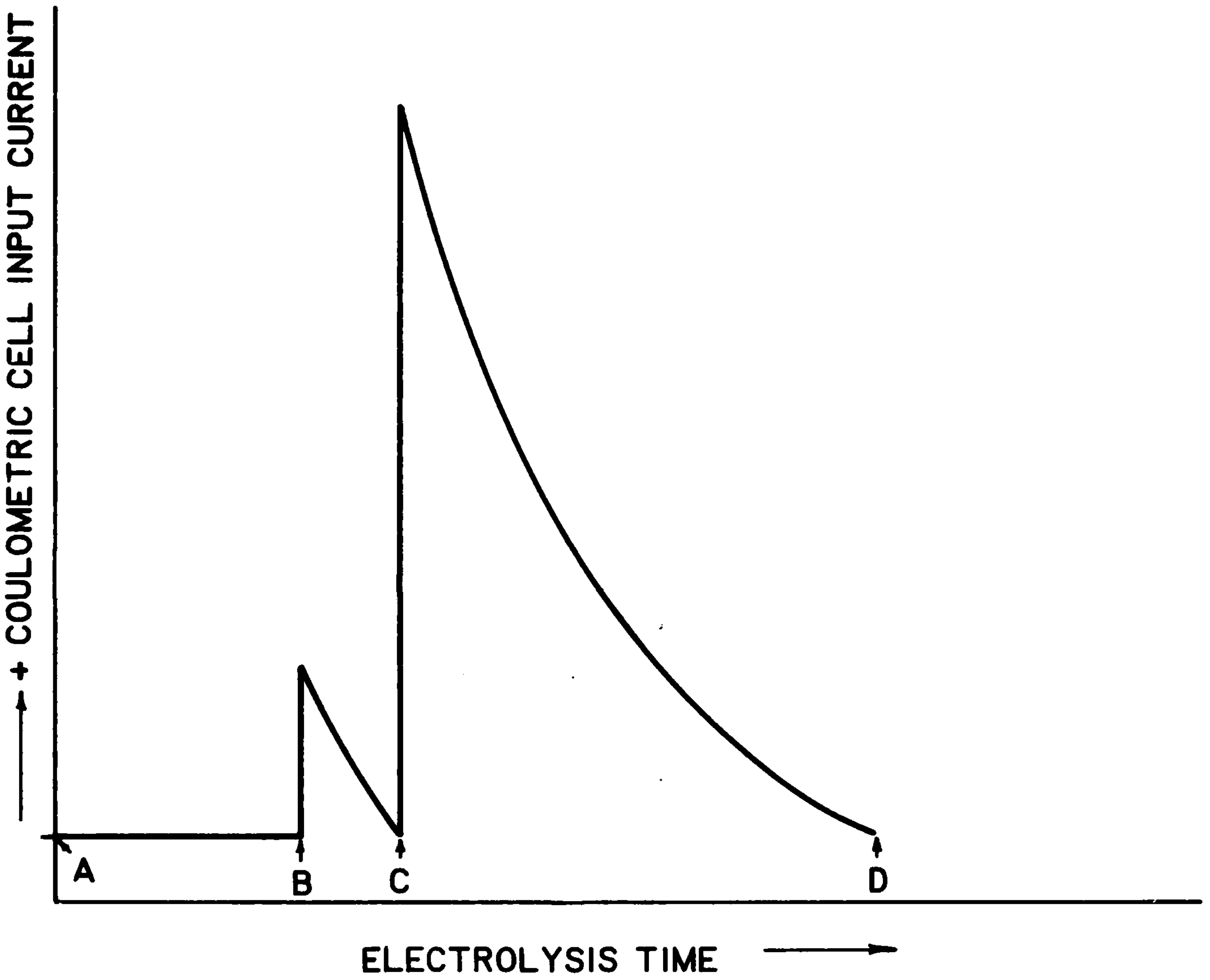

FIGURE 3: SCHEMATIC REPRESENTATION OF COULOMETRIC CELL INPUT CURRENTS DURING DEGASSING (A → B), PREREDUCTION (B → C), AND REDUCTION OF A TYPICAL SAMPLE (C → D)

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