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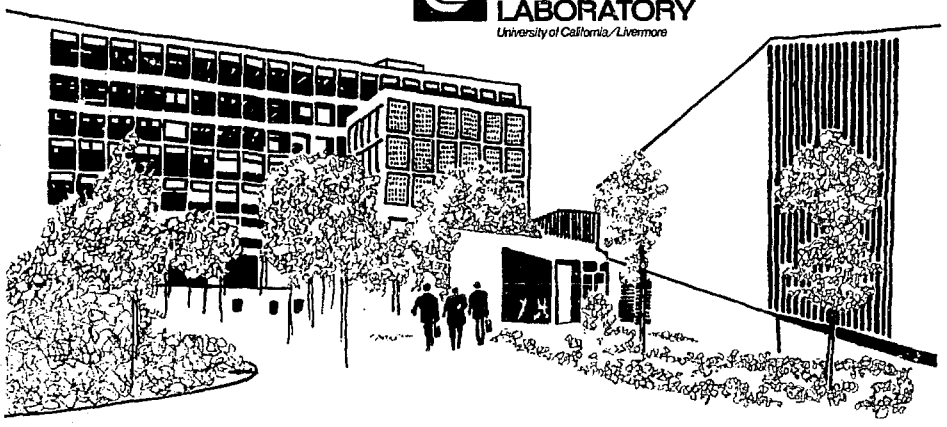
UCRL-52351

**AN AUTOMATED SAMPLE-PROCESSING AND  
TITRATION SYSTEM FOR DETERMINING  
URANIUM IN NUCLEAR MATERIALS**

J. E. Harrar, W. G. Boyle, J. D. Breshears, C. L. Pomernacki,  
H. R. Brand, A. M. Kray, R. J. Sherry, and J. A. Pastrone

November 15, 1977

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# AN AUTOMATED SAMPLE-PROCESSING AND TITRATION SYSTEM FOR DETERMINING URANIUM IN NUCLEAR MATERIALS

## ABSTRACT

The system is designed for accurate, precise, and selective determination of from 10 to 180 mg of uranium in 2 to 12 cm<sup>3</sup> of solution. Samples, standards, and their solutions are handled on a weight basis. These weights, together with their appropriate identification numbers, are stored in computer memory and are used automatically in the assay calculations after each titration. The measurement technique (controlled-current coulometry) is based on the Davies-Gray and New Brunswick Laboratory method, in which U(VI) is reduced to U(IV) in strong H<sub>3</sub>PO<sub>4</sub>, followed by titration of the U(IV)

with electrogenerated V(V). Solution pretreatment and titration are automatic. The analyzer is able to process 44 samples per loading of the sample changer, at a rate of 4 to 9 samples per hour. The system includes a comprehensive fault-monitoring system that detects analytical errors, guards against abnormal conditions which might cause errors, and prevents unsafe operation. In this report, we present a detailed description of the system, information on the reliability of the component subsystems, and a summary of its evaluation by the New Brunswick Laboratory.

## INTRODUCTION

Among the numerous methods proposed for the accurate assay of uranium in nuclear materials, the titrimetric method of Davies and Gray<sup>1</sup> as modified by workers at the New Brunswick Laboratory (NBL)<sup>2</sup> has emerged as the most selective and hence the most versatile technique. This method has been thoroughly characterized at NBL and elsewhere, and has been found to be especially

applicable to uranyl nitrate solutions; samples such as aluminum-, stainless-steel-, and Zircaloy-clad fuels; and samples containing niobium, hydrofluoric acid, and nitric acid.

The original Davies-Gray method involves the reduction of U(VI) to U(IV) by Fe(II) in strong H<sub>3</sub>PO<sub>4</sub>, oxidation of the excess Fe(II) with HNO<sub>3</sub> in the presence of Mo(VI) catalyst and sulfamic acid, dilution

of the solution, and then titration of the U(IV) with  $K_2Cr_2O_7$  to a visual end point. The method was improved at NBL by the addition of V(IV) to the solution to accelerate the attainment of equilibrium, thus enabling potentiometric end-point detection. The basic method also has been adapted by Goldbeck and Kerner<sup>3</sup> of NBL to a coulometric titration, in which the V(V) titrant is electro-generated at constant current by the oxidation of V(IV). This procedure, compared to the volumetric one, offers several advantages. It does not require a titrant solution, there is greater precision and lower systematic error in the measurement of the titrant quantity, it is easier to adapt to changing quantities of uranium titrated, and it is amenable to automation.

Because of the large number of assay samples processed by many nuclear laboratories, there has been a continuing need for the automation of a general-purpose procedure like that based on the Davies-Gray-NBL method. Other benefits such as more timely analyses, freedom from operator bias, reduced clerical time and errors, increased precision, and reduced operator intervention when processing radioactive samples also could be realized with automation. However, to achieve the maximum benefits of automation, all operations performed on

the samples, not just the titration itself, should be automated. Four basic steps are involved in the complete analysis: sample dissolution, sample solution preparation, titration, and calculation and presentation of the results. All of the work done to date has been directed toward mechanizing the last three steps.

Progress in the automation of the Davies-Gray-NBL method thus far has included adapting the volumetric, potentiometric titration to a Fisher Scientific Company Titralyzer,<sup>2</sup> Radiometer Company titration equipment,<sup>4</sup> and a Brinkmann-Metrohm titrator with programmable calculator control.<sup>5</sup> The coulometric titration also has been carried out with the Fisher Titralyzer.<sup>6,7</sup> Recently, workers at the Reactor Centrum Nederland<sup>8</sup> and the Hanford Engineering Development Laboratories<sup>9</sup> have succeeded in scaling down the volumetric titration and have designed the procedure for semiautomatic operation. The LLL titration system described here is based on the full-scale coulometric titration.<sup>3</sup> (When our system first was designed, we did not know if the procedure could be scaled down without an intolerable loss of accuracy and precision.)

Because of the instability of the U(IV), sample solutions must be handled individually, starting with the pretitration solution preparation,

and titrated immediately. Thus, the solution preparation and titration steps should be combined in the automated system. The solution handling presents some particularly difficult problems for automation. The large volumes of reagent solutions used (5 to 160 cm<sup>3</sup>), their extremely corrosive nature (e.g., 8 M HNO<sub>3</sub> and 13 M H<sub>3</sub>PO<sub>4</sub>), and the total volume of the titration solution (about 250 cm<sup>3</sup>) precludes the use of commercially available solution dispensers and discrete-sample analyzers.<sup>10,11</sup> In

previous work,<sup>2,4-9</sup> the addition of the reagent solutions before the titration and the post-titration rinsing have been accomplished with systems of valves, gravity-feed reservoirs, and pumps.

The design of the automated analysis system described here extends and departs from previous systems in several respects. Figure 1 is a photograph of the overall system and a simplified block diagram is given in Fig. 2. The system, complete with an automatic wet-chemical analyzer,

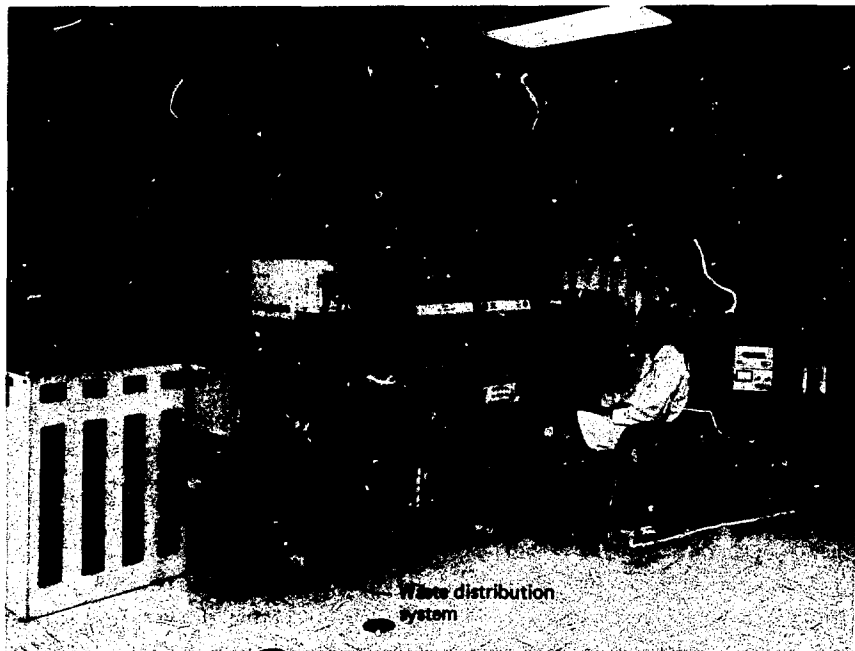


Fig. 1. LLL automated titration system for uranium.



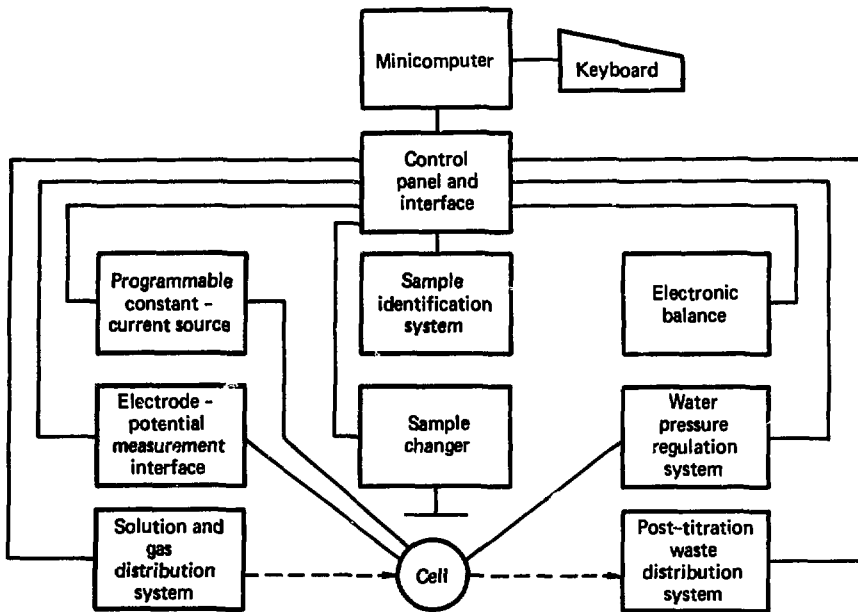


Fig. 2. Diagram of the automated titration system for uranium.

is able to handle all of the data-generating operations associated with the assay of solid or liquid samples containing uranium. Determination of uranium is accomplished by controlled-current coulometry with potentiometric end-point detection.

Figure 3 outlines the basic procedure for the assay of uranium materials by the Davies-Gray-NBL method. First, a subsample of solid material is weighed and then dissolved in an appropriate solvent (e.g., nitric acid). To reduce the systematic errors of the analysis, a weighed

aliquot is taken of the subsample solution. This aliquot usually is evaporated with sulfuric acid to remove interferences. In the automated system, the weight information is stored semiautomatically via an electronic balance or is entered at a keyboard. After the evaporation step, all succeeding operations are accomplished without operator attention.

The two principal operations — weighing the solid and solution samples and titrating the uranium in solution — have been integrated so that previously entered weight information,

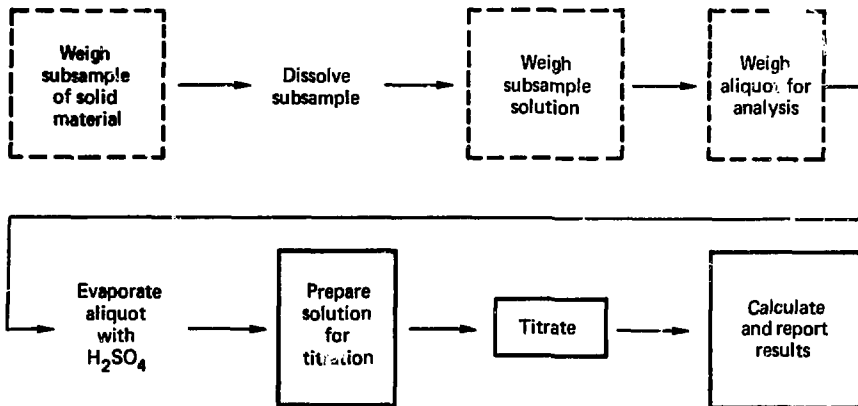


Fig. 3. Basic steps of the automated uranium assay procedure (solid and dashed boxes denote automatic and semiautomatic operations, respectively).

with appropriate identification numbers, can be extracted from a computer memory file and used with the titration results to automatically calculate the quantity and weight concentrations of uranium in the analyzed samples. A commercially available sample changer with a capacity of forty-four 300-ml beakers is used, together with an optical-reader electronic subsystem that reads coded labels denoting the positions of the beakers in the sample changer.

The apparatus for delivering the pretitration reagent solutions and discarding the waste solution uses pressurized solution containers and an appropriate valving arrangement, rather than a pump system. (Somewhat similar approaches to solution dispensing have been used recently in

liquid chromatography<sup>12</sup> and for titrant solution delivery.<sup>13</sup>) Titrations are performed by controlled-current coulometry using a specially designed electrolysis cell as well as electronic modules for programming the current and for measuring the electrode potentials.<sup>14</sup>

Another essential feature of the uranium titration system is an extensive fault-condition monitoring subsystem that guards against unsafe operating conditions and abnormal conditions that might cause incorrect analytical results. This fault-monitoring network includes sensors for solution spills or leaks, solution flows, gas and water pressures, and power outages. In addition, software is provided for detecting abnormal characteristics in the titration

itself and for determining whether the analyses of standard solutions are within quality-control limits. If any of the fault conditions should occur, the system is programmed to give an alarm and indicate and record the fault. The system then shuts down, goes on hold, or carries out certain preprogrammed actions, depending on the nature of the fault

condition and the status of the system when the fault occurred. In addition, this fault-condition subsystem automatically monitors many parameters more carefully than could be done manually, thus significantly increasing the credibility of the analytical results and minimizing the probability of incorrectly processing large numbers of samples.

## SYSTEM OPERATION

There are three basic steps in the overall operation of the uranium titration system: weighing the sample, loading the sample changer, and the actual analysis.

### WEIGHING AND STORAGE OF WEIGHT DATA

First, a series of weights, from which the weight concentration of uranium will be calculated, are entered into the computer memory file along with appropriate identification (ID) numbers. For unknown samples, three weights are entered: the subsample weight (the portion of the solid sample to be analyzed), the subsample solution weight (the solution resulting from the dissolution of the subsample), and the subsample solution aliquot weight (the aliquot of the subsample solution to be titrated). The operations and the ID

number coding are illustrated in Fig. 4.

For known standard solutions, the weight of the aliquot of standard solution and the concentration of the standard solution are entered; the computer calculates only the quantity of uranium in the standard aliquot and stores this value with the ID number for later use. The ID numbers for standards consist of one letter followed by 4 digits, e.g., A1234.

A sample computer printout illustrating the entry of data for a sample and for a standard is shown in Fig. 5. In this dialogue, the operator can type in a numerical value of the weight or cause an automatic entry of the weight from the electronic balance by typing a carriage return. The three weights for a sample usually are not all

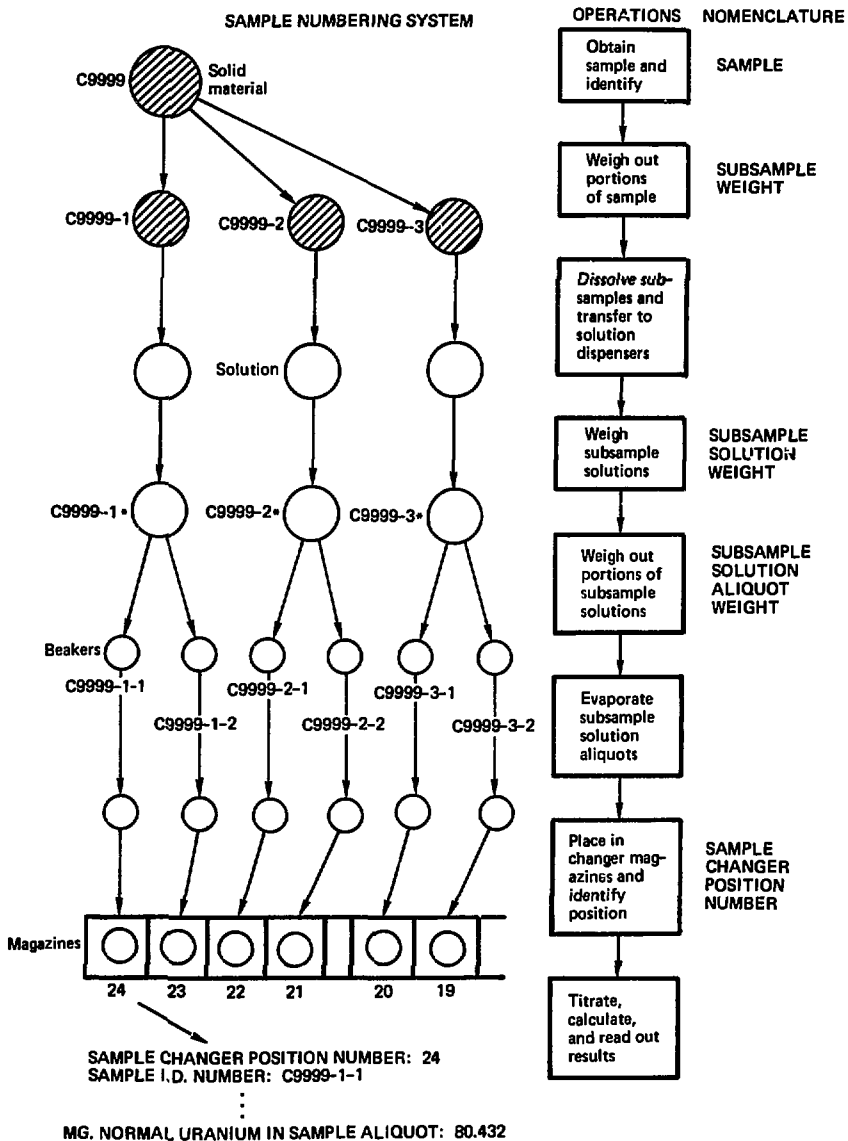


Fig. 4. Processing scheme for solid samples.

DATE ENTERED: 04-01-76  
I. D. NUMBER: E2049-1-2  
SUBSAMPLE WT., GM.: 000.32521  
SUBSAMPLE SOL. WT., GM.: 025.21800  
SUBSAMPLE SOL. ALIQUOT WT., GM.: 010.28540

DATE ENTERED: 04-01-76  
I. D. NUMBER: A0010  
STD. ALIQUOT WT., GM.: 009.43420  
STD. CONC., MG. URANIUM/GM. SOLN.: 10.952  
STD. QUANTITY OF URANIUM, MG.: 103.2300

Fig. 5. Entry of weight data for a sample and a standard.

entered at the same session because of intervening chemical pretreatments. In this case, each time a new weight is to be entered, the previously entered weights are automatically recalled and printed by the program, in response to the operator's typing of the appropriate ID number. With the automatic tare feature of the electronic balance, entry of a series of standard solution weights and aliquots of subsample solutions is very rapid.

#### LOADING OF SAMPLE CHANGER

After a group of samples and standards have been weighed and prepared for titration, the beakers are placed in the sample-changer magazines. The operator, interacting with the computer, then enters the required data into the computer memory files: namely, the ID number of each subsample solution aliquot or standard quantity of uranium and the numbers of the magazine positions in which he has placed beakers. The

input format for this step is illustrated in Fig. 6. In this dialogue, the computer requests the data indicated for each beaker. (The current month, day, and year are entered only once.) Later, when the sample changer operates during the analytical cycle, the sample identification subsystem identifies each beaker by position number as its solution is analyzed. After the titration is complete and the quantity of uranium calculated, the computer associates the uranium quantity via the position number to the previously entered ID number and weight information.

#### ANALYSIS AND DATA READOUT

After loading the sample changer and indexing the position numbers to the ID numbers, the hardware and software systems are ready for the titration step. At the initial startup, there is another computer-operator exchange, during which the operator

```
DATE: 04-01-76
SAMPLE POS. NUMBER::21
I. D. NUMBER: A0011

DATE: 04-01-76
SAMPLE POS. NUMBER::22
I. D. NUMBER: E2049-1-1

DATE: 04-01-76
SAMPLE POS. NUMBER::23
I. D. NUMBER: E2049-1-2
```

Fig. 6. Entry of sample-changer position numbers and ID numbers for a standard and two samples.

specifies certain parameters that govern the titration and data gathering. Figure 7 illustrates the operations that are required to initiate and execute the analytical cycle. (The rectangular blocks represent discrete operation status periods that provide the framework for the normal-operating and fault-monitoring software.) After each beaker is processed, the result of the analysis is printed out with the previously entered weight data as

well as with information on titration characteristics that may be useful for diagnostic purposes (see Figs. 8 and 9). For the standard solution (Fig. 9), an error is calculated and this value is compared with a previously set control tolerance. A system halt is initiated if the error is too large. With the positive sample identification features of this system, samples and standards can be loaded and processed in any proportion and in any order.

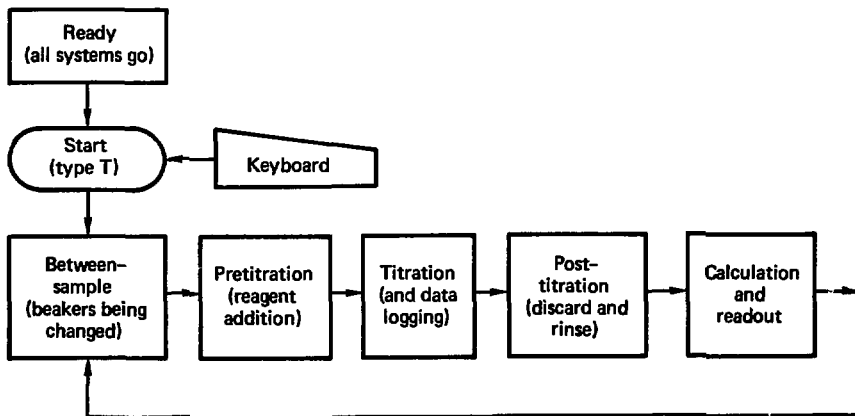


Fig. 7. Sequence of operations in the analytical procedure.

```

DATE: 04-02-76
TITRATION PARAMETERS:N.
SAMPLE POS. NUMBER: 22
I. D. NUMBER: E2049-1-1
SUBSAMPLE WT., GM.: 000.32521
SUBSAMPLE SOL. WT., GM.: 025.21800
SUBSAMPLE SOL. ALIQUOT WT., GM.: 009.59350
MG. NORMAL URANIUM IN SAMPLE ALIQUOT= 30.5172
GM. NORMAL URANIUM PER GM. SUBSAMPLE= 0.24668
SMALL SAMPLE
OPEN-CIRCUIT POTENTIALS, MV.=IND. ELEC. :- 27.90
                                GEN. ELEC. :- 28.70
FINAL PRE-ENDPOINT INTERVAL POTENTIALS, MV.=IND. ELEC. :- 13.30
                                GEN. ELEC. :- 600.10
IND. ELEC. ENDPOINT POTENTIAL, MV= 98.29
C1= 25 C2= 67 E. P. = 261.234 C3= 254

```

Fig. 8. Data readout for the analysis of a sample.

```

DATE: 03-31-76
TITRATION PARAMETERS:N.
SAMPLE POS. NUMBER: 27
I. D. NUMBER: A0005
STD. QUANTITY OF URANIUM, MG.: 085.98192
MG. NORMAL URANIUM IN STD. ALIQUOT, MG. = 85.9912
ERROR: 0.011%
OPEN-CIRCUIT POTENTIALS, MV.=IND. ELEC. :- 46.20
                                GEN. ELEC. :- 47.80
FINAL PRE-ENDPOINT INTERVAL POTENTIALS, MV.=IND. ELEC. :- 20.50
                                GEN. ELEC. :- 695.50
IND. ELEC. ENDPOINT POTENTIAL, MV= 100.34
C1= 0 C2= 113 E. P. = 364.886 C3= 457

```

Fig. 9. Data readout for the analysis of a standard.

## DESCRIPTION OF ELECTRONIC HARDWARE

A detailed block diagram of the uranium titration system, showing the various electronic and electromechanical modules and their functional relationships, is given in Fig. 10.

### COMPUTER SYSTEM

The supervisory computer system includes a Digital Equipment Corporation model PDP-8/e mini-computer with 24 K of core memory, a model LA-30 Decwriter keyboard, a fast paper-tape

reader and punch, a DK8-EP programmable real-time clock, an MI8-EP bootstrap leader, a KP8-E power-fail detector, and the associated interfaces (see Fig. 1). The accuracy of the programmable clock is critical to the analysis. The clock frequency is specified to be 10 MHz ( $\pm 0.01\%$ ) over the 0 to 55°C, 10 to 90% relative humidity operating range of the computer and was verified at 25°C by measurement with an electronic counter.

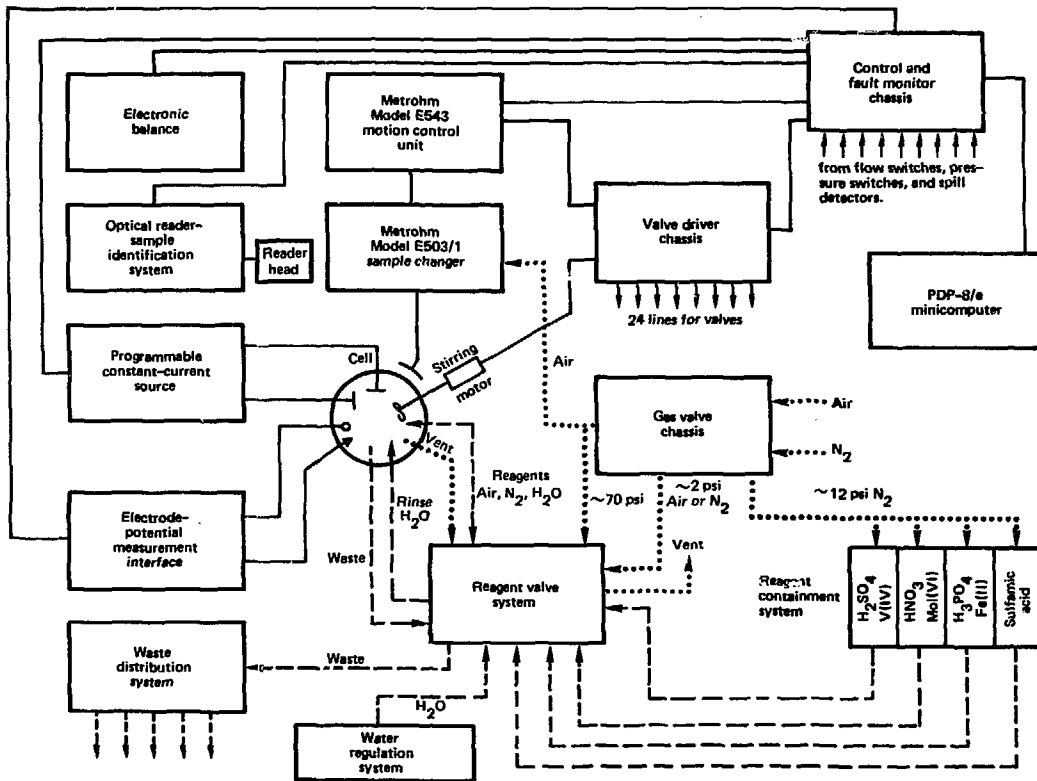


Fig. 10. Diagram of the automatic uranium titration system.



## CONTROL PANEL AND FAULT-MONITORING CHASSIS

This unit (see Figs. 11 and 12) incorporates most of the digital logic and interfacing that link the computer with the rest of the system. Signals from the various hardware fault-monitoring sensors arrive at this chassis. On the control panel, a graphic diagram of the solution, gas, water, and waste flow system is provided, together with switches that allow operator manipulation of the system valves to manually conduct some of the system functions. The array of lamps indicates valve status, fluid flow, operation status of the

system, and system faults as they occur.

## ELECTRONIC BALANCE

The electronic balance (see Fig. 1) is a Mettler Instrument Corporation model HE10/BE10 balance/control unit, with a BA28 digital display module. Binary-coded decimal (BCD) signals are taken from the BA28 module to the control panel interface where the weight information is logged in. The balance has a maximum capacity of 160 g, a readability of 0.1 mg, and an automatic tare feature that enables zeroing of the readout over the entire weight range.

## SAMPLE CHANGER

The samples to be titrated are acid solutions of uranium in volumes up to about 12 cm<sup>3</sup>, contained in special, lipless beakers. The beakers are queued for titration on a Metrohm Ltd. model E503/1 pneumatic sample changer<sup>15</sup> (see Fig. 1). The sample changer is under the direct control of a model E543 sample-changer control unit, which in turn is controlled by the computer. The beakers are transported on the sample changer in four-place plastic magazines (Fig. 13); there is space for 11 magazines in one loading of the sample changer. The regular titration station and all accessories were removed from the model E503/1 sample changer, leaving

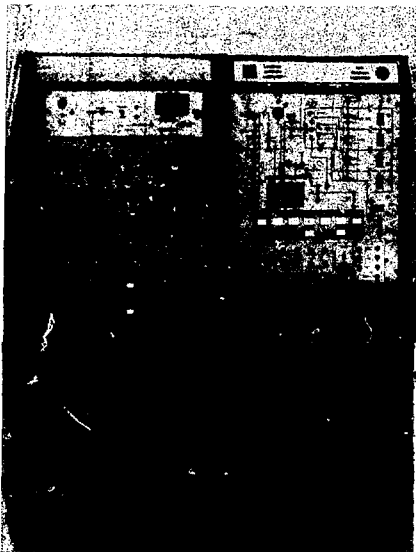


Fig. 11. System control console.

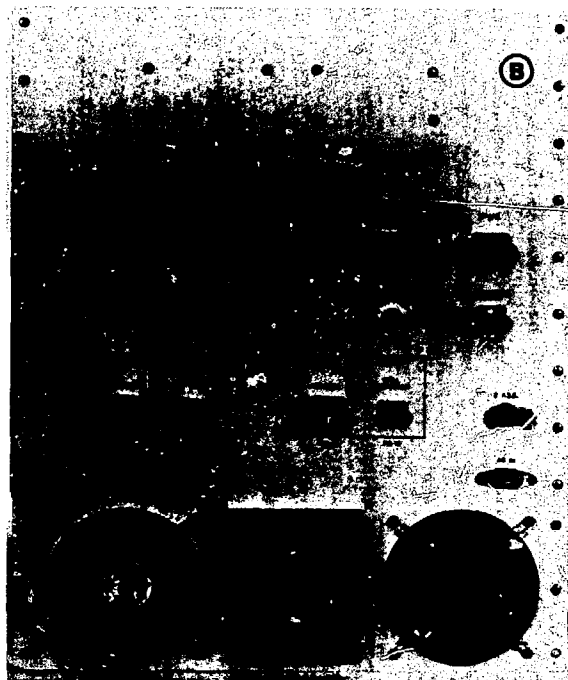
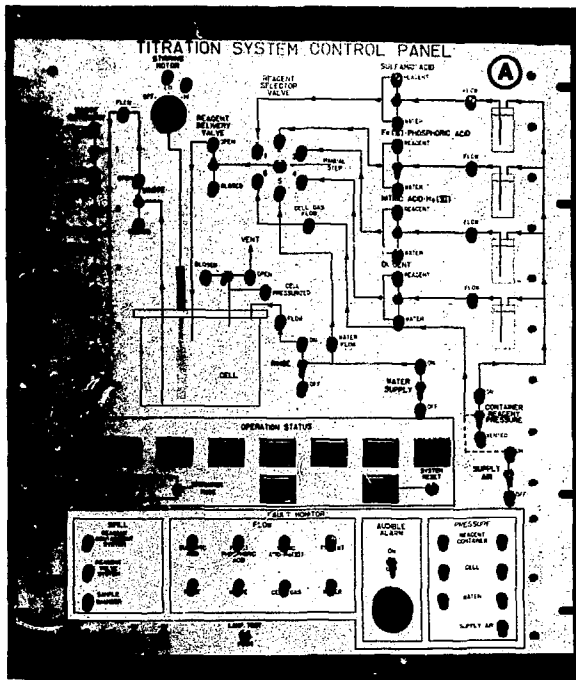


Fig. 12. Control panel and fault monitor chassis, front (a) and rear (b).

only the four support rods. A new titration station and the reagent valve system were attached to these rods.

#### SAMPLE IDENTIFICATION SYSTEM

The sample identification subsystem consists of three modules manufactured by the Mettler Instrument Corporation: a model CT211 optical code reader (Fig. 13), a model CT21 code reader control, and a model CT16 numerical display. Binary-coded decimal signals from the numerical display unit are taken to the control panel interface. Reflective, adhesive-backed, coded labels are affixed to the positions on the sample changer magazines. As the sample magazine is moved past the titration station, bringing a new sample into position, the optical reader (mounted at the titration station) deciphers the label. The

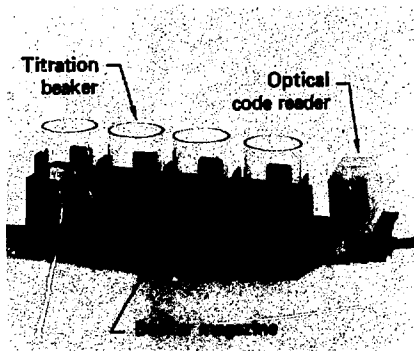


Fig. 13. Beakers in magazine with optical code reader.

number corresponding to the position of the beaker in the magazine is transmitted to the computer. These position numbers have been previously linked by the operator to the particular sample ID number. Eight-digit numbers can be accommodated by the reader system; presently however, only two-digit numbers (1 through 99) are used.

#### PROGRAMMABLE CONSTANT-CURRENT SOURCE

This module is described more completely in Ref. 14 and is illustrated in Fig. 14. It permits digital control of direct current to 500 mA with a resolution of approximately 30  $\mu$ A and a compliance voltage of more than 45 V. In addition, all instrument functions can be controlled manually with the front panel switches. A built-in digital panel meter enables the system to measure, visually indicate, and transmit (as BCD signals) either the delivered constant current (as the voltage drop across a built-in precision resistor) or the total output voltage of the source. Switching between these two measurements can be controlled externally. The long-term stability of the instrument calibration is 0.03% per year.<sup>14</sup>

#### ELECTRODE POTENTIAL MEASUREMENT INTERFACE

This unit (also described more fully in Ref. 14) provides a means

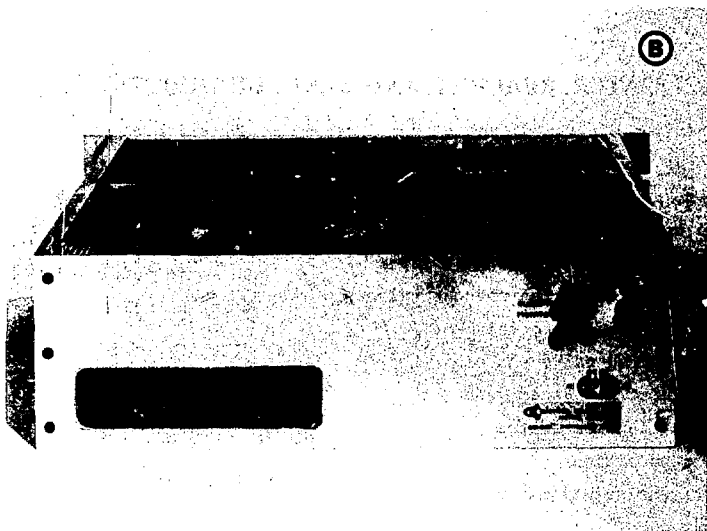
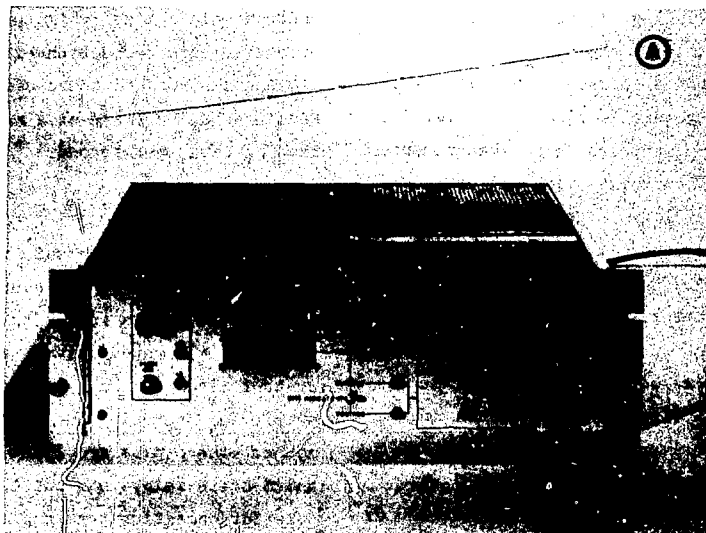


Fig. 14. Programmable constant-current source, front (a) and rear (b) panels.

for measuring and transmitting, to the computer, the generator and indicator electrode potentials vs a single reference electrode (Fig. 15). Switching between these measurements can be controlled manually or by external logic signals. The heart of this module is an Analog Devices model AD2004, 4-1/2-digit digital panel meter. This meter indicates voltages in the range of  $\pm 1.9999$  V with a resolution of 0.1 mV. It has a fully floating differential input with an impedance of more than 100 M $\Omega$ , a bias current of less than 1 nA, and a common mode rejection of 120 dB at 60 Hz. The analog and digital

sections are optically isolated. Automatic zero correction circuitry compensates for drift and offset. Readings can be taken at a maximum rate of eight per second.

#### VALVE DRIVER CHASSIS

The valve driver chassis (Fig. 11, below the control panel) contains solid-state relays for switching power to the system valves, the control circuit, and the dc power supply for operating the stirring motor. There also are 117-V ac solid-state relays and switched outputs for operating the sample changer and a water-pressure booster pump.

## GAS, WATER, REAGENT, AND WASTE DISTRIBUTION SYSTEMS

A detailed diagram of the flow system for the distribution of reagent solution, gas, water, and waste solution to and from the titration cell is given in Fig. 16. The most important components are the reagent valve system, the reagent containment system, the gas valve chassis, the water regulation system, and the waste distribution system.

The compositions of the pretitration reagent solutions<sup>6</sup> are as follows:

- Reagent 1: 1.5 M sulfamic acid.
- Reagent 2: 0.11 M ferrous sulfate, 13.3 M  $H_3PO_4$ , and

approximately 0.001% chromium from the preoxidation of the  $H_3PO_4$  with  $K_2Cr_2O_7$ .

- Reagent 3: 8.0 M  $HNO_3$ , 0.15 M sulfamic acid, and 0.4% ammonium molybdate.
- Diluent: 0.3 M  $H_2SO_4$  and 0.025 M  $VOSO_4$ .

#### REAGENT DELIVERY SYSTEM

The heart of the pretitration reagent delivery system is a six-position reagent selector valve (V5, Laboratory Data Control No. R6060V6AP-K). The valve is switched through its six positions during the

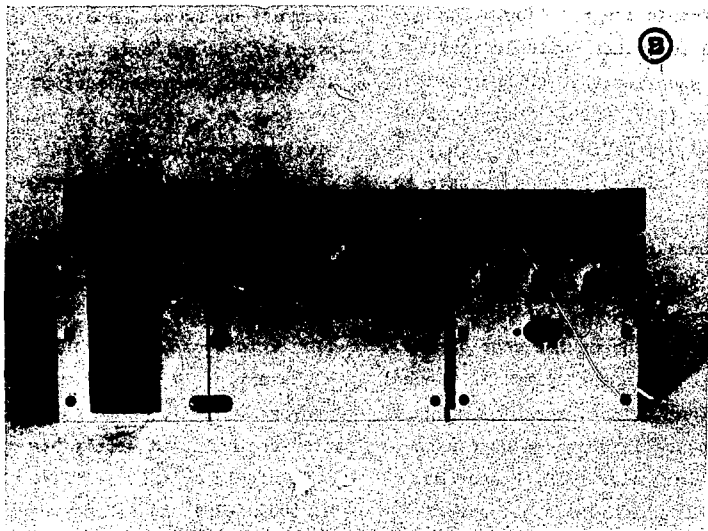
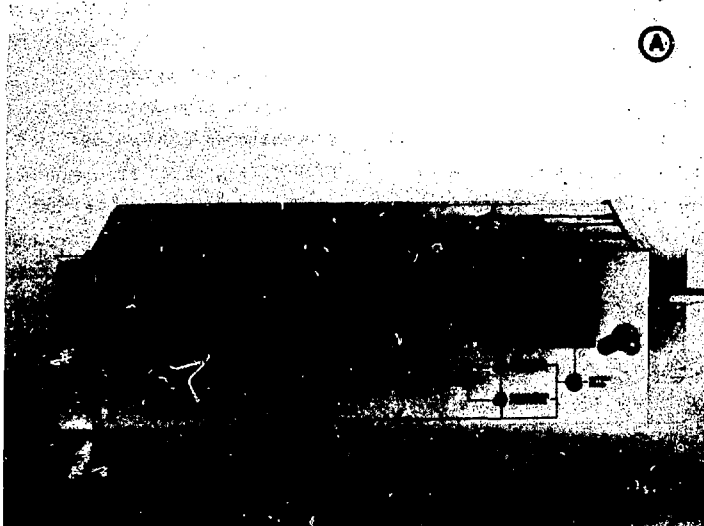


Fig. 15. Electrode potential measurement interface, front (a) and rear (b) panels.

course of the pretitration operations to deliver the appropriate reagent solutions to the cell. The quantity of each reagent is determined by the solution flow rates and by the length of time the reagent delivery valve (V3, Altex No. 201-03-Tefzel) is open. Valves V6 to V9 (three-way, Altex No. 201-04-Tefzel) are used to open their respective reagent lines to water to flush the system downstream. Valves V3, V5, and V6-V9 have a zero dead-volume, a 1.6-mm bore, and are pneumatically operated.

As shown in Figs. 10 and 16, the reagent containers are pressurized to 80 kPa (12 psi) with nitrogen gas to enable reagent flow. The nitrogen (or other suitable inert gas) is supplied through a pressure regulator (PCV, Circle Seal No. PVR-3-PM) and valve V10 which, when energized, allows the gas to pass to the reagent containers. The V10 valve vents the gas and hence relieves the reagent pressure whenever it is deliberately de-energized or, via an interlock, whenever the door of the reagent containment system is opened. Protection against excessive reagent gas pressure is provided by a pressure relief valve (PSV, Valcor No. 101T34-72) which vents at approximately 100 kPa (about 15 psi). Small deviations (0.7 kPa) in pressure that affect the accuracy of reagent delivery are monitored with a pressure

switch and gage (PSI, ACCO-Helicoid type IDC) which has both high and low adjustable set points.

Reagent flow is monitored with flowswitches (FS, Valcor No. SV400T2HF), which are magnetically activated reed switches that close when the solution flows exceed preset levels. Each reagent line also contains a check valve (CV, Mace No. CV2-23) that prevents reverse flow of the reagents when the system is depressurized.

Unrestricted flow at the driving pressure is allowed for the Fe(II)- $H_3PO_4$  and diluent reagents because these flow rates are satisfactory for accurate delivery. However, the flow rates of the sulfamic acid and  $HNO_3$ -Mo(VI) reagents must be reduced to acceptable levels with manual, micrometer-adjustment needle valves (V18 and V19, Gilmont micrometric-type).

Position 5 of V5 is supplied with water from the water manifold via the manual throttling valve (V20). Position 6 is connected to the source of clean air at 14 kPa (about 2 psi) of pressure. This, in turn, is taken from the main air supply via a pressure regulator (PCV, Veriflow No. HIR1005250PM) and a flow-regulating manual needle valve (V27). If the air pressure should exceed 35 kPa (5 psi), the safety valve (PSV, Codecal No. 1000-2) closes to protect the down-

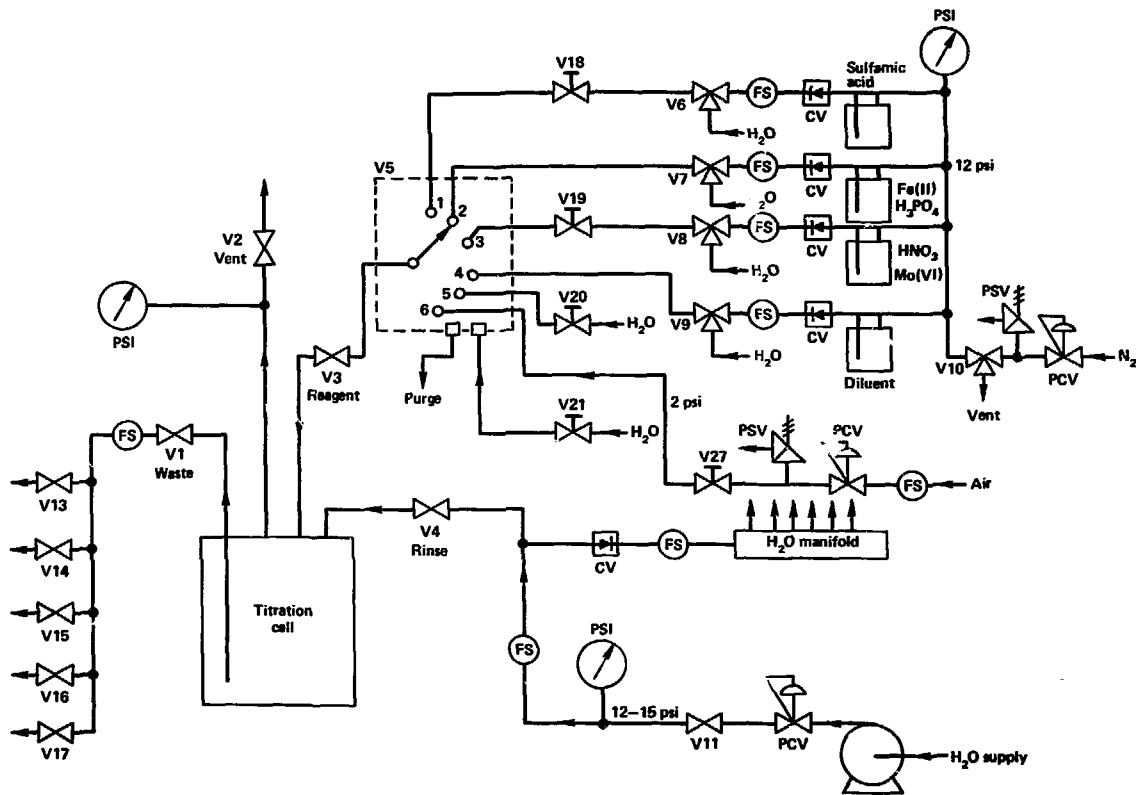


Fig. 16. Solutions, gas, water, and waste distribution system (CV = check valve, FS = flowswitch, PCV = pressure regulator, PSV = pressure relief valve, and PSI = pressure switch/gage).



stream apparatus. The supply air is switched on and off with a solenoid-operated valve (V12, not shown). A small trickle of water also is supplied to valve V5 to purge certain inside passages and to prevent the formation of crystals of solid material from the reagent solutions; this is accomplished with manual valve V21.

All materials that directly contact the reagent solutions are either glass or fluorocarbon plastic. Whenever possible, all other components in the analytical system that may contact corrosive vapors also are fabricated from inert plastics or from stainless steel. Valves V1-V9, together with the associated tubing and fittings, are assembled in a polyethylene box (Fig. 17) that is supported on the sample changer near the titration station.

#### REAGENT CONTAINMENT SYSTEM

Four glass reservoirs, one for each reagent, are housed in a polycarbonate and polyethylene plastic enclosure (Fig. 18). The reagent containers are fabricated from 15-cm-id glass process pipe rated at 207 kPa (30 psi). The capacity of the Fe(II)- $H_3PO_4$  container is about  $7 \text{ dm}^3$ ; the capacity of the other containers is about  $15 \text{ dm}^3$ . These quantities are sufficient for at least 100 determinations. Teflon screw caps fitted with Teflon-covered O-rings permit easy filling of the reservoirs (Fig. 18c). The level of solution in the reservoirs is monitored by visual observation through windows in the enclosure.

#### WATER REGULATION SYSTEM

A deionized or distilled water line is connected to the water regu-



Fig. 17. Reagent valve system, side (a) and top (b) views.



Fig. 18. Solution reservoir (a), and side (b) and top (c) views of the reagent containment system enclosure.

lation module (Fig. 19). This unit contains a pump (Micropump model 10-84-316) to boost the pressure (as necessary) to that required for cell rinsing, a pressure regulator (PCV, Valcor No. 100T32-54), a solenoid-operated shutoff valve (V11), and a

flowswitch (FS, Valcor No. SV400T8) to monitor the high flow (about  $1 \text{ dm}^3/\text{min}$ ) during rinse. The no-flow pressure of the water [50 to 100 kPa (7 to 15 psi)] is monitored with a dual set-point pressure switch and gage (PSI, ACCO-Helicoid type IDC).

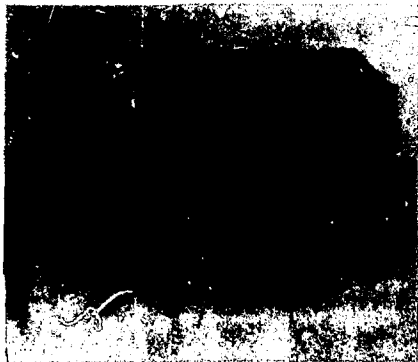


Fig. 19. Front panel of the water regulation system.

Within the reagent valve system, water is routed via a manifold (Fig. 16), a check valve (CV, Mace CV2-34), and a second water flowswitch (FS, Valcor No. SV400T2) to monitor the flow of water to position 5 of valve V5.

#### WASTE DISTRIBUTION SYSTEM

This module (Fig. 20) is a manifold of five low-cost (Noryl plastic body) solenoid-operated valves (V13-V17, Skinner No. V426DA0-JV011).

The valves are programmed to route the waste solution from the titration cell into various containers. Waste valve V1, and the flowswitch (FS, Valcor No. SV400T2HF) that registers the flow of waste, are located in the reagent valve system module.

#### GAS VALVE CHASSIS

The gas valve chassis (Fig. 21) contains filters for purifying the

supply air that operates the pneumatic valves and the sample changer. This unit also contains regulators for the purified air, the cell pressurization gas, and the nitrogen gas for pressurizing the reagent containers, as well as sensors and gages for monitoring the various system gas pressures and the flow of the cell gas. The cell gas pressure is measured with an ACCO-Helicoid-type IDC gage/switch (PSI, Fig. 16) connected to the cell vent line. The gas valve chassis also includes six solenoid-operated four-way valves (Humphrey No. 062-4E1) for switching air to pneumatic valves V3, V5, and V6-V9. The gas valve chassis, the water regulation chassis, and all of the electronic instrumentation except the minicomputer are housed in the system control console (Fig. 11), a 1.5-m-high double relay rack.



Fig. 20. Waste distribution system.

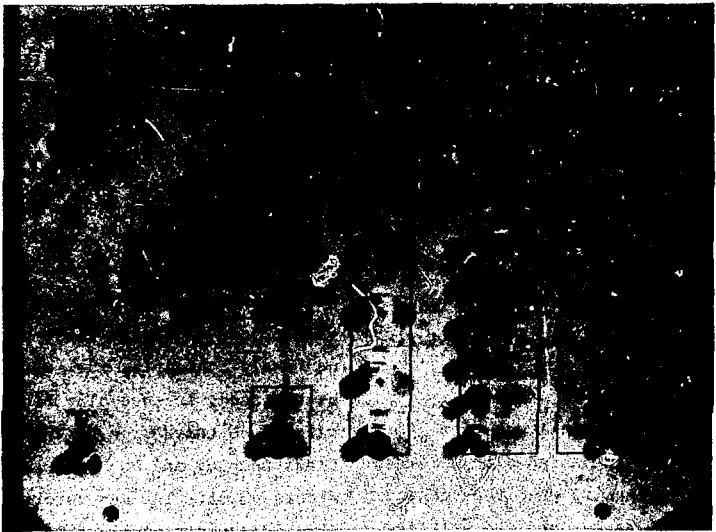
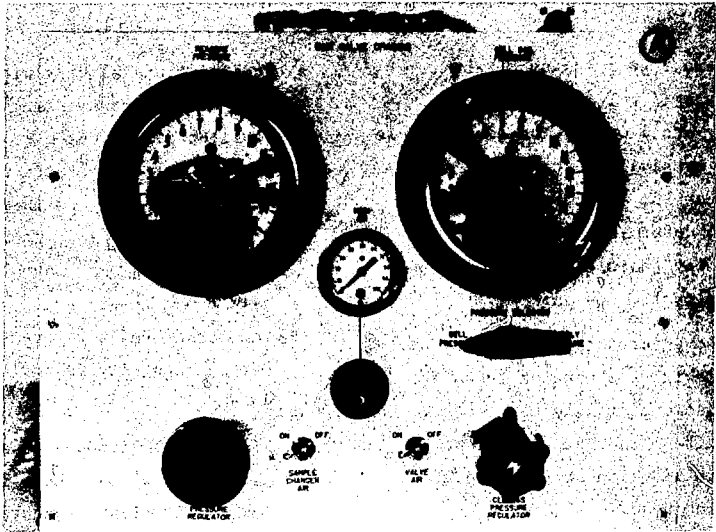


Fig. 21. Gas valve chassis, front (a) and rear (b) panels.

## TITRATION CELL ASSEMBLY

The exact positioning of the components (e.g., the electrodes, stirrer, etc.) within the electrolysis cell is crucial for the proper functioning of the system and for the accurate determination of uranium. Several key features are incorporated into the system design:

- The generator and counter-electrode separator tubes are placed coaxially to create a uniform current and potential distribution at the generator electrode.
- The indicator electrode and the reference electrode salt-bridge junction are located outside the principal current-flow path on an equipotential line; thus there is minimum interference with the potential measurement by the current flow.
- All four of the electrode assemblies are located so that they do not contact the solution during the pretitration.
- The solution delivery-tube assembly is designed to eliminate splashing when the reagents are delivered, and the stirring impeller is designed to give maximum stirring without splashing.
- The solution-delivery wire, waste tube, and stirring impeller are oriented so that they do not contact the new sample solution when the beaker is first raised into position, thus ensuring that, should the sample not be processed because the beaker fails to pressurize, sample integrity is not breached.
- Finally, all components are assembled so that there is a reasonably tight pressure seal within the cell when the titration beaker is in place. Thus the cell is pressurized to signal the start of the pretitration and to dispose of the spent titration solution through the waste tube.

A diagram of the titration cell designed to meet these criteria is shown in Fig. 22. The glass beaker (Fig. 23a), enclosing these components and containing the solution to be titrated, is specially fabricated with close tolerances by the Wilmad Glass Company and has a capacity of about 300 ml. The generator electrode (Fig. 23a) is a double-thickness (Fig. 22) of expanded gold (Exmet No. 8AU10-5/0), affixed to a 2-mm-diameter platinum rod. It may be possible to

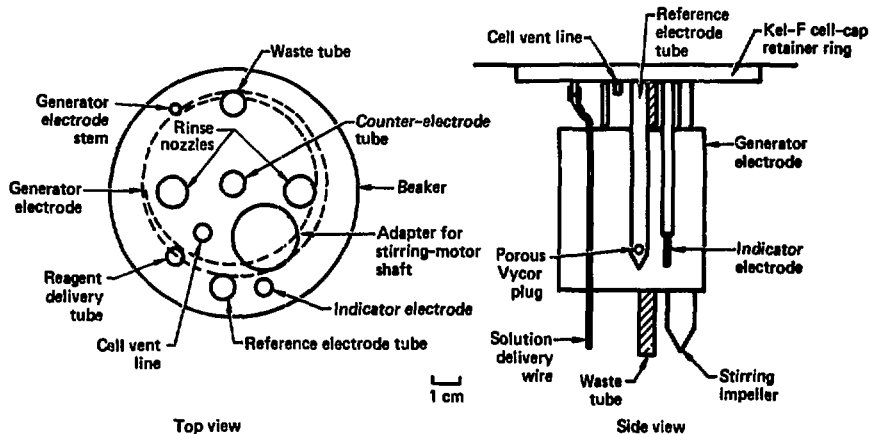


Fig. 22. Titration cell assembly.

use platinum gauze. However, experiments at the New Brunswick Laboratory<sup>16</sup> and preliminary studies conducted at LLL have revealed that negative errors in the titration then result, apparently because of a catalytic oxidation of the U(IV). The counter electrode (Fig. 23b) is a spiral of platinum wire that is enclosed in a tube, the lower section of which is either porous Vycor (Corning Glass No. 7930) or a Nafion (DuPont) ion-exchange membrane.<sup>17</sup> Both 1-mm wire gold and platinum indicator electrodes (Fig. 23c) have been used, the former sealed in heat-shrinkable Teflon and the latter sealed in glass or used bare. The reference electrode, a Radiometer type K601 Hg-Hg<sub>2</sub>SO<sub>4</sub> electrode, is held above the cell in a tube that is

connected to the salt-bridge tube (Fig. 23c). The salt-bridge tube is Kel-F with a force-fitted piece of porous Vycor rod as the solution junction which is oriented (Fig. 22) away from the generator electrode.

Reagent solutions are delivered from valve V3 to the cell through 3.2-mm-od Teflon tubing, to which is attached a gold wire (Fig. 23d). This wire eliminates splashing of the dense, viscous Fe(II)-H<sub>3</sub>PO<sub>4</sub> solution upon delivery. In addition, the flow rates of the Fe(II)-H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub>-Mo(VI) solutions are adjusted so that they flow down the wire, thus ensuring that no Fe(II) remains unoxidized by the HNO<sub>3</sub>. The waste and vent tubes are 6- and 3.2-mm-od Teflon tubes, respectively (Fig. 23d). The glass stirring impeller (Fig. 23c) is

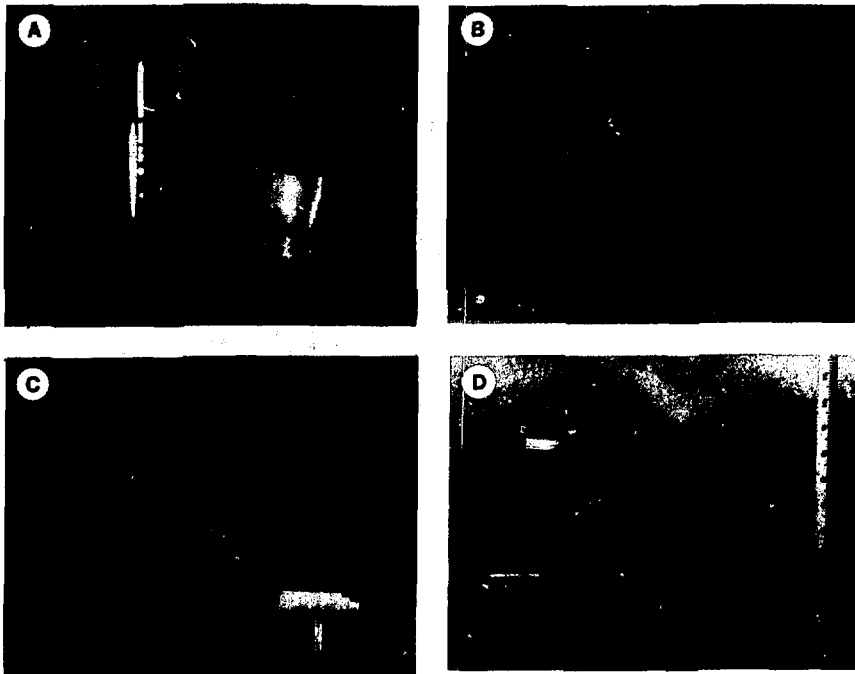


Fig. 23. Titration cell components. From left to right in (a), beaker and generator electrode; from top to bottom in (b), counter electrode and separator tube; from top to bottom in (c), indicator electrode, salt-bridge tube, and reference electrode; and from bottom to top in (d), stirrer, waste tube, and delivery tube.

a flat blade, approximately 2 mm thick, about the same height as the generator electrode and tapered at the end. The impeller is rotated by a 12-V dc tachometer-feedback, speed-regulated motor (Barber-Colman No. FYQM-63260). The motor and the Kel-F coupling shaft are contained in a hermetically sealed enclosure. Three states — off, low speed (about 1300 rpm), or high

speed (about 3600 rpm) — can be selected manually or by the computer program. The cell components are rinsed by a spray of water from two Teflon Bete-Fog (120 deg) full-cone spray nozzles mounted in the cell cap.

The titration cell assembly is mounted as shown in Fig. 24 on a special Kel-F platform at station No. 4 of the sample changer. When

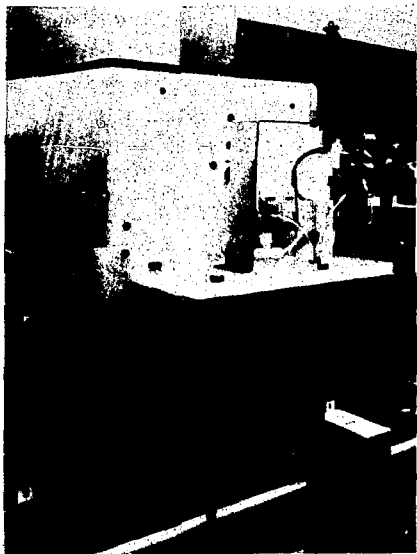


Fig. 24. Titration station.

the beaker is raised, its rim presses against an inert Viton elastomer gasket in the cell cap to create the pressure seal. A polycarbonate-plastic cylindrical enclosure around the cell components serves as a safety shield and protects the components from damage in the event of misalignment in the raising of the beaker.

## SOFTWARE DESCRIPTION

The system software is designed to interact with the operator and electronic balance for the acquisition and storage of sample ID and weight information. Interactive software allows the operator to specify the titration conditions. The software also controls the mechanical operations of sample queuing, pretitration reagent addition, post-titration solution disposal, and cell rinsing. The instruments for regulating the electrolysis current, acquiring the titration data, and reading the coded

sample position labels are all controlled by systems software. In addition, software routines process the titration data to obtain the analytical results and output the analysis reports. System software also monitors the fault-detection circuits, detects abnormal analysis conditions, and when faults and errors arise, carries out preprogrammed actions and generates specified error messages.

The basic software was written to be used with a modified version of



the Digital Equipment Corporation interpretive language, 8K FOCAL. Two large overlays were written in assembly language to operate with 8K FOCAL: NBLWT for handling the weighing and recording of sample weight and identification information, and AUTVAL for most of the other system hardware control functions and fault-monitoring functions except those associated with the actual titration.

Two FOCAL user programs were designed for this system. One is the fundamental weighing and titration program for routine operations. The other is a test program which provides several operator-selected options for the analysis cycle, but which does not have the capability of weight information manipulation or calculation. With either program, the operator has the option, via the startup dialogue, of conducting the titrations with preset parameter values (e.g., electrolysis current levels, number of data points) or with values selected in response to queries from the computer. For troubleshooting, the system can be operated by the test program in an automatic mode in which the sample changing as well as the pretitration and post-titration valve sequencing are carried out with water instead of reagent solutions.

Two 4-K segments of core memory

are allocated for storage of the sample or standard weights and ID numbers. Depending on the proportion of standards and samples, there is storage capacity for 340 to 1024 entries.

Several special function calls were created to be used in commands of the form of  $S U=FSET( )$ ,  $S U=FCUR( )$ ,  $F U=FVAL( )$ . These commands then were written into the user programs to manipulate the weight information and to control the electronic instrumentation, the timing of the operations, and the sequence of the mechanical operations. For example, certain  $FVAL( )$  arguments can be used to list the weight data storage and to delete entries. The level of the electrolysis current, the sequence of titration-curve data taking, and the timing of the data taking are established by the arguments of  $FCUR( )$  and  $FSET( )$ . The states of the 17 valves, the stirring motor and the valve timing are determined by a numerical code in the arguments of a series of  $FVAL( )$  statements. Because these functions are part of the user program, they can be readily changed under the rules of FOCAL programming. [Listings of the programs and additional information about their operation are available upon request from the authors (J. E. Harrar or J. D. Breshears).]

## SEQUENCE OF OPERATIONS FOR AUTOMATED ANALYSIS

The overall sequence of operations in the analytical cycle is diagrammed in Fig. 7 and the execution of the pretitration and post-titration procedures can be visualized by referring to Fig. 16. During normal sample processing, valves V10, V11, and V12 remain energized to, respectively, pressurize the reagent containers, supply water, and supply air. Also, valves V6-V9 are switched to the reagent lines. To ready the system for the analysis, valves V1, V3, V4, and V13-V17 must be closed, V2 must be open, V5 must be aligned at position 6, and valves V6-V12 must be configured as described above.

### BETWEEN-SAMPLE PERIOD

To start the sample processing, the operator types the letter T on the teletypewriter. This commands the sample changer to advance the magazines containing the sample beakers. Typing T also causes the cell vent valve (V2) to close and the reagent delivery valve (V3) to open. The reagent selector valve (V5) is at position 6 and thus when V3 is opened, air at 14 kPa (about 2 psi) flows out of the reagent delivery tube at the titration station. Valve V2 is closed; thus, when a beaker is brought to the titration

station, lifted and pressed against the gasket, and a good seal is formed, 14 kPa of pressure quickly develops in the beaker. This increase in pressure is detected by the cell pressure switch and serves as the pneumatic signal that a beaker is in place, ready for sample processing. Verification of beaker pressurization in this manner also ensures that during the post-titration, solution disposal by cell pressurization will function properly.

### PRETITRATION

The pretitration sequence begins as soon as the cell pressurization signal is received. The cell vent valve (V2) is reopened, the stirrer is turned on at low speed, the reagent delivery valve (V3) is closed, and the reagent selector valve (V5) is advanced to position 1. After 2 s to permit the operation of V5, the reagent delivery valve is opened for about 4 s to allow 5 cm<sup>3</sup> of sulfamic acid to flow into the beaker. In a similar manner, 45 cm<sup>3</sup> of Fe(II)-H<sub>3</sub>PO<sub>4</sub> solution is delivered at position 2. A 30-s delay then occurs to allow the reduction of U(VI) to U(IV). Next, 10 cm<sup>3</sup> of the HNO<sub>3</sub>-Mo(VI) reagent is delivered at position 3, followed by a 3-min delay to

permit complete oxidation of the excess Fe(II). Then, 160 cm<sup>3</sup> of diluent is added, after which the stirrer is switched to high speed. At position 5 of V5, about 5 cm<sup>3</sup> of water is delivered in approximately 2 s to flush the diluent out of the line, leaving it clean for the next sample. As the reagent delivery valve is closed and V5 is advanced to position 6, the signal is given to start the titration.

#### TITRATION

No switching of valves occurs during the titration period except when a fault condition is detected. However, it is possible to use an inert-gas blanket over the solution during the titration, by merely substituting the inert gas for the

air at position 6 of V5 and by keeping V3 open.

Figure 25 illustrates the sequence of data acquisition and current control in the coulometric titration. Before the start of electrolysis, a measurement is made of the open-circuit generator electrode potential vs the reference electrode and of the indicator electrode potential vs the reference electrode. These data are stored for later readout with the titration results (see Figs. 8 and 9), which is accomplished by the electrode-potential-measurement interface. The programmable constant-current source then is switched to the reaction cell and electrolysis begins at 300 mA (I1, Fig. 25).

Data acquisition continues with 1-s intervals between measurements of

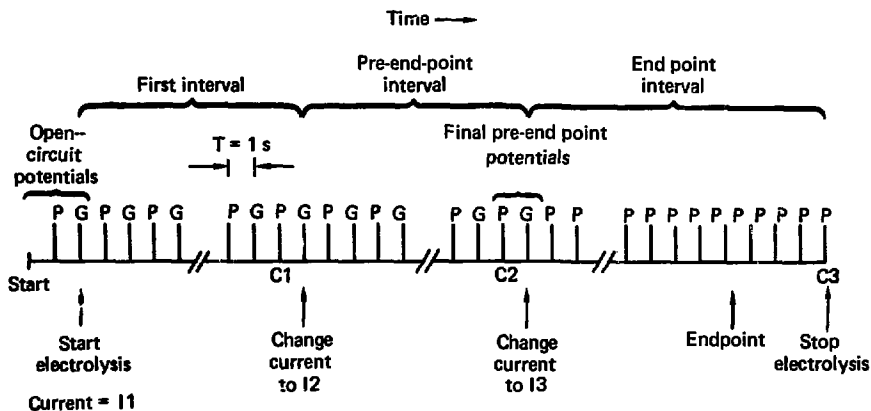


Fig. 25. Titration data acquisition and current control scheme (P = indicator electrode potential, G = generator electrode potential).

the indicator and generator electrode potentials. After each measurement of the indicator electrode potential, the data are smoothed using an algorithm that is the digital-filter equivalent of an analog, single-pole, RC filter. The equation is<sup>18</sup>

$$Y(t) = (1 - \alpha)X(t) + \alpha Y(t-1),$$

where  $Y(t)$  is the output of the filter (the calculated smoothed point),  $X(t)$  is the input or most recent data point,  $Y(t-1)$  is the previous filter output, and  $\alpha$  is a coefficient selected to obtain a particular time constant or degree of smoothing. The value of  $\alpha$  is given by

$$\alpha = e^{-1/n},$$

where  $n$  is the number of data points corresponding to the desired time constant. In the titration system, we use  $\alpha = 0.81873$ . This is equivalent to a time constant of 5 data points or 10 s for the 2-s interval sampling of the indicator electrode potential. The most recent data point is then subtracted from the previously smoothed point. This difference in volts is divided by the difference in coulombs corresponding to the two data points to obtain the slope of the curve (V/C).

The calculated slope is compared with a value of +0.0001 V/C; when this is exceeded, a calculation is made to

determine whether 21 C of electricity ( $Q$ ) have been passed. If so, a quantity of uranium in the sample greater than approximately 50 mg is indicated and no action is taken. If  $Q$  is less than 21 C, a quantity of uranium less than about 50 mg is indicated and the current is reduced to 100 mA (12, Fig. 25) so the end point will not be approached too rapidly. Such a sample is designated a "Small Sample" in the data readout (see Fig. 8). Smoothing and slope calculation then continue until the indicator-electrode potential begins to change rapidly. When a preset value of "Pre-Endpoint Slope" is exceeded, the electrolysis current is reduced to 10 mA (13, Fig. 25), and measurements are taken only of the indicator-electrode potentials. These data in the end-point interval are processed later to locate the end point in the titration. In the end-point interval, the titration is continued past the inflection point of the curve until the slope of the curve drops below a preset value.

During each cycle of data acquisition, several conditions of the titration are monitored by the FOCAL program. After each reading of the indicator electrode potential, the actual electrolysis current is measured and compared with the nominal current to determine whether it is within a tolerable error band. Also,

the total quantity of electricity passed is not allowed to exceed 150 C. Thus after each reading of the generator electrode potential, the value is compared with an allowable upper positive limit. In addition, the total output voltage of the constant-current source is measured during each data cycle and is not allowed to exceed the compliance limit of 45 V. Should any of these fault conditions occur, the titration is terminated, the post-titration sequence is initiated, and appropriate error messages are printed out.

#### POST-TITRATION

Upon termination of a normal titration, the data are held in memory for processing after the post-titration operations are executed. This sequence begins by opening the reagent delivery valve (V3) to reintroduce air in the system, closing the cell vent valve (V2), as well as opening the waste valve (V1) and the appropriate waste category valve (V12-V17). In about 30 s, all the spent solution from the titration is forced out of the cell into a waste container. Then, the rinse valve (V4) is opened for 5 s and the cell components are sprayed with water. A 5-s delay for drainage occurs and the cell components are sprayed again for 5 s. During the rinse periods, the beaker is still pressurized so

that the rinse solution flows out as waste.

#### CALCULATION AND READOUT

After the second rinse, the nearly empty sample beaker remains in position at the titration station. The titration data are processed to locate the inflection point in the curve, the end point is calculated, and the titration information is printed out. The indicator-electrode potential data in the end-point interval are first smoothed with a ten-point moving average to reduce the noise even further. Then, successive differences using the averages are calculated, and the maximum difference (peak) in the first derivative of the titration curve is found. This is the preliminary estimate of the end point.

With the estimated end point, the original data are convolved with a 9-point Savitsky-Golay function<sup>19</sup> to yield the second derivative of the data. The Savitsky-Golay algorithm midpoint is started 15 points before the estimated endpoint; the computation is continued for 30 points with 10 data points between each point of the convolute. The result of the Savitsky-Golay convolution is a set of data with values ranging from positive to negative. The zero-crossing corresponds to the inflection point in the original data. To locate this

zero-crossing, 13 points that encompass the zero-crossing are taken, a least-squares-line equation is found for the 13 points, and the value of the abscissa is computed from the zero of this equation.

After the end point is determined, the quantity of electricity (in coulombs) corresponding to this end point and the quantity of uranium (in milligrams) are computed. This is accomplished by computing the sum

$$Q = \sum_{1}^{n} i_n t_n,$$

where  $i_n$  is the current level and  $t_n$  is the time duration of current flow, both in the  $n$ th interval. Normal readouts of titration data are shown in Figs. 8 and 9. In these outputs,

C1, C2, and C3 refer to the total numbers of points taken at the ends of the various titration intervals (see Fig. 25) and E.P.<sub>n</sub> denotes the interpolated end point in numbers of points. Approximately 30 s are required to process the data and print out the results.

#### RETURN TO BETWEEN-SAMPLE PERIOD

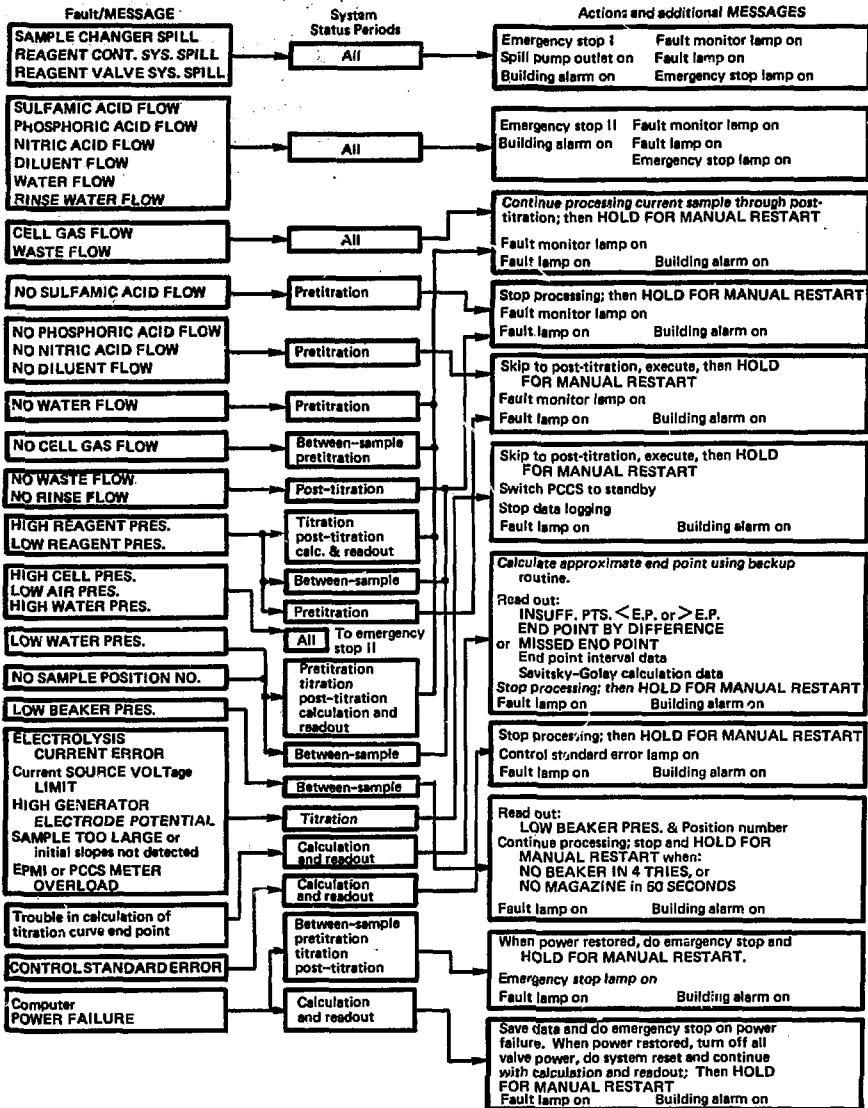
If the analysis continues to function properly and accurate results are obtained, the waste valves are closed, allowing the pressure in the cell to increase. This signals the sample changer to lower the old beaker and bring a new one to the titration station. The valves return to the configuration described for the first between-sample period, and the system continues with the next sample.

## FAULT-MONITORING SYSTEM

The uranium analyzer incorporates a comprehensive fault-monitoring system based both on hardware- and software-sensing mechanisms. The faults which can be detected during automatic operation and the system action that is taken when a fault is detected are summarized in Fig. 26. The messages that are printed out are shown in upper-case letters.

The fault monitoring scheme coordinates the shutdown procedure, if

any, to the status of the system when the fault occurred. Thus only catastrophic conditions such as solution spills justify an emergency stop or a complete shutdown similar to the power-off configuration. Actions for faults that do not affect the sample currently in process (e.g., low reagent pressure during titration) are postponed until the sample analysis is complete. If a noncatastrophic fault occurs when at least



Note: Condition HOLD FOR MANUAL RESTART always has emergency stop fault-monitoring still enabled.

Fig. 26. Diagram of fault, error message, and action taken for the titration system.

one reagent has been added to the sample or during the titration itself, the sample is presumed to be worthless and the program jumps to the post-titration sequence. This minimizes contact between the titration mixture and the cell components in case the system should remain on hold for a long period of time. Similarly, in every instance where a "hold for manual restart" condition is executed, the system goes to a safe configuration where the cell components have been rinsed, the emergency-stop fault monitoring is still enabled, and (in most situations) a beaker is still in position at the titration station. Thus, if a spill or flow fault should subsequently occur while the system already is holding from a previous fault, the emergency-stop routines still can be executed.

Solution spills are detected by sensing the decrease in open-circuit resistance between pairs of wires at the sample-changer titration station and in the reagent container enclosure and a grid in the bottom of the reagent valve enclosure. Both an accidental flow and a lack of flow when called for by the operating program constitute flow faults. For example, during the pretitration reagent addition, as each step of the program is executed, the status of the flowswitches is checked to verify that the proper flows take place.

This feature mitigates the need for solution level detectors in the reagent containers.

Abnormalities in the titration curve resulting from indicator electrode fouling or interferences in the sample may cause difficulties when calculating the end point. Various abnormal situations can arise, all of which terminate sample processing and generate various combinations of the error messages shown in Fig. 26. These faults cause all of the data on the indicator electrode potentials in the end-point interval to be printed out. If no zero-crossing is found in the second-derivative calculation, the quantity of uranium is calculated from the estimated end point obtained from the differencing technique and is so indicated on the printout. However, the end-point-by-difference also may not be found. Information on the cause of the abnormality is given in messages which state that there were insufficient numbers of data points either before or after the end point. The control standard error routine is initiated when the result of a standard solution analysis is outside the allowable control limits. (This tolerance, like all of the software-detected faults, can be easily changed in the FOCAL program.)

If a power failure to the computer occurs during calculation and readout,



all necessary data are saved and several pointers are set. Thus when power is restored, program operation can continue without error; after the data readout, a "hold" is executed. If power failure occurs in other

periods of system operation, the emergency stop configuration is commanded immediately when power is restored, because, in most cases, system operation cannot be resumed safely without operator interaction.

## PRELIMINARY STUDIES OF SYSTEM PERFORMANCE

A comprehensive study of several of the factors affecting the automated analysis has been published in Ref. 20; some of the results are summarized here.

### SOLUTION DELIVERY SYSTEM

No detailed studies have been conducted to determine the allowable variation in the delivered volumes of the four pretitration reagent solutions. However, previous work on the method in which  $K_2Cr_2O_7$  was used as the titrant<sup>2,21</sup> as well as experience in the present work<sup>20</sup> indicate that for chemical reasons at least, very close control is not required. For the automated system, however, variations in the solution volumes must be restricted so that the mixing characteristics of the solution during the reduction, oxidation, and titration steps are not adversely affected and so that the final total volume of solution in the cell is not markedly changed. Positioning of the solutions during the various stages

of the automated analysis also requires that the sample volumes range from approximately 2 to 12 cm<sup>3</sup>. Thus we have set the following tolerances for the four reagent solutions: sulfamic acid,  $5 \pm 1$  cm<sup>3</sup>; Fe(II)- $H_3PO_4$ ,  $45 \pm 3$  cm<sup>3</sup>;  $HNO_3$ -Mo(VI),  $10 \pm 2$  cm<sup>3</sup>; and diluent,  $160 \pm 5$  cm<sup>3</sup>.

In the present system, the most important factor affecting the reproducibility of the solution delivery is the change in flow rates caused by variations in the level (i.e., head) of the solution in the reagent containers. The pressure of the gas used to pressurize the containers is regulated to within  $\pm 2.5\%$  and the reproducibility of the solution delivery at constant head is within  $\pm 1\%$ .<sup>20</sup> However, the variation in solution head during normal operation usually is approximately 30 cm and can be as large as 56 cm for reagents 1, 3, and 4. The 56-cm drop in solution level causes a considerable change in the effective pressure (about 7% for pure water

and greater for the more dense reagent solutions).

The expected effect of the head change was verified directly<sup>20</sup>; in addition, the reagent solution flow rates were monitored over a 1.5-y period, during which time there were no readjustments of the mechanical components. We found that with a 30-cm head variation, the variations in delivered volume were:  $\pm 0.14 \text{ cm}^3$  for sulfamic acid,  $\pm 1.4 \text{ cm}^3$  for  $\text{Fe(II)-H}_3\text{PO}_4$ ,  $\pm 0.34 \text{ cm}^3$  for  $\text{HNO}_3$ - $\text{Mo(VI)}$ , and  $\pm 5.4 \text{ cm}^3$  for the diluent. Because these values compare well with the stated specifications and the reliability of the present delivery system has been excellent, we have seen no need to consider a more elaborate system incorporating flow regulation.

#### REAGENT SOLUTION PURITY

The purities of two of the reagent solutions,  $\text{Fe(II)-H}_3\text{PO}_4$  and diluent, are critical to the accuracy and the precision of the results obtained with this analyzer. In the course of this work,<sup>20</sup> we discovered that in some lots of reagent-grade concentrated  $\text{H}_3\text{PO}_4$ , a substance was present that caused the generator electrode to operate at a higher potential where the current efficiency for the oxidation of  $\text{V(IV)}$  to  $\text{V(V)}$  is significantly lowered. This in turn

caused a positive error in the analysis and, in extreme cases, resulted in degradation of the gold electrode. The identify of the contaminating substance is unknown; it may be the same material that has caused problems in fuel-cell studies with concentrated  $\text{H}_3\text{PO}_4$ .<sup>22</sup> However, the generator electrode potential in the analyzer system is closely monitored, enabling contaminated lots of  $\text{H}_3\text{PO}_4$  to be easily detected and avoided.

A potential source of negative error in the uranium determination is the presence of  $\text{V(V)}$  in the diluent. Vanadium(V) may be present in the  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  salt used to prepare the diluent or it may be produced by air oxidation of the  $\text{V(IV)}$  in the diluent solution. We did not detect any  $\text{V(V)}$  in seven lots of two different sources of  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ ; however, a very slow oxidation of  $\text{V(IV)}$  by air does occur but can be decreased by increasing the concentration of acid in the diluent.<sup>20</sup> Thus we minimized the oxidation of  $\text{V(IV)}$  by making the diluent  $0.30 \text{ M}$  in  $\text{H}_2\text{SO}_4$  and by pressurizing the reagent containers with nitrogen to prevent contact with air. Pressurizing the reagent containers with an inert gas also improves the stability of the  $\text{Fe(II)}$  reductant, but air oxidation of this reagent is quite slow.

## TITRATION TECHNIQUE

Extensive studies were conducted<sup>20</sup> on the current efficiency of the electrolysis and on the titration efficiency<sup>23</sup> of this analysis. Curves of the generator electrode potential as a function of current level, under controlled-current conditions, were obtained in both the presence and absence of U(IV). In addition, measurements were made, using a controlled-potential coulometry, of the background current in the potential region where the generator electrode operates. We found that a considerable fraction of the U(IV), in addition to the V(IV), is directly oxidized early in the titration when the U(IV) concentration is high. Thus the current efficiency for V(V) generation is lower than 100% in the presence of uranium, although the titration efficiency remains close to 100%.

Under the particular electrolysis cell conditions chosen, the background current becomes excessive at a potential of about +0.75 V vs the Hg-Hg<sub>2</sub>SO<sub>4</sub> reference electrode (approximately +1.18 V vs SCE). The potential of the generator electrode is not constant during the titration; typically it rises from about 0.6 to approximately 0.7 V vs Hg-Hg<sub>2</sub>SO<sub>4</sub> when analyzing more than 50 mg of uranium. Because of this, and because the

background current may not be additive, the precise effect of the background current on the uranium determination is not known. However, the accuracy of the determination is undoubtedly influenced by the fact that a 6-min electrolysis of a blank solution at +0.7 V requires the passage of a charge that is equivalent to 0.20 mg of uranium.

An important constraint in this analytical method is that after the dilution step, there is a slow oxidation of U(IV). Therefore, the titration must be completed in a minimum time to avoid a significant negative error.<sup>1-3,16,21</sup> On the other hand, if the titration is rapid, there is a danger in overshooting the equivalence point because of either slow chemical reactions or sluggish potentiometric measurement response near the equivalence point. In the original coulometric method of Goldbeck and Lerner,<sup>3</sup> the titration was carried out to a specific end-point potential with an intermittent pulsing of the constant current (usually 300 mA, with low duty cycle), beginning at a preset potential that preceded the end point by about 1 min.

In the present system, there is a continuous flow of current, with feedback actuation of current change to decreasing levels as the titration proceeds. To avoid reliance on a

fixed potential of a reference electrode and on constancy of the end-point potential with varying sample media, the end-point anticipation and current control are based on the slope of the titration curve (V/C), rather than on absolute potentials. To optimize the titration over the complete sample range (approximately 10 to 150 mg uranium) the electrolysis current for small samples (50 mg) differs from that for larger samples. For samples below about 50 mg (detected automatically by an early change in slope), the electrolysis current is decreased from 300 to 100 to 10 mA. Larger samples are titrated at two current levels, 300 and 10 mA. The slope detection parameters are selected so that as much of the uranium as possible is titrated as rapidly as possible but without overshooting the end point. The titration control scheme is similar in principle to that used by previous workers (e.g., Refs. 24 and 25) and in some commercial instruments except that, in this case, the current levels are discrete and the feedback actuation is controlled by the software.

An analytical method is most useful if it can be designed so that it involves no systematic error and thus is subject to as few arbitrary parameters as possible, both in operation and in data manipulation. The systematic error is lower if the

method can be placed on an absolute basis; i.e., if the calculation of the quantities of analyte is based solely on electrical calibrations of the instrumentation (current and time), which are traceable to National Bureau of Standards calibrations. In theory, the controlled-current coulometric technique accomplishes this goal. However, the method locating the titration end point may introduce significant error. The uranium analyzer was designed to store the titration curve data and to take enough data past the equivalence point so that many means of calculating the end point are possible.<sup>26</sup> Goldbeck and Lerner<sup>3</sup> originally established the accuracy of this titration with standard solutions of uranium; the end-point potential was determined from the inflection point of the titration. Additional evidence corroborating the validity of this approach was obtained in the present work.<sup>20</sup>

We investigated whether there is an intrinsic difference between the inflection point of the titration curve and the equivalence point for this particular titration. Using an equation of Goldman<sup>27</sup> which, except for the involvement of hydrogen ions in the reaction, is directly applicable, we established that the inflection point of the theoretical titration curve is within 0.01% of the

true equivalence point for the range of concentrations encountered.<sup>20</sup> The actual experimental titration curves, however, do not exactly conform to the shape predicted by the equation. Nevertheless, there appear to be no significant grounds for rejecting the inflection-point technique in favor of another.

#### COMPARISON OF THE TWO END-POINT CALCULATION TECHNIQUES

The basic technique to locate the titration end point involving the Savitsky-Golay algorithm is supplemented by a routine based on a differencing approach. This backup routine is initiated automatically if a valid end point is not found with the primary calculation. To determine the accuracy of the differencing technique, we compared the two routines, performing both calculations on the same sets of "normal" titration data (see Table 1). The difference between the two techniques is very small but the backup routine almost always yields lower results than does the Savitsky-Golay algorithm. Although for these data, the differencing technique is quite adequate, the primary routine should be more reliable in the long run because it is more immune to noisy and spurious data.

#### ACCURACY OF THE CONSTANT-CURRENT SOURCE

Theoretically, one of the advantages of coulometry is that there is no need to frequently standardize the titrant. However, to fully realize this benefit, an extremely stable constant-current source is essential. We evaluated the constant-current source used in our uranium analyzer and found that the drift in calibration over the 30- to 500-mA range was less than 0.03% per year.<sup>14</sup> (The accuracy of the instrument is based on a National Bureau of Standards traceable 1- $\Omega$  resistor with an accuracy specification of 0.01%.) This performance is quite satisfactory for the analytical precision we desire.

Table 1. Comparison of Savitsky-Golay and differencing techniques for calculating titration end points.

Calculated end point, mg uranium	
Savitsky-Golay	Differencing
113.140	113.115
113.114	113.103
113.039	113.029
56.639	56.625
34.005	33.993

## EVALUATION BY THE NEW BRUNSWICK LABORATORY

The automated titration system was designed and built for the New Brunswick Laboratory (NBL) of the U.S. Department of Energy (formerly at New Brunswick, New Jersey and now at Argonne, Illinois). Their evaluation of the precision, accuracy, and reliability of the system recently has been published<sup>28</sup>; only highlights are presented here. At NBL, a detailed evaluation was made with standards containing from 40 to 140 mg uranium. The computer program was changed slightly so that all samples were determined using the "large sample" electrolysis current sequence (300 and 10 mA). Also, the slope detection was modified to select different pre-end point slope values for different sample sizes.

To determine the accuracy and precision of the analyzer, NBL made a series of runs over 15 d using three replicates each day at each of six uranium levels (see Table 2). The value at each level therefore represents 45 determinations. There is a significant, increasingly negative bias occurring in the titration of the larger quantities of uranium. The cause of this bias has not yet been discovered, but is believed to be due to an interaction between the catalytic loss of U(IV) and the current efficiency of the

titration for the particular size of generator electrode employed. Due to the high precision obtained, NBL recommends that either the results be corrected using a recovery data calibration or that the sample size be limited to 50 mg.

A variety of uranium-containing samples also were analyzed and representative results from Ref. 28 are given in Table 3. The only problem encountered with these samples involved the effect of HF. The indicator electrode response is more sensitive in the presence of HF. As a result, insufficient numbers of data points sometimes were obtained when titrating samples of ore concentrate. Early attempts to titrate

Table 2. Accuracy and precision of analyses of uranium standards at the New Brunswick Laboratory.<sup>28</sup>

Uranium titrated, mg	Mean recovery, %	Relative standard deviation, %
40	100.00	0.04
60	99.95	0.05
80	99.90	0.03
100	99.88	0.04
120	99.86	0.03
140	99.81	0.04

a solution of U-Zr-Er alloy in HF also resulted in an error greater than 1%. The effect of fluoride on the titra-

tion and a method to prevent etching of the beakers by high concentrations of HF must be addressed in further study.

## SYSTEM RELIABILITY

The prototype system was operational in its nearly final form in the spring of 1975; some of the subsystems were functional in the previous year. The system was tested almost continually until the spring of 1976, when it was shipped to the New Brunswick Laboratory for a year of thorough evaluation. A brief description of the reliability of various subsystems follows.

### ELECTROCHEMICAL CELL

The continual measurement, display, and recording of the titration variables gives the system operator a graphic early warning of specific difficulties, thus minimizing downtime. The reference-electrode salt-bridge has never malfunctioned. In addition, the location of the four electrodes and measurement of their potentials with the floating, differential-input meters have proved very satisfactory. Interrupting the passage of electrolysis current at 300 mA or decreasing the current (to 100 or 10 mA) does not measurably affect the potentiometric measurement. Flame cleaning,

followed by  $\text{HNO}_3$ -quenching of the platinum indicator electrode is occasionally required; however, the gold generator electrode has never required cleaning. Similarly, the Nafion-membrane counter-electrode tube has required no maintenance. The stirrer shaft and bushing have been replaced twice.

### GAS, WATER, REAGENT, AND WASTE DISTRIBUTION SYSTEM

Except for the flowswitches, the gas, water, solution, and waste distribution subsystems have been quite reliable. The reagent solution delivery system uses the liquid-chromatography-type valves and pressurized containers; this design appears to be quite successful. None of the valves has yet required replacement, reagent delivery volumes have been constant over long periods of time, and no corrosive chemical spills have been caused by the delivery system. On the other hand, the flowswitches, which indicate the flows of the various fluids in the system, have not been as reliable as desired.

Table 3. Comparison of uranium analyses by manual and automated methods.<sup>28</sup>

Sample type and number	Percent uranium found		Percent difference, $\frac{A - M}{M} \times 100$
	NBL manual titration (M)	Automated titration (A)	
<u>UO<sub>2</sub></u>			
EU 3340 A	87.54	87.50	-0.05
EU 3429 A-1	83.91	83.98	+0.08
<u>UO<sub>3</sub></u>			
EU 3829 A	82.94	82.99	-0.06
EU 3832 A	82.93	82.82	-0.13
<u>UF<sub>6</sub></u>			
E 1191-1-2	67.58	67.62	+0.06
E 1192-1-1	67.63	67.62	-0.01
<u>U<sub>3</sub>O<sub>8</sub></u>			
E 2782-1-1	85.67	85.62	-0.06
E 2783-1-1	85.67	85.58	-0.11
<u>U Nitrate</u>			
EU 3591-1-1	13.10	13.07	-0.23
EU 3592-1-1	13.69	13.68	-0.07
<u>U-Al</u>			
EU 3659 A	10.82	10.82	0.00
EU 3661 A	10.82	10.81	-0.09
<u>Ore Concentrates</u>			
F 8200-1	81.00	81.02	+0.02
F 8201-2	80.78	80.85	+0.09
<u>Stainless Steel</u>			
E 2440-1-1	0.475	0.478	+0.63
E 2441-1-2	0.398	0.400	+0.50



Too often, they have stuck in the "on" condition, giving a false indication of a fluid flow. Because the flowswitches have been much less reliable than the operations they were intended to monitor, we are modifying this approach. The only other components that have deteriorated and required replacement are the polyurethane, pneumatic-valve tubing and the polycarbonate windows of the reagent containment enclosure.

#### ELECTRONIC SYSTEMS

With few exceptions, there have been no more than the usual electronic

malfunctions and most have resulted in minimum downtime. The most serious problem occurred when the programmable constant-current source, after nearly four years of operation, experienced a power supply failure. This was quickly corrected but we did not discover for some time that the failure also had altered the value of the precision resistor that is used to calibrate the constant current. We also experienced difficulties with several of the commercially built instruments; however, with replacement modules and factory service, these problems were corrected.

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