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SEMI-AUTOMATED URANIUM ANALYSIS BY A MODIFIED DAVIES-GRAY PROCEDURE

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Westinghouse Hanford Company, operator of the Hanford Engineering Development Laboratory (abbreviated HEDL), is prime contractor to the U.S. Department of Energy for construction and operation of the Fast Flux Test Facility. This engineering test reactor is an important test facility for future breeder reactor concepts. Important to the operation of the FFTF is extensive chemical analysis of the fuel material. Over two million of these pellets are required for a single core loading. (The energy equivalent of one of these pellets will satisfy the energy needs of a typical residence for a full year.) Analyses of these materials as well as other nuclear fuel cycle materials requires reliable, rapid analytical methods.

To rapidly and reliably determine uranium in these and other fuel materials we have recently developed a semi-automated implementation of the Davies-Gray uranium titration. As illustrated in Figure 1, the Davies-Gray method is essentially a three step procedure. First uranium is reduced quantitatively from +6 valence to +4 valence by excess of iron (II) in strong phosphoric acid in the absence of nitrite. Prior to the uranium reduction nitrite is destroyed by addition of sulfamic acid. In the second step iron (II) is selectively oxidized to iron (III) by nitric acid in the presence of Mo (VI) catalyst. Finally after dilution to reduce phosphate concentration, the uranium is titrated to U (VI) by standard dichromate. The original sluggish colorimetric endpoint determination used by Davies and Gray is seldom used since New Brunswick Laboratory discovered that addition of vanadium (IV) just prior to titration sufficiently improves reaction rate to allow a potentiometric endpoint determination. One of the advantages of the Davies-Gray uranium titration is that it is quite specific for uranium, most common impurity elements do not interfere with the analysis, and specifically high levels of Pu, Th, and Fe are tolerated.

At HEDL we have further modified this procedure (Figure 2), reduced the sample size yet maintained high precision by weight addition of the majority of titrant, we have automated individual segments of the procedure to increase sample throughput, we've reduce the volume of liquids produced in the operation, a very important consideration since all wastes are radioactive and must be solidified for long term disposal, and we've stabilized reagents to allow methods use on a discontinuous basis with minimal delay.

To assure that the three major steps of titration: Uranium reduction, excess iron oxidation, and uranium titration are quantitative, the reagent volumes, concentrations, and reaction times must be carefully controlled. We have simplified the method by combining reagents, separating and simultaneously performing the pre-titration chemistry and the titration on succesive samples to greatly reduce the time required for analysis, we've reduced liquid volume by a third, and we add the majority of the titrant as a concentrated dichromate weight solution requiring only 1 to 2 ml for the titration. (Figure 3)

The analytical flow is shown conceptually in Figure 4. The sample, aliquoted by weight to a beaker, is placed on a pre-titration station where reagents are automatically added to adjust the uranium valence and destroy excess Fe (II). As the Sample is transferred to the titration station it is both diluted and vanadium is added by simply adding dilute vanadyl sulfate from a wash bottle. Meanwhile, a second sample is placed on the pre-titration station and the automatic sequence is activated. The first sample then has weight titrant added to a point near the potential break. The remaining titrant is added automatically by volume to a dead-stop potentionmetric endpoint. Approximately six minutes are required to complete the automatic pre-titration sequence. This is sufficient time to titrate the preceeding sample, weigh the titrant dropper bottle, remove the titrated sample, and rinse the electrodes and delivery tip. Figure 5 shows an overall view of the apparatus which is contained in a glovebox for radioactivity control. Also shown are the electronic controllers, reagent reservoirs, electronic balance used for weighing, and the calculator used to compute results.

The two portions of the analytical procedure, the pre titration valence adjustment chemistry and the titration, have been separated physically into two stations within one glove box module, (Figure 6). The pre titration station (shown in Figure 7) employs a solid state time-controller which sequentially opens three solenoids allowing gravity feed of reagents from reservoirs outside the glove box and delivery to the sample beaker on a magnetic stirrer in the box. Total flow is controlled by a combination of needle valve setting and solenoid opening interval. The solenoids and needle valves have only "Teflon" surfaces in contact with the reagents. The solution reservoirs (shown in Figure 8) are contained within plastic safety trays and shield on the top of the glove box. The reagents are protected from concentration changes due to air entry by traps which are "fermentation locks" attached to the top of each reservoir. A constant liquid-height system is used for one very viscous reagent to assure constant volume delivery. It is a separatory funnel, closed on top, with an extended "drip tip". As liquid drains out of the lower reservoir air flows up the "drip tip" relieving the vacuum in the separatory funnel keeping the level in the reservoir constant at the tip. Polyethylene tubing is used to carry milder reagents and Teflon tubing is used to carry the more reactive nitric acid - Mo (VI).

The titration station (Figure 9) consists of a magnetic stirrer titration platform, reference and PT-wire electrodes, dichromate delivery tube, and digital volt meter which continuously displays solution potential. The volume titrant delivery is controlled and recorded by a Brinkmann digital burette and associated controllers (Figure 10). The 1 ml micro burette delivery rate is controlled by a differential controller which delivers titrant proportionally to the difference between solution potential and the preset end point. The digital recorder prints an automatically advancing sequence number and the volume of titrant delivered for each titration. The volume titrant is delivered through a 4-m long "Teflon" tube. The valve sequence-timer which controls the pre-titration reagent flow was custom built by Brinkmann Instrument Company.

Precision and accuracy of the method are illustrated in the next two Figures. Calibration with solutions prepared from NBS-SRM 960 uranium metal shows a slight positive bias amounting to +0.03 mg U whose cause is presently undetermined (Figure 11). All results are corrected by subtracting the current value of this correction determined for a running average of ten calibration values. Figure 12 shows typical results obtained for mixed uranium-plutonium oxide fuel pellet lots. Note that these results reflect not only the precision of the analytical method, they also reflect the pellet-to-pellet variation within each fuel lot. The overall pooled relative standard diviation for the analysis of 23 fuel pellet lots is 0.126%

Figure 13 highlights other modifications which have been made to improve the long-term (1-2 week) standby stability of this method. The vanadyl sulfate solution is stored in "Teflon" or glass only. Storage of vanadyl solution in polyethylene or other plastics leads to a titrable cumulative change in the vanadyl solution oxidation state causing a long-term drift in the calibration of the method. Also the oxidizing and reducing reagents are protected from air by an Ar cover-gas which flows continuously over the solutions. The Pt electrode is stored in 4N HNO_3 and refreshed before use by soaking 10 minutes in freshly drawn reducing reagents. Electrode response has been retained for 1 year with no need for flaming or other treatment to restore responsiveness.

By adopting this modified method at HEDL, a single operator can efficiently, rapidly, and reliably determine uranium with a minimum of radioactive waste produced.

Fig. 1

CHEMICAL REACTIONS OF THE DAVIES–GRAY URANIUM ANALYSIS

- NITRITE REMOVAL:

$$NH_2SO_3^{-} + NO_2^{-} \longrightarrow N_2 + H_2O + SO_4^{-2}$$

- URANIUM REDUCTION:

$$UO_2^{+2} + 2\,Fe^{+2} + 4\,H^{+} \xrightarrow{H_3PO_4} U^{+4} + 2\,Fe^{+3} + 2\,H_2O$$

- IRON OXIDATION:

$$Fe^{+2} + HNO_3 + 2\,H^{+} \xrightarrow{Mo^{+6}} Fe^{+3} + HNO_2 + H_2O$$

- URANIUM TITRATION:

$$3\,U^{+4} + Cr_2O_7^{-2} + 2\,H^{+} \longrightarrow 3\,UO_2^{+2} + 2\,Cr^{+3} + H_2O$$

- POTENTIOMETRIC ENDPOINT (NBL MODIFICATION):

$$6\,VO^{+2} + Cr_2O_7^{-2} + 2\,H^{+} \longrightarrow 6\,VO_2^{+} + 2\,Cr^{+3} + H_2O$$

Fig. 2

HEDL MODIFICATIONS TO DAVIES-GRAY PROCEDURE

- SAMPLE SIZE REDUCED TO 10 - 30 mg U
- ANALYTICAL SEGMENTS AUTOMATED TO INCREASE THROUGHPUT
- LIQUID WASTE VOLUME REDUCED THREEFOLD
- WEIGHT ADDITION OF MAJORITY OF TITRANT
- REAGENTS STABILIZED FOR DISCONTINUOUS OPERATIONS

Fig. 3

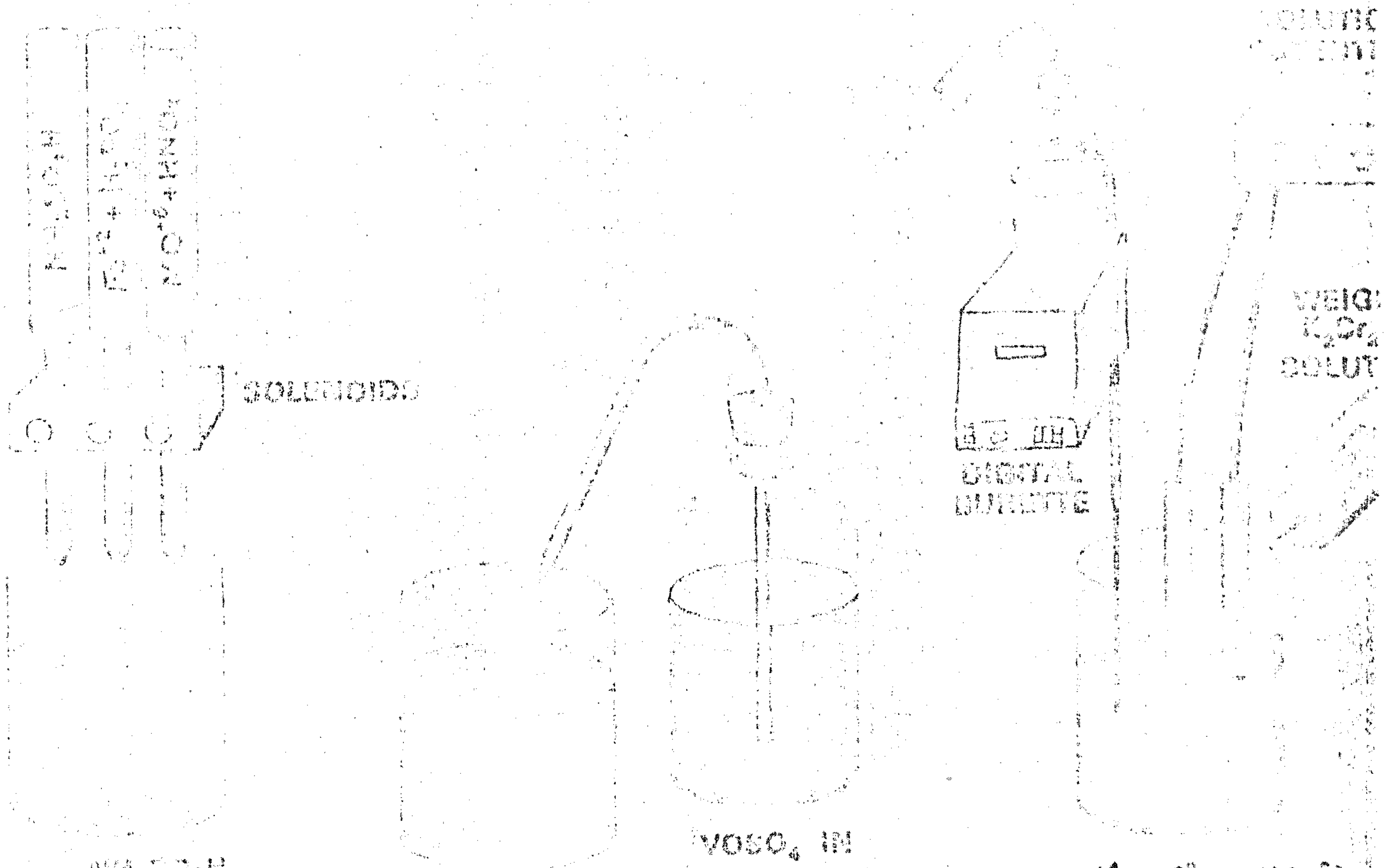
DAVIES–GRAY MODIFICATIONS

ORIGINAL - NBL	HEDL MODIFIED
8 REAGENT ADDITIONS	5 REAGENT ADDITIONS
~50 mℓ TITRANT	~2 mℓ TITRANT
250 mℓ TOTAL VOLUME	80 mℓ TOTAL VOLUME
10 - 15 min / ANALYSIS	6 - 7 min / ANALYSIS

Fig. 4

URANIUM ASSAY BY MODIFIED DAVIES-GRAY TITRATI

PRE-TITRATION STATION **DILUTION** **TITRATION STATION**



$UO_2^{+2} + Fe^{+2} \xrightarrow[H_3PO_4]{NH_2SO_3H} U^{+4}$

(EXCESS $Fe^{+2} + HNO_3 \xrightarrow[Mo^{+6}]{} Fe^{+3}$)

$U^{+4} + Cr^{+6} \longrightarrow UO_2^{2+}$

($VO^{+2} + Cr^{+6} \longrightarrow VO_2^{+}$ ENDP

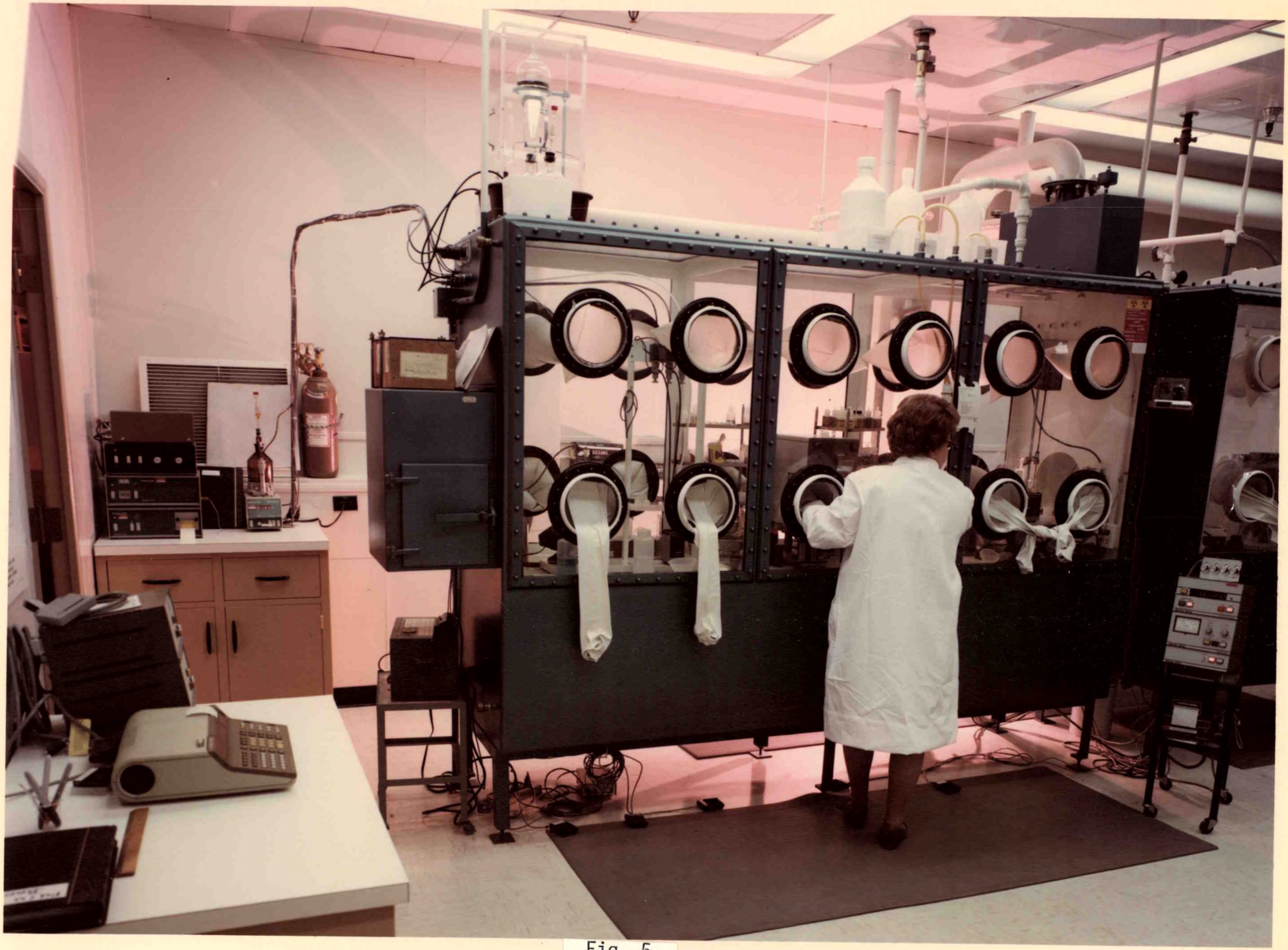


Fig. 5

Fig. 6

Fig. 7

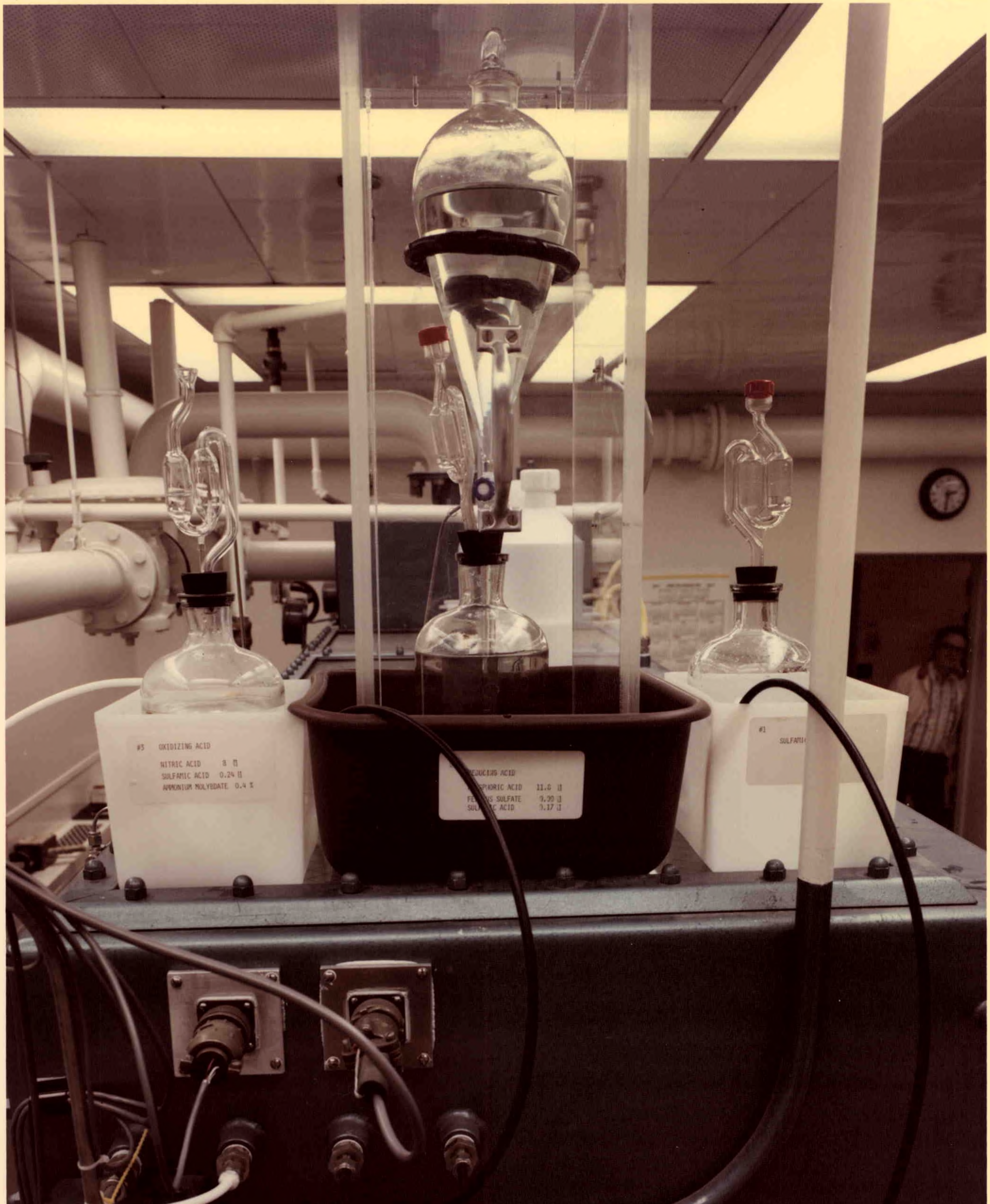
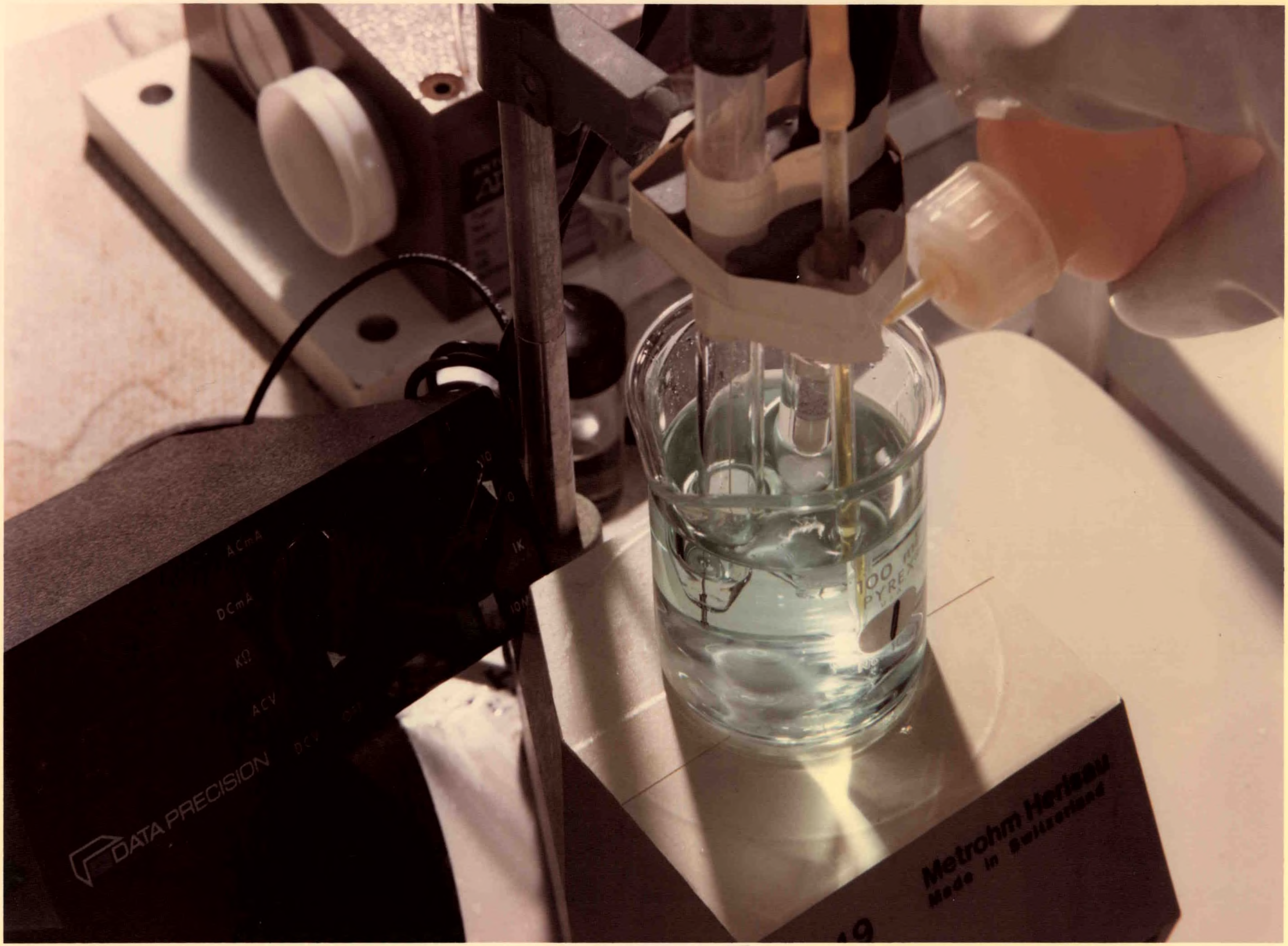

#3 OXIDIZING ACID
NITRIC ACID 8 M
SULFAMIC ACID 0.24 M
AMMONIUM MOLYBDATE 0.4 %
#1

Fig. 8



ACmA
DCmA
KΩ
ACV
DATA PRECISION
1K
10M
100 ml PYREX
Metrohm Herisau
Made in Switzerland

Fig. 9

Titrator E 526
Metrohm Herisau
Brinkmann
Dualprint E533
U titrations
Dosimat E 535
Metrohm Herisau
ARGON
UNION CARBIDE CORPORATION

Fig. 10

Fig. 11

CALIBRATION DATA FOR URANIUM STANDARDS

U ADDED, mg	U FOUND, mg	DIFFERENCE, mg
28.297	28.293	-0.004
27.650	27.690	0.040
32.068	32.081	0.013
19.060	19.060	0.000
30.874	30.896	0.022
36.702	36.723	0.021
18.863	18.899	0.036
18.926	18.989	0.063
20.221	20.272	0.051
16.796	16.819	0.023

AVERAGE DIFFERENCE = 0.026 s_i = 0.021   RSD = 0.12%

Fig. 12

URANIUM CONCENTRATION FOR (U, Pu) O_2 FUEL PELLET ANALYSES

	LOT 1	LOT 2	LOT 3
	66.16	66.14	65.88
	66.05	66.12	65.88
	66.04	66.10	65.95
	66.16	66.26	65.82
	66.09	66.16	65.93
	66.09	66.08	65.51
	65.88	66.03	65.88
	65.94	66.29	65.92
	66.08	66.16	65.91
	66.05	66.06	65.88
$\overline{X}$	66.054	66.140	65.856
s_i	0.088	0.083	0.127
RSD	0.13%	0.12%	0.19%

Fig. 13

IMPROVEMENTS TO REAGENT STABILITY

- VANADYL SULFATE STORED IN GLASS OR TEFLON ONLY
- REDUCING REAGENT AND OXIDIZING ACID UNDER CONTINUOUS ARGON COVER-GAS
- Pt ELECTRODE STORED IN 4 N HNO_3, REFRESHED IN FRESHLY DRAWN REDUCING REAGENT