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# ANALYTICAL CHEMISTRY DIVISION
# QUARTERLY PROGRESS REPORT
## for Period Ending March 26, 1952

M. T. Kelley, Director
C. D. Susano, Associate Director

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| ORNL-867 | Period Ending October 10, 1950 |
| ORNL-955 | Period Ending January 10, 1951 |
| ORNL-1068 | Period Ending March 26, 1951 |
| ORNL-1113 | Period Ending June 26, 1951 |
| ORNL-1129 | Period Ending September 10, 1951 |
| ORNL-1233 | Period Ending December 26, 1951 |

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# ABSTRACT

## ANALYTICAL CHEMISTRY DIVISION
## X-10 SITE

A method for improved damping to eliminate current fluctuations in the polarographic wave is described. The dropping-mercury frequency and its harmonics are selectively eliminated by means of four parallel-T RC filters together with a reduced amount of the usual RC damping. The composite filter is useful for derivative as well as regular polarograms. Two methods of derivative polarography have been studied – the resistance-condenser (RC) and the tachometer methods. Circuit diagrams and illustrative polarograms are shown. Also, a stray pickup filter for the input of the polarograph's preamplifier was developed. Its use results in improved instrument stabilization.

Two methods for the determination of aluminum in "23" process feed solutions have developed. The evaluation of the vacuum-fusion method for oxygen in thorium is discussed. Progress in the fundamental study of the polarography of technetium is reported. A new method is proposed for the colorimetric determination of copper. The factors affecting the reductimetric titration of iron with mercurous nitrate were studied. Certain problems in the assay of plutonium are discussed, for example, the quantitative removal of iron from plutonium solutions, the possible use of Thoron reagent for determining plutonium, and the assay of plutonium on a weight basis.

The decay scheme of $K^{42}$ has been studied, with establishment of the branching ratio and the half-life and verification of earlier reports on the gamma energy. Mercury, thallium, or lead x rays have been found in the decay of $Tl^{204}$, indicating a more complex decay scheme than the accepted simple beta decay. A sodium iodide scintillation spectrometer has been set up and is proving of considerable value in the determination of gamma energies and in the identification of gamma emitters. The technique of using scintillation counting for measurement of gamma activity in process samples appears promising. The present method involves the use of an ionization chamber. Methods of causing the energy response of a scintillation counter to approximate that of an ionization chamber are now under investigation. Further work on radiochemical determination of the HRE flux and on elimination of $Xe^{135}$ is in progress. Solvent extraction of anionic species of uranium, yttrium, zirconium, hafnium, tin, and antimony shows promise in analytical separations.

A proposed price schedule for activation analysis service has been submitted to the ORNL Director and to the AEC as a result of increased interest by industrial organizations in such a service. Anionic solvent

extraction with methyldioctylamine has been employed as a separation technique in the activation analysis study of zirconium and hafnium. New applications of activation analysis are described.

A procedure for the spectrochemical determination of traces of boron in the presence of large amounts of iron is given. Also, improvements in the spectrochemical determination of beryllium in thorium metal and of traces of cesium in $Rb_2CO_3$ and in $H_2O$ are discussed.

Two successful preparations of aluminum phosphide that gave yields of 90 and 91% AlP, were made. A series of lithium halide phosphors was prepared for the Physics Division.

In relation to the analytical chemical control of the HRE, an inventory list of the Princo Densitrol equipment is presented. The evaluation of one of the low-temperature units in a laboratory test loop, the technique of pressurizing the metal plummets with gas, and problems encountered thereby are discussed. The effect of neutron irradiation on neutron-absorbing borosilicate glasses after extended irradiation and annealing periods is described. Absorbance curves for the glasses are shown. Of the inorganic materials tested for corrosion resistance in 0.17 *M* uranyl sulfate solution, fused titania and synthetic sapphire are reported to have high resistance. Corrosion data on samples of these materials are presented.

The results of an electron microscopy study of oxide films formed on Carpenter-443 chromium steel containing approximately 1.25% copper are summarized. Work now in progress on oxide films formed on type-347 stainless steel under a variety of conditions is mentioned along with other work for the HRP. Observations with the electron microscope of the surface of electropolished thorium disclosed a crystalline precipitate in the metal matrix. Copper crystals are now being studied to show structure details beyond the range of the optical microscope, that is, spiral terrace effects, etc. Brief mention is made of a proposed study of radiation damage to thin metal films and of the results of a trial run using sputtered aluminum films. Suggestions are made for a remote-control technique for preparing replicas of irradiated metal surfaces for optical and electron microscopy. Use of the Welch densitometer with a traveling stage to determine the uniformity of radioactive sources is described.

## ANALYTICAL CHEMISTRY DIVISION
## Y-12 SITE

The development of methods for the determination of impurities in lithium hydroxide has been continued. It has been found that traces of chromium and vanadium can be separated from alkali hydroxides and concentrated into a small volume by ion-exchange techniques, thus these impurities are rendered determinable by colorimetric or polarographic methods.

Work has been initiated on the development of a satisfactory procedure for the electrodeposition of bismuth on aluminum. Attempts to deposit a satisfactory bismuth plate of sufficient thickness have proved unsuccessful.

Studies have continued of methods for the determination of both major and trace constituents of ternary and quaternary eutectics composed of the fluorides of alkali metals, beryllium, and uranium. A titrimetric determination of beryllium, preceded by an ion-exchange separation of uranium and beryllium, appears to be an improvement over previous methods. Ion-exchange techniques have also been used in connection with the determination of total alkali metals in the eutectics, and the new procedure is more rapid and accurate than that previously available. An improved method for the determination of fluoride has been developed.

Established methods have been adapted for the determination of silicon, nitrate, chloride, sulfate, and sulfide in the individual components of the fluoride eutectics. In addition, $UF_4$ is being analyzed for $UO_2$ and $UO_2F_2$.

The development of methods for the analysis of $UO_2SO_4$ for trace elements has continued. A colorimetric method for the determination of nitrate, without separation, has proved to be more sensitive than the chromous reduction-Kjeldahl distillation procedure. Methods for the determinations of copper, carbon, and free acid have been adapted for use, and further investigation has been made of the methods previously studied for the determination of zirconium and ruthenium. A direct spectrophotometric method has been adapted for the determination of uranium(IV). An amperometric method of titration of fluoride in trace quantities has been studied.

The uranium determination by direct titration with chromous sulfate has been tested in the presence of iron and molybdenum with favorable results. The complete absorption spectrum of uranyl sulfate in both the visible and ultraviolet regions has been measured.

More than 95% of the analytical service work was carried out in connection with two projects: HRP, and Raw Materials. Trends with respect to sample types for each project are discussed. A total of 24,687 determinations was reported. A tabulation of determinations, indicating the distribution by project, is included.

# PUBLICATIONS

## ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

A. D. Horton, P. F. Thomason, and F. J. Miller, "Spectrophotometric Determination of Inorganic Fluorides," *Anal. Chem.* **24**, 548 (1952).

G. W. Leddicotte and F. L. Moore, "A New Solvent Extraction Method for the Separation of Niobium and Tantalum" (a note to the editor), *J. Am. Chem. Soc.* **74**, 1618 (1952).

## ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

D. L. Manning, W. K. Miller, and R. Rowan, Jr., *Chemical Determination of Impurities in Lithium Hydroxide*, Y-B31-323 (Jan. 17, 1952).

J. C. White, *Effect of pH and Concentration of Ammonium Persulfate on Colorimetric Determination of Nickel by Dimethylglyoxime Method*, Y-B31-324 (Jan. 17, 1952).

C. D. Susano, *Analysis of Zirconium Hydride*, Y-B31-334 (Feb. 27, 1952).

H. P. House and C. D. Susano, *Clarity of Borated Water*, Y-B31-336 (March 5, 1952).

# ANALYTICAL CHEMISTRY DIVISION – X-10 SITE

## RESEARCH AND DEVELOPMENT

### IONIC ANALYSES

P. F. Thomason

**A Method for Improved Damping to Eliminate Current Fluctuations in the Polarographic Wave: Selective Elimination of the Dropping-Mercury Frequency and Its Harmonics by Means of Four Parallel-T RC Filters Together with a Reduced Amount of the Usual RC Damping** (M. T. Kelley, D. J. Fisher). In the course of the developmental work on derivative polarography,(1) it was realized that the presence of the large, fluctuating slopes of each oscillation corresponding to each growth and fall of the drops of the mercury electrode constitutes a severe problem for the derivative circuit. It is the slope of the average currents during the life of consecutive drops that is of interest. Conventional RC damping cannot be employed to completely damp out the drop oscillations without changing the form of the polarographic wave to an intolerable degree. A frequency-selective filter that will remove the drop oscillations from the record with negligible effect on the form of the polarographic wave is needed so that at any time the input to the derivative circuit will be the average current.

For the frequencies corresponding to the fundamental and the several harmonic values of the drop times ordinarily employed in polarography, LC filters are impractical because of the very large inductance, but high-$Q$ inductors, needed. James of the Instrument Development group, Instrument Department, suggested that the parallel-T RC filter might be useful for this purpose. The principles of this filter, or null network, have been described.(2,3,4) Such a filter would be useful in regular polarography also, since it would permit simplification of the measurement of wave height through a simple extension of linear portions of the recorded wave and would enable nearly all of a given polarograph current range to be utilized by the average-current wave height. In the case of the RC-derivative method, such a filter should allow the use of lower RC products that give faster response to input changes and less prolonged peaks in the normal process of decay of the RC-derivative circuit over several RC time intervals. In the case of the tachometer-derivative method, the filter would enable the use of less RC damping of the tachometer output voltage, which would also result in a correspondingly faster response time. In addition, the amount of RC damping required in the polarograph itself would be greatly reduced.

A single-section parallel-T RC filter is shown in Fig. 1. The filter completely rejects a frequency, $f$, given by $f = 1/2\pi RC$, where the symbols are the same as those defined by Fig. 1. The network should operate from a source impedance that is small compared with R and into a load that is large compared with R.

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(1) D. J. Fisher and M. T. Kelley, "Differential Polarography," *Analytical Chemistry Division Quarterly Progress Report for Period Ending December 26, 1951*, ORNL-1233, p. 1-4.

(2) L. Stanton, "Theory and Application of Parallel-T Resistance-Capacitance Frequency-Selective Networks," *Proc. Inst. Radio Engrs. and Waves and Electrons* **34**, 447 (1946).

(3) A. Wolf, "Note on a Parallel-T Resistance-Capacitance Network," *op. cit.*, 659.

(4) F. E. Terman, *Radio Engineers' Handbook*, p. 918 and 945, McGraw-Hill, New York, 1943.

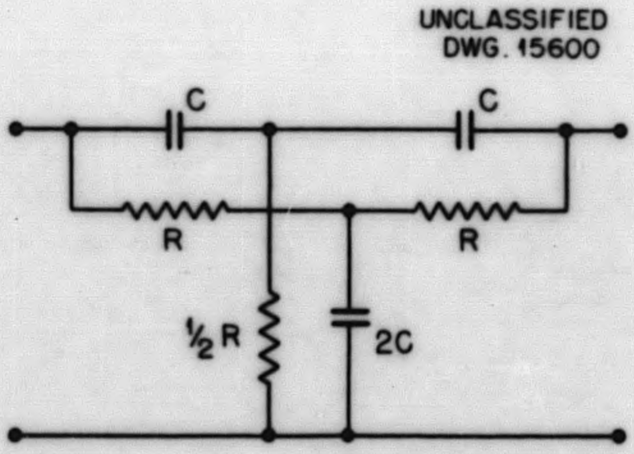

**Fig. 1. Circuit Diagram of a Single-section Parallel-T RC Filter.**

A practical composite filter for polarographic use consists of an RC filter and four parallel-T RC filters that reject, in order, the tenth, fourth, and second harmonics, and the fundamental frequency of the D.M.E. If the design null frequency of the fourth parallel-T RC filter corresponds to the lowest drop time used, the filter will be equally effective for faster dropping rates as well, because the composite filter is a low-pass device. From Fig. 2, prepared by Smith of the Instrument Department, it is seen that the composite filter has a much sharper cutoff than an RC damping circuit (RC filter) alone; that is, the combination becomes frequency-selective and rejects the dropping-mercury frequency and its harmonics but passes the polarographic wave frequency virtually unattenuated. Thus it is not necessary to provide ganged, variable resistors to tune the filter; fixed resistors and condensers are satisfactory, and the only control needed is a switch to throw the filter in and out of the polarograph circuit. Although the filter was developed for use in the ORNL polarographs, models Q-1160 and Q-983, it can be used in any polarograph. Specific polarograph impedances must be considered when selecting filter component values.

The filter removes over 99% of the otherwise-recorded excursions caused by the rise and fall of each drop of the D.M.E. The measured wave height is not identical with that obtained without the filter. However, without the filter, mid-points of recorded oscillations are being arbitrarily taken as indicative of average current.⁽⁵⁾ The recorded half-wave potential is retarded about 20 mv, but this known retardation is not a disadvantage since it can be taken into consideration.

The circuit of the practical quadruple parallel-T RC filter is shown within the dotted line of Fig. 3. The design null frequency is 0.2 cps. The tenth harmonic rejection filter section, in addition to the other three sections, is found to be useful. If the RC-derivative circuit is to be used, it is switched in at points *A* and *B*. The output of this filter may indicate more nearly a true average of the current flowing at any time than do the mid-points of recorded oscillations without the filter.

The forms of the polarographic waves for a solution of 50 $\mu$g of uranium(VI) per milliliter in 0.1 *M* $HNO_3$ that were recorded with and without the quadruple parallel-T RC filter are shown in Fig. 4 *a* and *b*. A plot of wave height vs. uranium(VI) concentration calculated from polarograms obtained with the composite filter is shown in Fig. 5. The measured wave heights are as reproducible as those obtained without the parallel-T RC filter. For example, on the duplicate polarograms reported in Fig. 5, wave heights of 69.8 and of 69.0 were obtained.

It is planned to have a number of the quadruple parallel-T RC filters constructed for use with ORNL polarographs that are in current operation.

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(5) I. M. Kolthoff and J. J. Lingane, *Polarography*, p. 39, Interscience, New York, rev. 1946.

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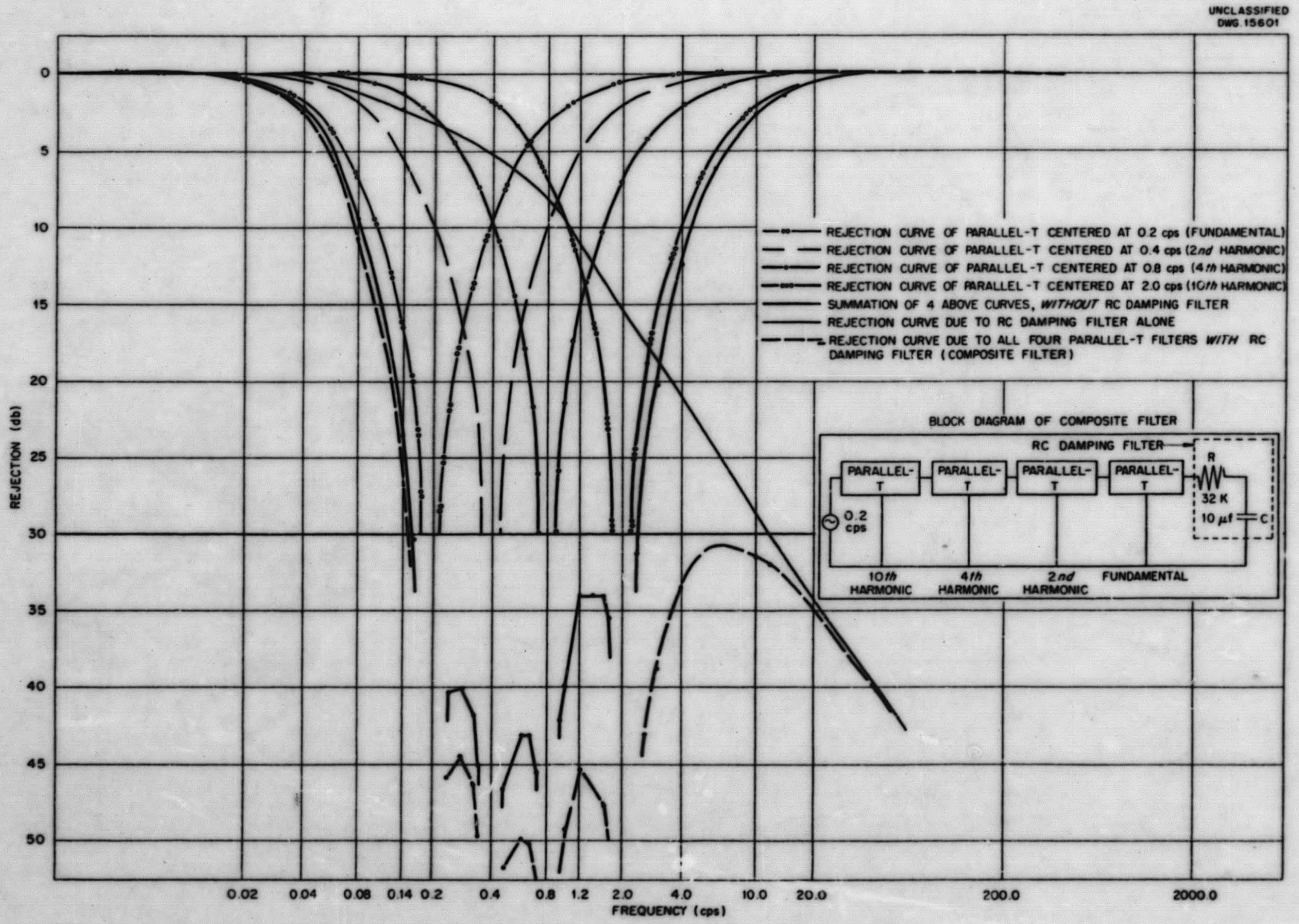

Fig. 2. Rejection Curves for Composite Filter.

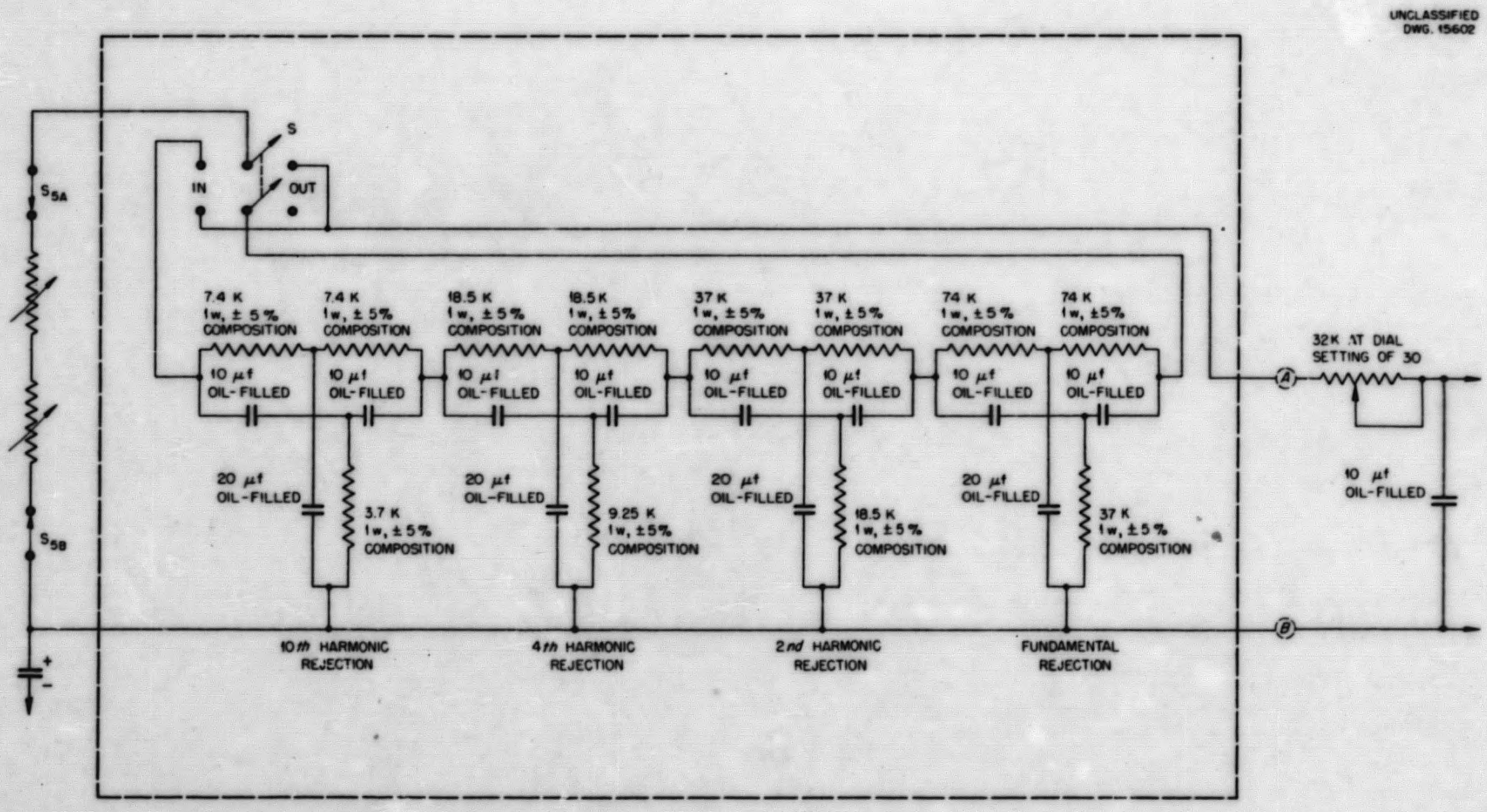

**Fig. 3. Circuit Diagram of Quadruple Parallel-T RC Filter.** Circuit outside of dotted line is within polarograph Model Q-1160.

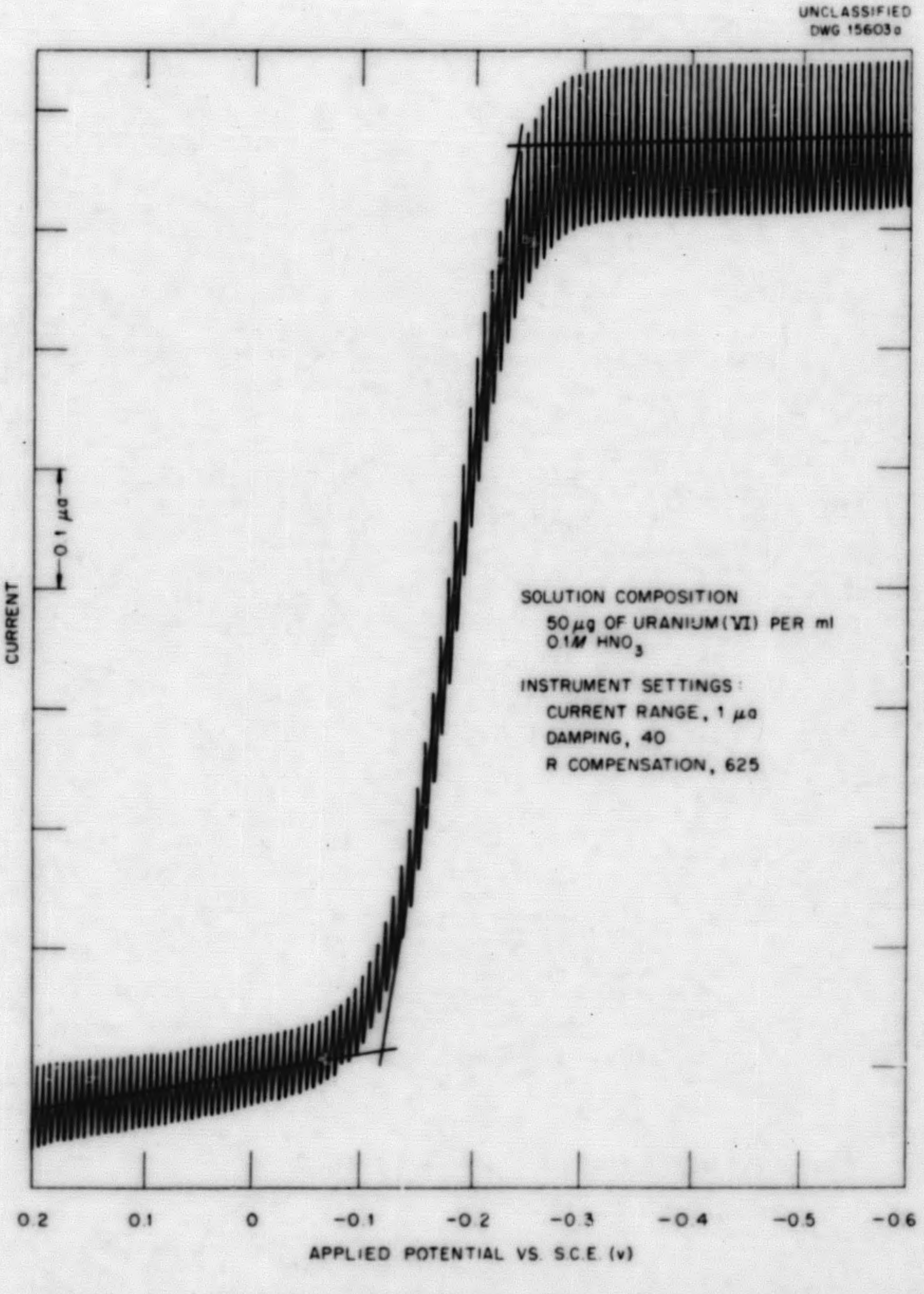

Fig. 4a. Uranium(VI) Polarogram Obtained Without Use of the Quadruple Parallel-T RC Filter.

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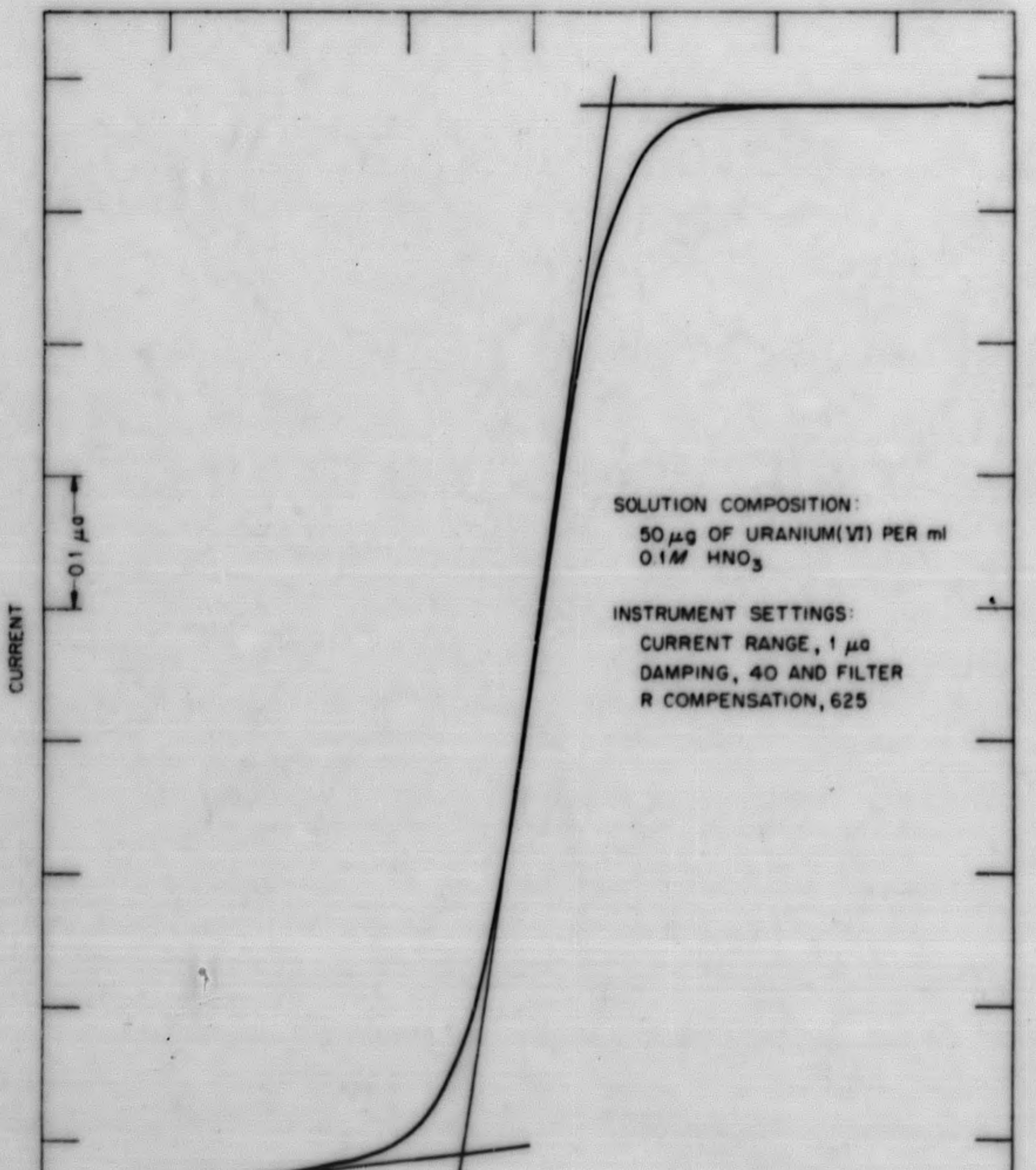

**Fig. 4*b*. Uranium(VI) Polarogram Obtained with Use of the Quadruple Parallel-T RC Filter.**

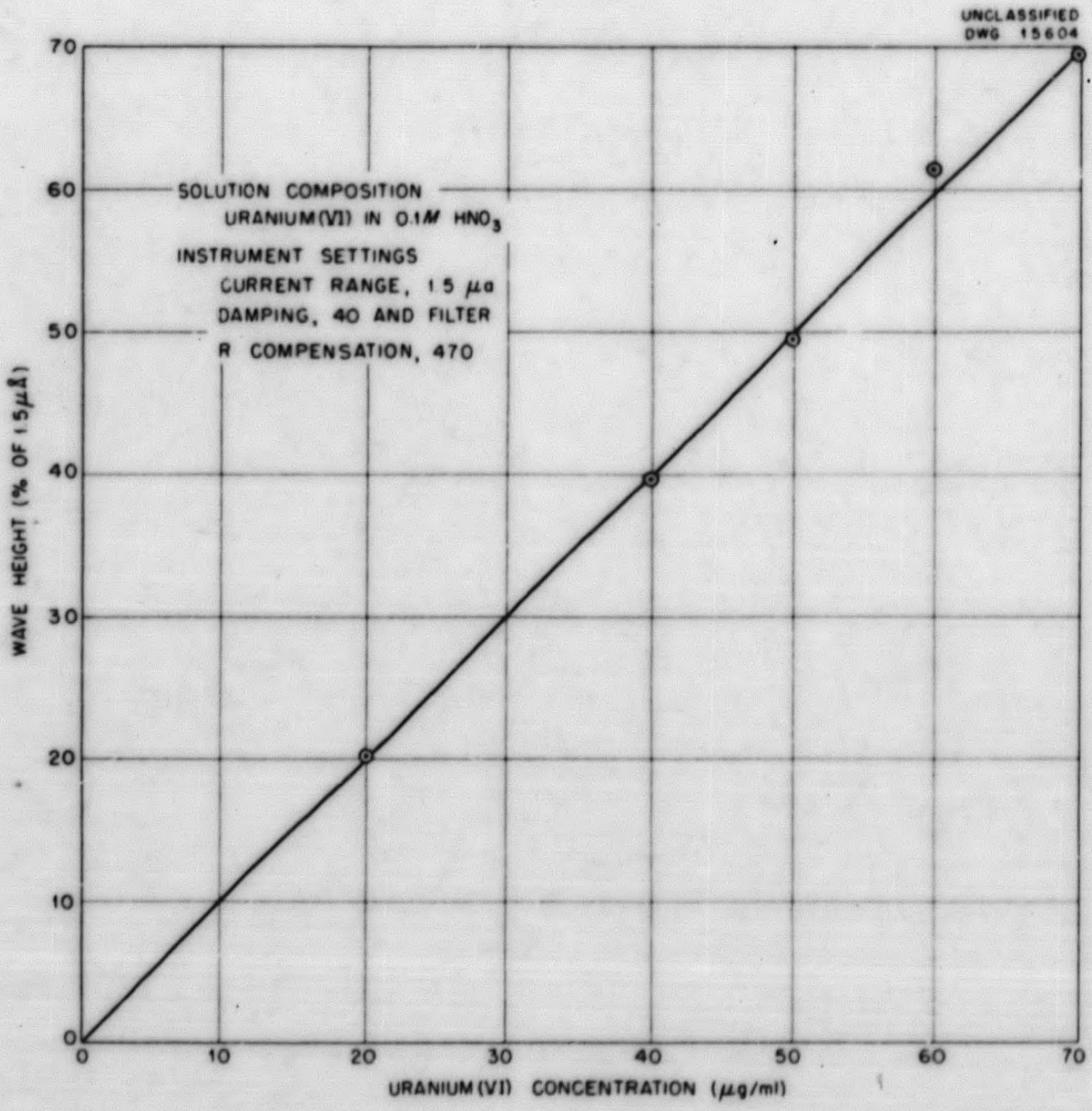

**Fig. 5. Plot of Wave Height vs. Uranium(VI) Concentration from Polarograms Made with Quadruple Parallel-T RC Filter.**

**Derivative Polarography: Tachometer Method** (M. T. Kelley, D. J. Fisher). In a previous quarterly report[1] it was stated that the tachometer derivative polarography method would be investigated. In this method, a tachometer (d-c voltage generator) is mechanically coupled to the shaft of the Brown balance motor of the polarograph recorder. The tachometer rotation rate, and hence its voltage output, is directly related to the balance motor rotation rate. The output voltage of the tachometer is therefore a direct measure of the slope at each point on the current vs. applied potential curve being recorded by the polarograph. A Brown potentiometer, external to the polarograph, is used to record the voltage output of the tachometer. Since the chart drive of this external recorder is operated by a synchronous motor, as is the applied potential drive, the tachometer output voltage, which is directly proportional to the slope of the polarographic wave at each point, is plotted against applied potential. This is the relationship demanded for derivative polarography. Two polarograms are obtained simultaneously, that is, a regular wave and a derivative peak, each on a separate potentiometer chart. The general method of obtaining a derivative by use of a tachometer was pointed out by Manning of the Instrument Development group, Instrument Department.

In the derivative device being developed for use with the ORNL polarograph, model Q-1160, the tachometer is coupled mechanically to the balance motor of the polarograph. The mechanical coupling device, which was designed and built by Tallackson of the Mechanical Development group, Instrument Department, contains a spring-loaded split gear coupled directly to the shaft of the balance motor. This directly coupled gear drives a smaller gear pinned to the tachometer shaft so that the tachometer rotation rate is related to the balance motor rotation rate by a constant factor that is greater than unity. The potentiometer records the slope at each point on the polarographic wave vs. applied potential. It is desirable to use a high-speed balance motor in the potentiometer, so that peak height and peak width as recorded will not be affected by the rate of response of the balance motor.

The circuit used to record the output voltage of the tachometer is shown in Fig. 6, and a parts list is presented in the following:

Battery – dry cell, 1.5 v
Tachometer – J36, d-c voltage generator, Eastern Air Devices, Inc.
Potentiometer – external Brown Electronik, low-impedance input, 10-mv range, 4.5-sec balance motor
Switch, $S_1$ – single-pole, triple-position, nonshorting, lever-type, damping control switch
Switch, $S_2$ – SPST momentary-contact, push-button type, damping discharge switch
Condenser, $C_1$ – 400 μf, 6 v, nonpolarized
Condenser, $C_2$ – 1000 μf, 25 WVDC, Mallory WP059. (It is suggested that two, equal, electrolytic condensers connected back-to-back be used for $C_2$ and for $C_3$.)
Condenser, $C_3$ – 4000 μf, 25 WVDC, Mallory HC2540
Resistor, $R_1$ – 30 K, 1 w, composition
Resistor, $R_2$ – 27 K, 1 w, composition
Potentiometer, $R_3$ – sensitivity control, 1K
Resistor, $R_4$ – 18 K, 1 w, composition
Potentiometer, $R_5$ – 100 ohms, 4 w, WW zero-set control.

The output of the tachometer is RC-damped by $R_1$ with $C_1$, $C_2$, or $C_3$. Rapid excursions of the tachometer resulting from adjustments of the polarograph preliminary to a run can charge the RC damping circuit well away from the point corresponding to the initial slope of the polarographic wave. After adjustments of the polarograph are made and prior to the applied-voltage scan, immediate restoration of the initial level of RC can conveniently be achieved by momentarily closing $SW_2$. Should excess damping be used, the damped output will lag behind the tachometer output voltage. Usually a time constant of 12 sec is suitable for damping. The damped tachometer output is applied across the potential divider, $R_2$ and $R_3$. It is convenient to vary the zero position of the potentiometer by using the battery and $R_4$ and $R_5$, which provide a stable, variable, d-c voltage. For ready comparison of the two records, the two chart drives are started so that

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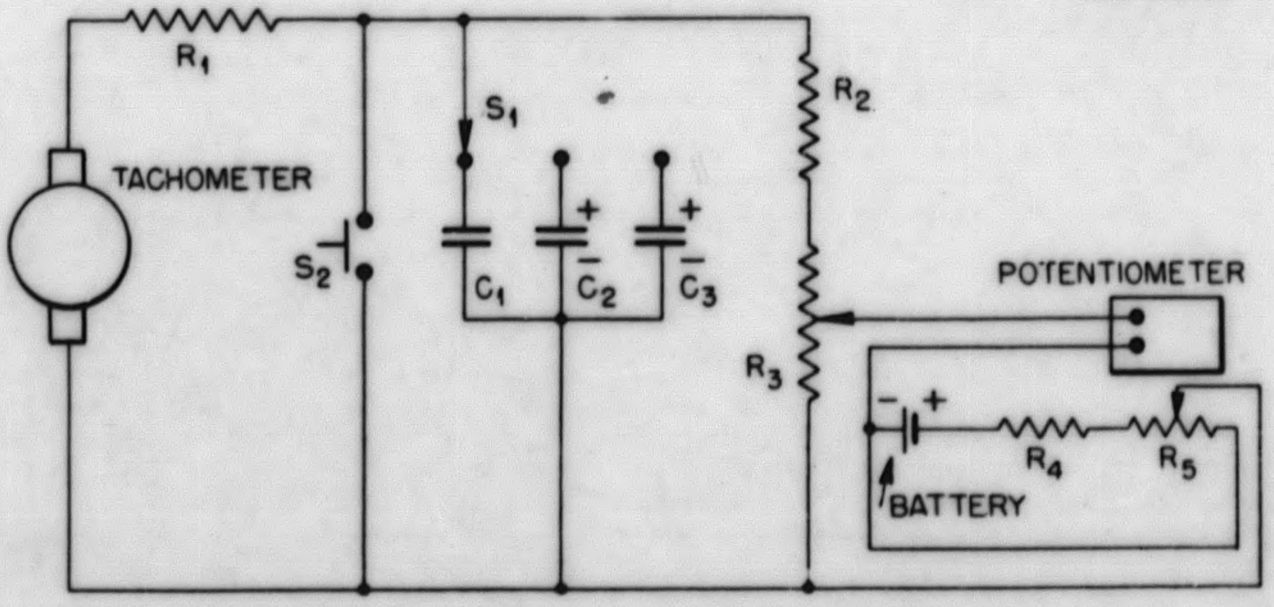

Fig. 6. Circuit Used in Tachometer Method of Derivative Polarography.

both records begin at a heavy, printed, ink line when the polarograph scan switch is thrown to the *on* position.

In typical tachometer derivative polarograms, when the slope of the polarographic wave is constant the instantaneous, damped, tachometer output is not constant but varies above and below an average value that is related directly to the slope. This fluctuation is caused in part by the normal behavior of the balance motor, which hunts to an extent that its pen record varies only negligibly but enough that the tachometer output fluctuates about an average value. A reduction of this variation will be attempted. When the slope of the polarographic wave goes through a maximum at the inflection point, which is at the half-wave potential,(1) the potentiometer records a peak. The peak is about 20 mv beyond the half-wave potential. For waves of reversible reductions, such as that of uranium(VI) at -0.18 v (S.C.E.), the peak as recorded is very nearly symmetrical. Also, the relationship between peak height and concentration is found to be linear, as predicted(1) from the Ilkovic equation. When the initial and final slopes of the polarographic wave are equal, the derivative record has a common base line. It appears that the peak height obtained by this derivative method for 50 μg of uranium(VI) per milliliter in 0.1 *M* $HNO_3$ is not appreciably altered by the presence of 3.5 μg of copper(II) per milliliter. Specific experimental data are not included with this report because development of the method is not considered to be completed.

The observed facts suggest that the recorded peak may be a close approximation to a plot of the slope of the wave vs. the applied potential. The tachometer derivative peak for uranium(VI) is more nearly symmetrical than the presently obtained RC-derivative peak for uranium(VI), and it also occurs at more nearly the true half-wave potential. From data taken with the methods in their present state of development, it seems that the tachometer-derivative method can quantitatively separate waves of closer half-wave potentials than can the RC-derivative method.

**Derivative Polarography: RC Method** (M. T. Kelley, D. J. Fisher). Further development of the RC-method of derivative polarography, described previously,[1] has been carried out. The selective elimination of the D.M.E. frequency and its harmonics by means of a quadruple parallel-T RC filter described in this report has resulted in improved RC-method derivative polarograms. The existence of a damping problem in derivative polarography has been pointed out elsewhere.[6,7] According to T. S. Lee,[7] "Derivative curves were proposed by O. Müller and J. Heyrovsky for the dropping-mercury electrode but have been found to be impractical, chiefly because of the fluctuations in current caused by the growth and fall of the drop." Therefore, the composite filter described above is useful for derivative as well as for regular polarograms. When the filter is used for regular polarograms it is necessary to switch the derivative resistor out of the circuit. The present developmental circuit for RC-derivative polarography is shown in Fig. 7. The switch completely removes the RC-derivative circuit from the ORNL polarograph, model Q-1160, when in the *out* position.

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[6] J. J. Lingane and R. Williams, "Derivative Polarography. I. Characteristics of the Leveque-Roth Circuit," *J. Am. Chem. Soc.* 74, 790 (1952).

[7] T. S. Lee, University of Chicago, private communication to V. F. Raaen, February 25, 1952.

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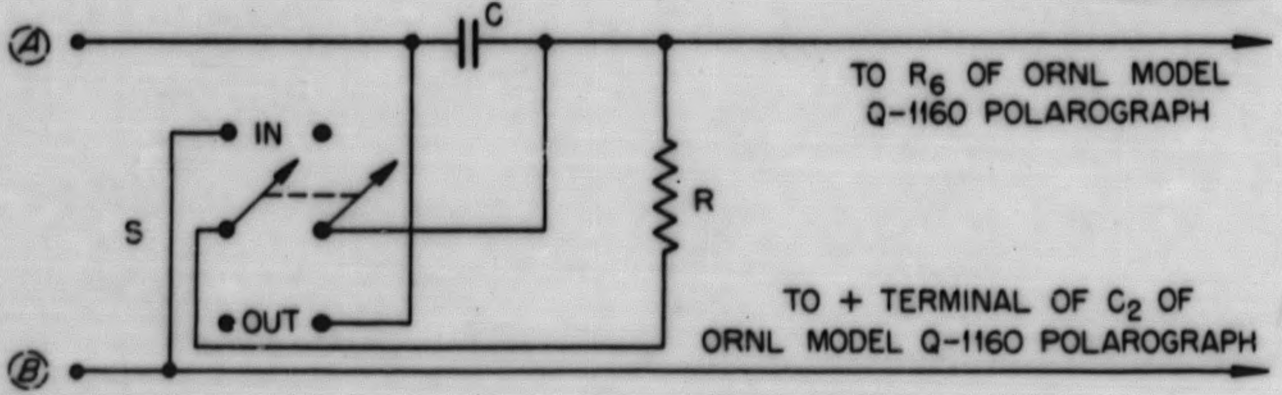

POINTS *A* AND *B* ARE IDENTIFIED IN FIG. 3 THIS REPORT
S SWITCH, DPDT TOGGLE SWITCH
FOR 0- TO 5-mv-RANGE BROWN RECORDER IN ORNL POLAROGRAPH
C = OIL-FILLED CONDENSER, 20 $\mu$f
R = WIRE-WOUND RESISTOR, 1 megohm, 1%
FOR 0- TO 1-mv-RANGE BROWN RECORDER IN ORNL POLAROGRAPH
C = OIL-FILLED CONDENSER, 10 $\mu$f
R = WIRE-WOUND RESISTOR, 0.2 megohm, 1%

Fig. 7. Circuit Used in RC Method of Derivative Polarography.

The RC-method derivative polarograms presently obtained are reproducible. The average of seven uranium(VI) peak heights obtained by analysis of a solution of 50 $\mu g$ of uranium(VI) per milliliter in 0.1 *M* $HNO_3$ is 73.8 chart divisions (0.0148 $\mu a$) with a maximum deviation of 1.5 chart divisions when using a Brown recorder of 0- to 1-mv range. The form of a typical RC-method derivative polarogram made with the use of the quadruple parallel-T RC filter is shown in Fig. 8.

It appears that solutions of up to 1 $\mu g$ of copper(II) per milliliter will not enhance the peak height of the RC-method derivative polarograms obtained with the present circuit for solutions of 50 $\mu g$ of uranium(VI) per milliliter in 0.1 *M* $HNO_3$.

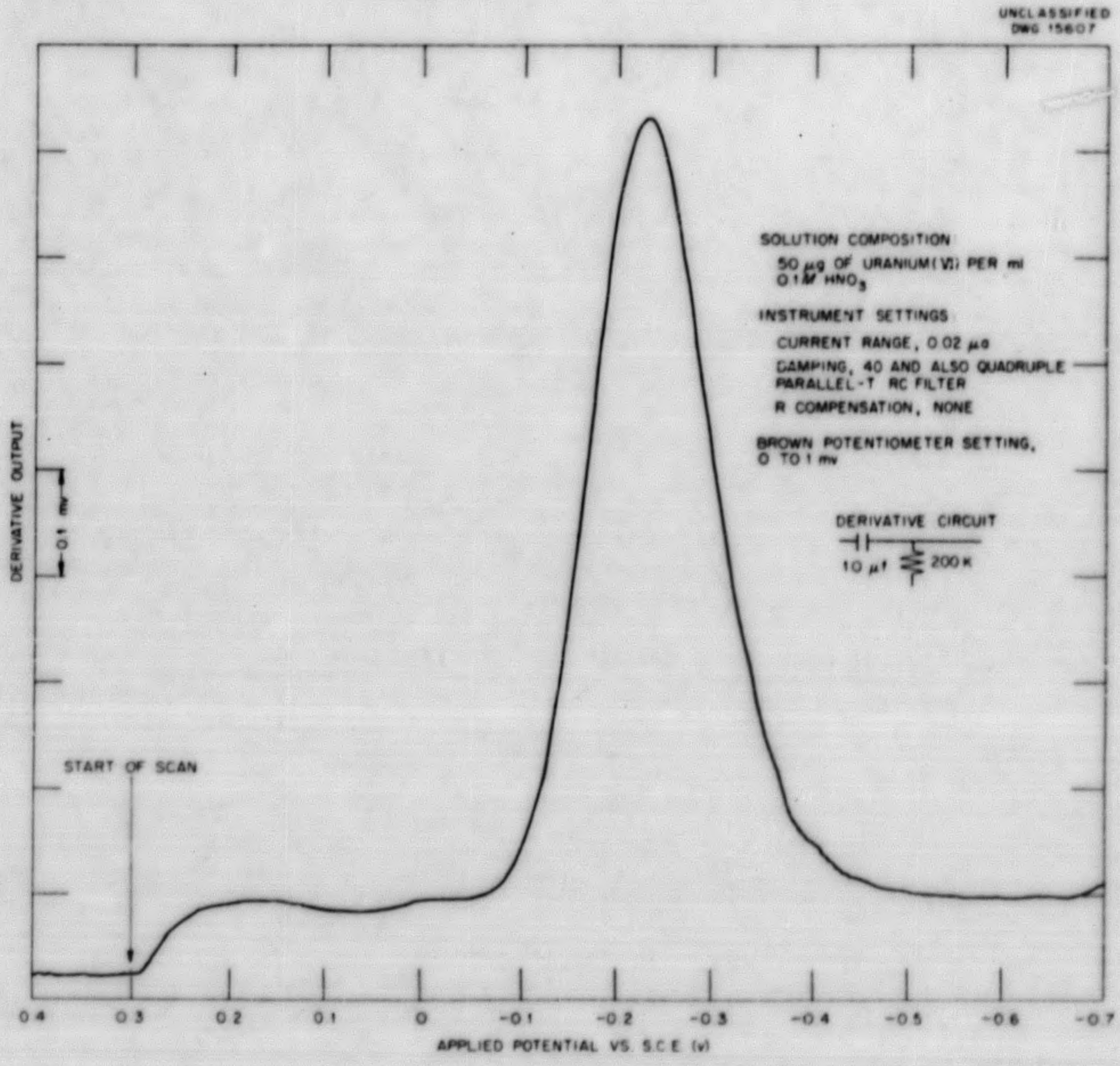

Fig. 8. RC-Method Derivative Polarogram of Uranium(VI) Made with the Use of the Quadruple Parallel-T RC Filter.

Methods for using smaller time-constant RC-derivative circuits are to be investigated. It is believed that smaller time-constants will result in faster response of the circuit to the incoming signal so that there may be improved resolution of peaks occurring at closely adjacent half-wave potentials, such as those of uranium and copper.

**Stray Pickup Filter for Input of ORNL Polarograph Preamplifier** (M. T. Kelley, D. J. Fisher). It is possible for random 60 and 120 cps pickup on the polarographic cell assembly to overload at times the preamplifier that was developed for the ORNL polarograph, model Q-1160. Shown in Fig. 9 is the circuit of a double-section, parallel-T, RC filter, tuned to reject 60 and 120 cps, that has been installed at the input terminals of the preamplifier of an ORNL polarograph. The following is a parts list of the circuit:

Resistor, $R_1$ - 25 K, 1 w, composition
Potentiometer, $R_2$, $R_5$ - 70 K
Potentiometer, $R_3$, $R_6$ - 50 K
Resistor, $R_4$ - 51 K, 1 w, composition
Condenser, $C_1$, $C_2$, $C_4$, $C_5$ - 0.05 $\mu$f, tubular
Condenser, $C_3$, $C_6$ - 0.1 $\mu$f, tubular

The filter is tuned, prior to installation, by an audio-oscillator and an oscilloscope. The first rejection section is tuned to 120 cps by means of $R_2$ and to maximum rejection by $R_3$. The second rejection section is tuned to 60 cps by adjustment of $R_5$ and to maximum rejection by $R_6$. Random disturbances of the recorded wave, particularly with a 0- to 1-mv-range Brown potentiometer, seem to be less frequent with the filter than without it.

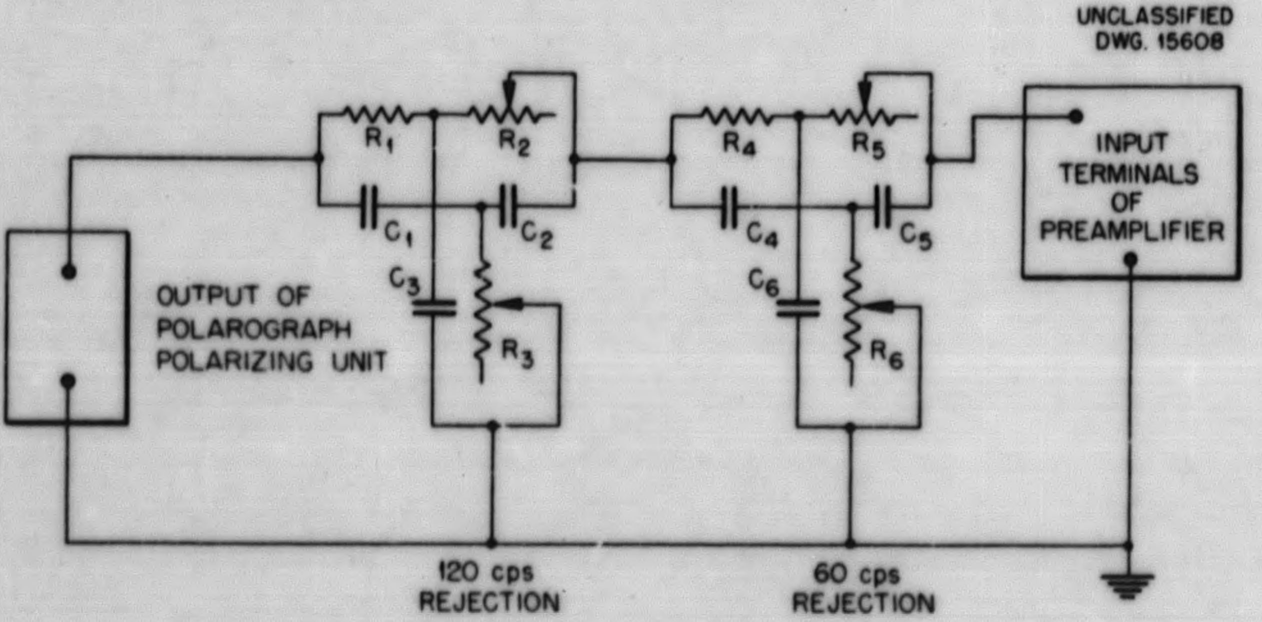

Fig. 9. Circuit Diagram of Stray Pickup Filter for Input of ORNL Polarograph Preamplifier.

**Polarography of Technetium** (H. H. Miller). Work has been continued on the polarographic behavior of technetium.(8) Experiments by Lingane(9) on the polarography of rhenium are being repeated for the purpose of comparing the data. The work has not been completed and will be reported later.

*Supporting Electrolyte of 4M $H_2SO_4$.* A solution of $1.61 \times 10^{-4}$ *M* $NH_4TcO_4$ in 4 *M* $H_2SO_4$ was polarographed over the potential ranges of 0.0 to −1.2 v and −0.8 to −1.6 v vs. S.C.E. The polarogram is shown in Fig. 10. No well-defined wave was observed; however,

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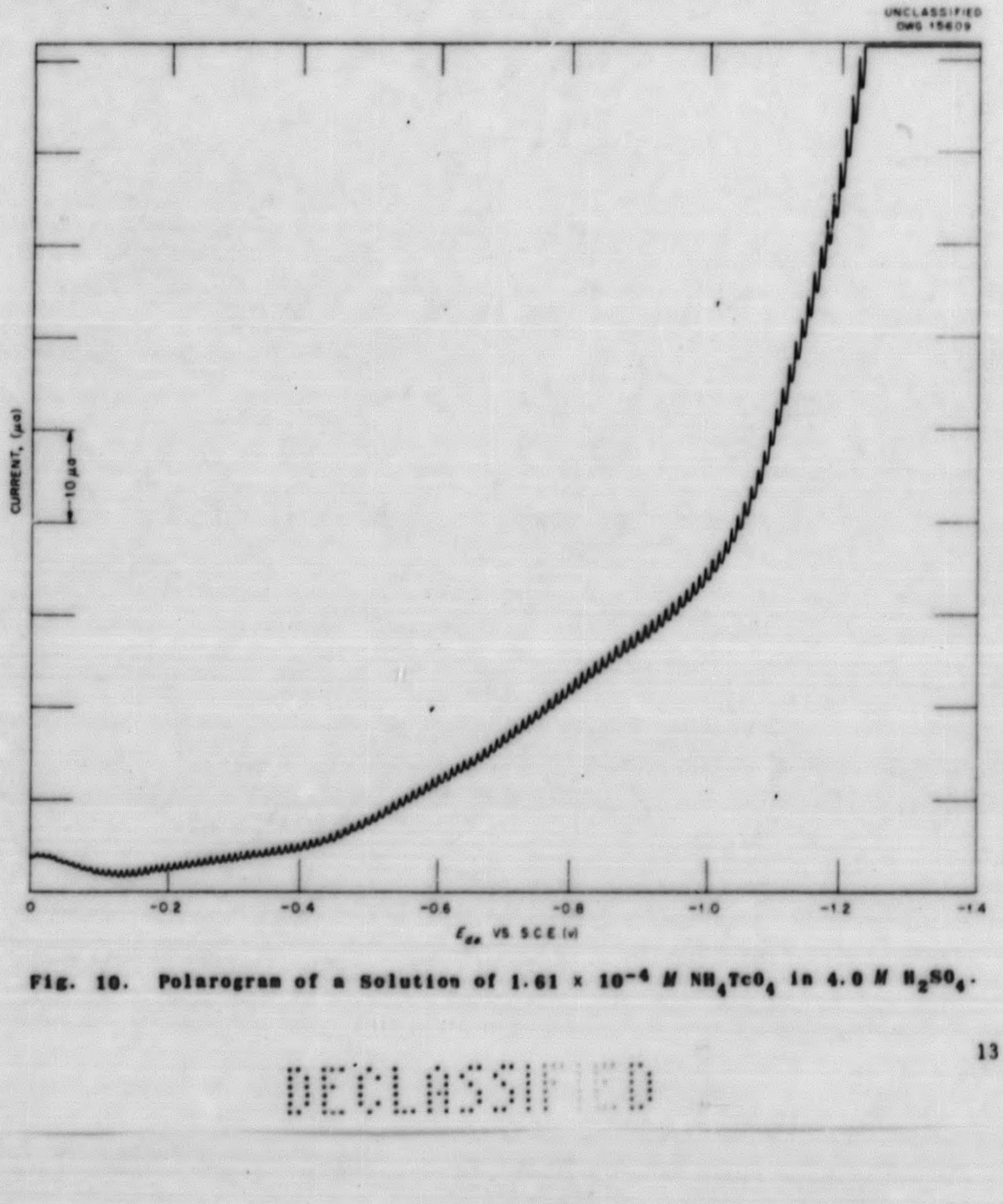

Fig. 10. Polarogram of a Solution of $1.61 \times 10^{-4}$ *M* $NH_4TcO_4$ in 4.0 *M* $H_2SO_4$.

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(8) H. H. Miller, "Polarography of Technetium," *Analytical Chemistry Division Quarterly Progress Report for Period Ending September 10, 1951*, ORNL-1129, p. 11.

(9) J. J. Lingane, "Polarographic Investigation of Rhenium Compounds. I. Reduction of Perrhenate Ion at the Dropping Mercury Electrode," *J. Am. Chem. Soc.* **64**, 1001-1007 (1942).

as the potential became more negative, the current gradually increased until the hydrogen wave was reached. The slope of the curve indicates that the pertechnetate ion is being reduced just prior to the hydrogen wave. The hydrogen wave prevents the pertechnetate wave from attaining a limiting diffusion current.

*Concentration of Pertechnetate in 0.1 M KCl vs. Diffusion Current.* To establish whether a linear relationship exists between concentration of pertechnetate and the diffusion current, polarograms were obtained by using 0.1 *M* KCl, pH approximately 10, as the supporting electrolyte. The concentration range was from $3.2 \times 10^{-5}$ to $3.2 \times 10^{-4}$ *M* $NH_4TcO_4$ [3.2 μg of technetium(VII) per milliliter of 0.1 *M* KCl]. Figure 11, which is a plot of technetium(VII) concentration vs. diffusion current, shows a straight-line relationship which indicates that this medium could be used for quantitative analytical determinations of technetium. It is interesting to note that 3 μg of technetium(VII) per milliliter of 0.1 *M* KCl gives a diffusion current of about 0.7 μa, which is a large, measurable wave on the ORNL high-sensitivity polarograph, model Q-1160. Therefore the limit of detection could be extended to a concentration much lower than 3 μg of technetium(VII) per milliliter of 0.1 *M* KCl.

A differential polarogram (RC-differential circuit(1)), run by D. J. Fisher, of a solution containing 31.9 μg of technetium(VII) per milliliter of 0.1 *M* KCl, pH approximately 10, is shown in Fig. 12. On comparison with a differential uranium polarogram, the symmetrical polarogram indicates that the technetium(VII) reduction may be reversible because of the similarity to the wave for uranium(VI) ⟶ uranium(V).

**Determination of Uranium in Plutonium Solutions.** Nontechnical personnel of the division were trained in the use of the polarographic method(10) for determining uranium in plutonium solutions.

**Indirect Determination of Aluminum in "23" Process Feed Solutions by Use of a Cation-exchange Resin** (P. F. Thomason). As an alternative to the volumetric method described by J. M. Chilton (in the following section) for determining aluminum in the presence of thorium, a fast method for the "shotgun" estimation of aluminum in "23" feed solutions has been developed. A 100-μl aliquot of "23" process feed solution estimated to be 1.5 *M* in $Th(NO_3)_4$, 1.0 *N* in $HNO_3$, and 0.5 *M* in $Al(NO_3)_3$ was passed through the small Dowex-50 resin column shown in Fig. 13, and the liberated $HNO_3$ was titrated with standard 0.1 *N* NaOH to the methyl-red end point. The acid liberated by $Th(NO_3)_4$ plus the original free $HNO_3$ obtained by previous analyses for thorium and free $HNO_3$ is subtracted from the total liberated acid, and the difference is equivalent to the aluminum adsorbed on the resin. Since this indirect method for aluminum depends on accurate thorium and $HNO_3$ analyses, the accuracy is only ±5 to 7%, which seems to be adequate for this purpose. The method has the added advantage of removing the fission products from the feed sample and thus allowing easy manipulation in the determination of the total liberated acid. The amount of acid liberated by the adsorption of the fission products can be ignored since the fission products are present in very small amounts.

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(10) H. H. Miller, "Polarographic Determination of Uranium in Plutonium Solutions," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950, Part II. Analytical Chemistry*, ORNL-686, p. 21-23.

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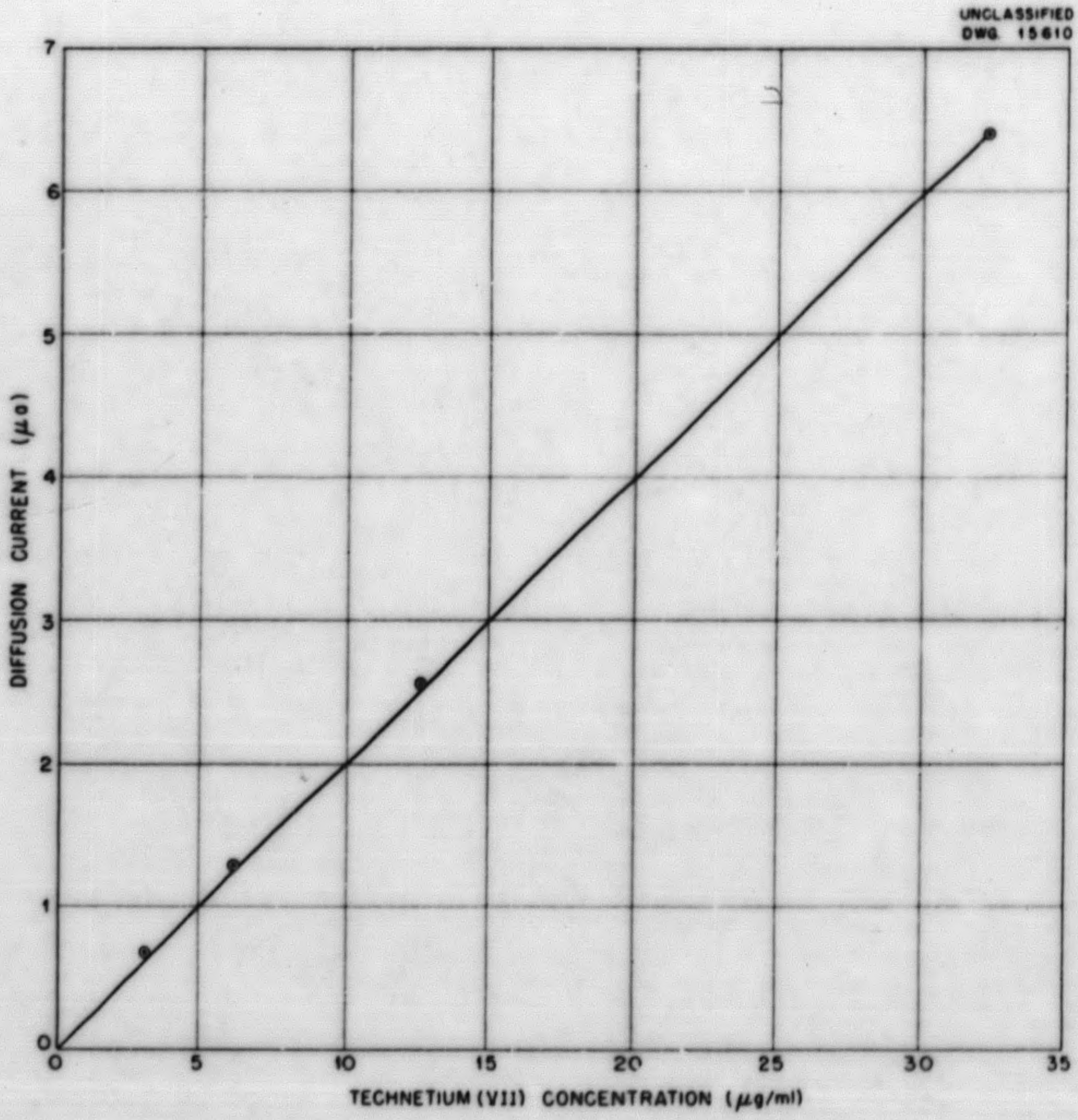

**Fig. 11. Plot of Technetium(VII) Concentration vs. Diffusion Current.** Solutions of $NH_4TcO_4$ in 0.1 *M* KCl, pH approximately 10.

The method was tested in the following manner. A standard solution of $Th(NO_3)_4$ was prepared from reagent-grade $Th(NO_3)_4$ and standardized gravimetrically. A solution of $Al(NO_3)_3$ was also prepared in a similar manner. The free acid content of the separate solutions was determined by the usual oxalate method,(11)

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(11) M. T. Kelley, P. F. Thomason, L. T. Corbin, S. A. Reynolds, C. L. Burros, and E. J. Frederick, "Free Acid in Radioactive UNH Solutions (Method No. 3)," *Manual of Analytical Procedures for the* $U^{235}$ *Recovery Process*, ORNL-983 (Aug. 20, 1951).

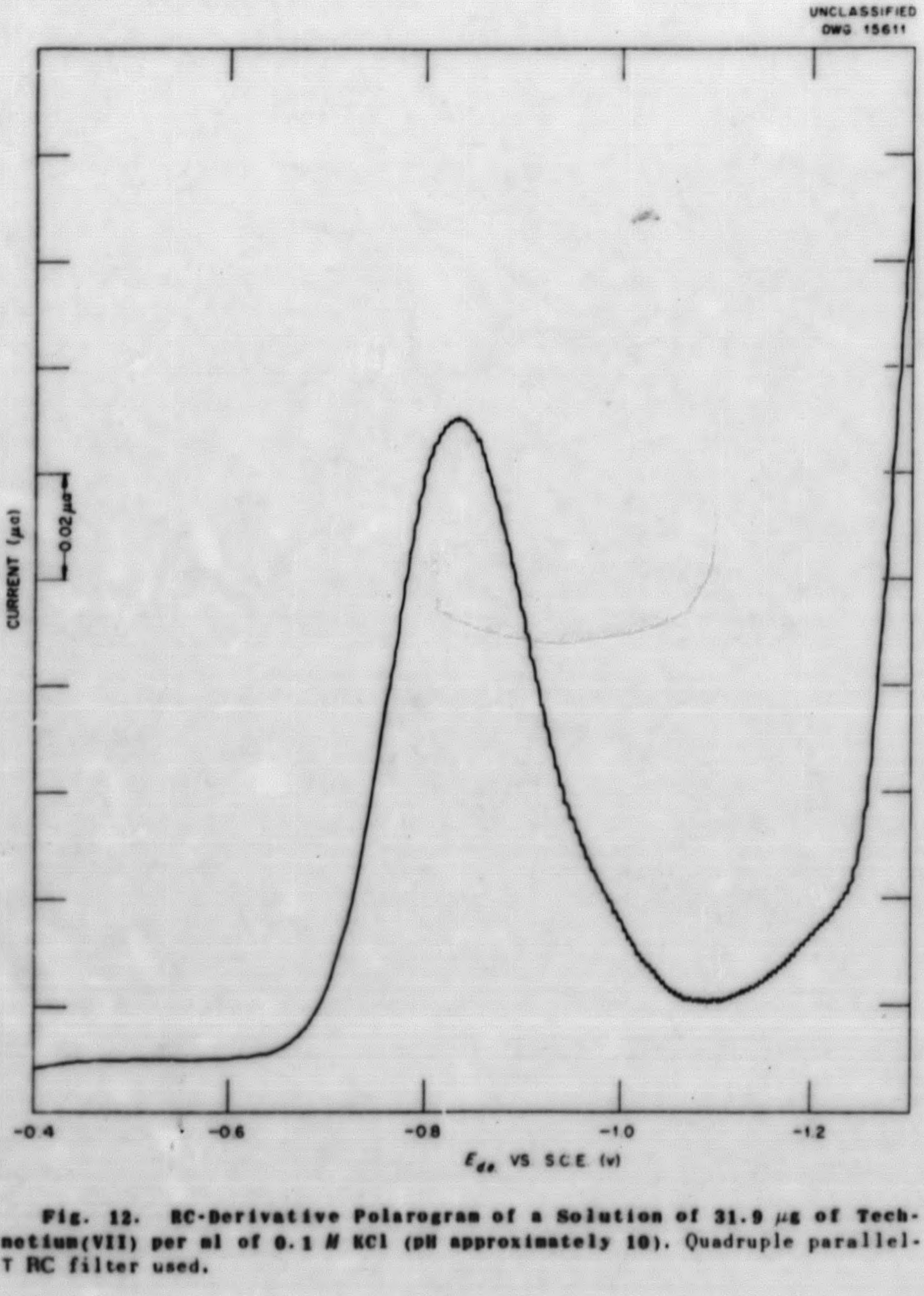

**Fig. 12. RC-Derivative Polarogram of a Solution of 31.9 μg of Technetium(VII) per ml of 0.1 N KCl (pH approximately 10).** Quadruple parallel-T RC filter used.

and they were found to contain no free acid. One-milliliter aliquots of a 0.1 *M* $Th(NO_3)_4$ solution were passed through the resin, and the liberated acid was titrated with 0.0997 *N* NaOH by using a micrometric 5-ml syringe buret. Five-milliliter aliquots of a 0.0333 *M* $Al(NO_3)_3$ solution were treated in the same manner. The results are shown in Table I. Synthetic feed samples made from mixtures of these solutions were also analyzed, and the acid liberated agreed with the theoretical amount within ±5%.

From these data it can be seen that thorium(IV) and aluminum(III) are both readily adsorbed on the Dowex-50 resin. The following equations indicate the general mechanism of the adsorption:

$$Th(NO_3)_4 + 4\ H^+\ (\text{cation resin}) \xrightarrow{\qquad} Th\ (\text{cation resin}) + 4\ HNO_3$$

$$Al(NO_3)_3 + 3\ H^+\ (\text{cation resin}) \xrightarrow{\qquad} Al\ (\text{cation resin}) + 3\ HNO_3$$

$$\underline{H}NO_3 + H^+\ (\text{cation resin}) \xrightarrow{\qquad} H^+\ (\text{cation resin}) + \underline{H}NO_3$$

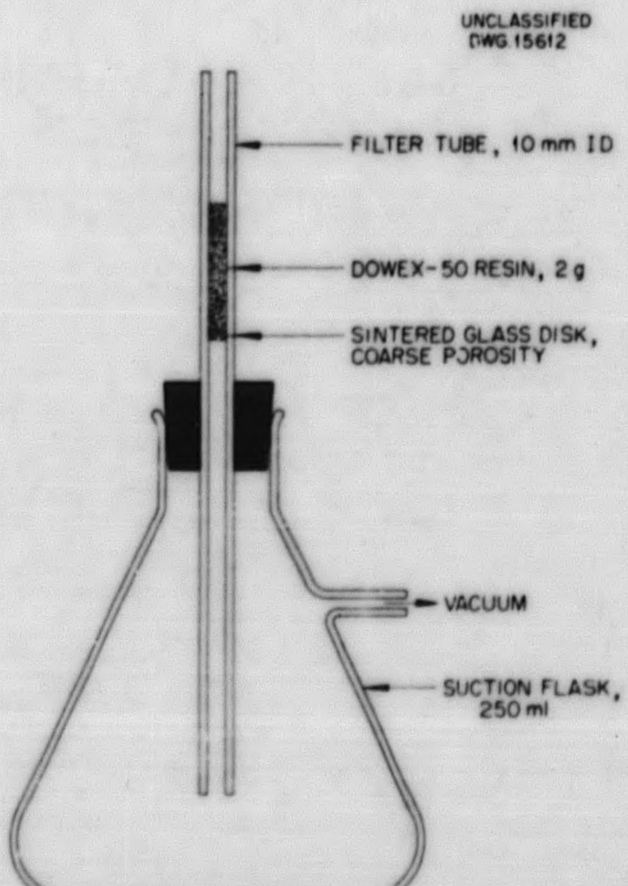

**Fig. 13. Resin Column for the Determination of Aluminum in Uranium Feed Solutions.**

**Volumetric Determination of Aluminum in the Presence of Thorium** (J. M. Chilton). A request was received from the Thorex Process group for a method of determining aluminum in highly radioactive samples containing large amounts of thorium. The acid-base titration method already described(12) was investigated further by use of microburets and smaller volumes of samples. It was found that the analysis of samples containing thorium and aluminum did not give reproducible results when phenolphthalein was used as the colorimetric indicator. The procedure was therefore modified to conform more closely to that described by Ringbom.(13) The pH during the course of the titrations was followed by means of a glass electrode. It was found that the first end point corresponds to the phenolphthalein color change and the second end point to the phenol-red color change. It was also found that under these conditions each thorium ion was

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(12) J. M. Chilton, "Determination of Aluminum in BaLa Process Samples," *op. cit.*, ORNL-1233, p. 17.

(13) A. Ringbom, "Volumetric Determination of Aluminum," *Svensk Papperstidn.* **50**, No. 11A, 145 (1947); *C. A.* **43**, 8949 (1949).

Table 1

ACID LIBERATED FROM $Th(NO_3)_4$ AND $Al(NO_3)_3$ SOLUTIONS WHEN PASSED THROUGH DOWEX-50 RESIN

| SOLUTION | SOLUTION ALIQUOT (ml) | AMOUNT OF 0.0997 *N* NaOH REQUIRED TO TITRATE LIBERATED ACID (ml) | |
|---|---|---|---|
| | | Calculated | Found |
| $Th(NO_3)_4$, 0.1 *M* | 1.0 | 4.00 | 3.97 |
| $Th(NO_3)_4$, 0.1 *M* | 1.0 | 4.00 | 4.00 |
| $Al(NO_3)_3$, 0.033 *M* | 5.0 | 5.00 | 4.98 |
| $Al(NO_3)_3$, 0.033 *M* | 5.0 | 5.00 | 4.97 |

equivalent to three hydroxyl ions rather than to four. The procedure developed was issued to the Laboratory and Semi-Works Control group for use in analyzing the Thorex Process samples.

**Determination of Oxygen in Thorium by Vacuum-Fusion Analysis (W. J. Wolkowitz).** The development of a method for determining oxygen in thorium metal by vacuum-fusion analysis is near completion. Oxygen in the concentration range 0.006 to 0.20 wt % has been successfully recovered from standard samples. The samples were prepared in 85-g quantities by arc melting thorium metal with the proper amounts of thorium dioxide and then remelting four times to ensure homogeneity. The analytical results are given in Table 2.

Table 2

OXYGEN IN THORIUM METAL DETERMINED BY VACUUM-FUSION ANALYSIS

| SAMPLE | OXYGEN IN THORIUM (wt %) | |
|---|---|---|
| | Added | Recovered |
| 1 | 0.006 | 0.007 |
| 2 | 0.013 | 0.011, 0.014 |
| 3 | 0.022 | 0.024, 0.025 |
| 4 | 0.05 | 0.047 |
| 5 | 0.08 | 0.07, 0.08 |
| 6 | 0.20 | 0.17, 0.22 |

Several standard samples with oxygen content in the range 0.22 to 1.5 wt % were prepared by the above method. Analysis of these samples by vacuum fusion gave erratic results, and the work is being repeated. In addition, a melt of 8 g of thorium metal has been prepared with thorium dioxide added to give an oxygen content of 0.485 wt %. The melt has been cut into eight equal samples, and each section is to be analyzed. If satisfactory oxygen recovery is obtained, a new melt containing approximately 0.8 wt % oxygen will be prepared. Similar experiments will be made until the upper limit of sensitivity of the method is established. It is expected that the upper limit will be at about 1.5 wt % oxygen.

**Colorimetric Determination of Copper** (J. M. Chilton). Since several samples have been received from the homogeneous reactor project for copper determination, an investigation was made of the feasibility of utilizing the reaction of copper(II) with potassium iodide in acid solution to liberate a quantity of free iodine equivalent to the copper(II). The free iodine was extracted in an organic solvent, $CCl_4$, and determined colorimetrically.

The absorption spectrum of iodine in $CCl_4$ was determined, and the absorption was found to follow Beer's law. Standard solutions of copper, both with and without uranium present, were analyzed by this method. It was found that each microgram of copper gives an optical density of approximately 0.003 when a total volume of 2.0 ml of $CCl_4$ is used for extraction.

**Studies of Factors Affecting the Reductimetric Titration of Iron with Mercurous Nitrate** (F. J. Miller, J. M. Chilton). A study of the precision of the titration was made by titrating 0.60 to 8.4 mg of iron with a 0.0683 *N* $HgNO_3$ solution by using a bright platinum indicator electrode vs. S.C.E. The results indicate that a reliability $(d/\sqrt{n})$ of 0.04 is obtainable. Studies of the effect of pH of the sample on the titration showed that the titration was successful over a pH range of 0.7 to 2.1.

The interference of fluoride and aluminum ions was also studied. Aluminum(III) in a milligram ratio to iron of 1:0.6 showed no interference. Fluoride in a milligram ratio to iron of 120:0.6 interfered slightly; in a ratio of 60:0.6 no interference was noted.

An attempt was made to determine plutonium in a synthetic sample as an analog of the iron titration. The synthetic solution was made to contain the indicated approximate quantities of the following ions:

| | |
|---|---|
| Plutonium | 0.084 mg/ml |
| Lanthanum | 3.0 |
| Fluoride | 3.0 |
| Aluminum | 4.0 |

The solution was approximately 1 *N* with respect to $HNO_3$. The sample was oxidized with sodium nitrite without heating; crystals of sulfamic acid were added to destroy the excess of sodium nitrite. Titration of 5 aliquots gave varying results, with the maximum deviation being of the order of 7.0%.

**Quantitative Removal of Iron from Plutonium Solutions** (F. J. Miller). Samples submitted for plutonium assay have contained varying quantities of iron. In the titration of plutonium to a potentiometric end point with cerium(IV), the iron is not differentiated from the plutonium. Consequently, the iron is an additive interference and should be removed. An attempt was made to separate the iron by a lanthanum fluoride precipitation of the plutonium, but the results with this procedure were not encouraging. Iron was not completely separated and some loss of plutonium was evident.

Hahn, who reported(14) the separation of metals by using a mercury microcathode, was successful in separating

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(14) R. B. Hahn, *Separations with a Micro Mercury Cathode*, AECD-3300 (Dec. 1951).

copper and iron from aluminum, uranium, and zinc. This method offered promise and was investigated. Hahn prepared a cathode by spot welding silver foil to a platinum wire, and he used a platinum wire for the anode. Since this type of electrode assembly was unsuitable for carrying out electrolysis in a 5- or 10-ml volumetric flask, a more convenient type of electrode, shown in Fig. 14, was prepared.

The electrode is cleaned thoroughly and then electrolyzed in a 10% mercurous nitrate bath until the silver wire is completely covered with mercury and drops of liquid mercury begin to fall.

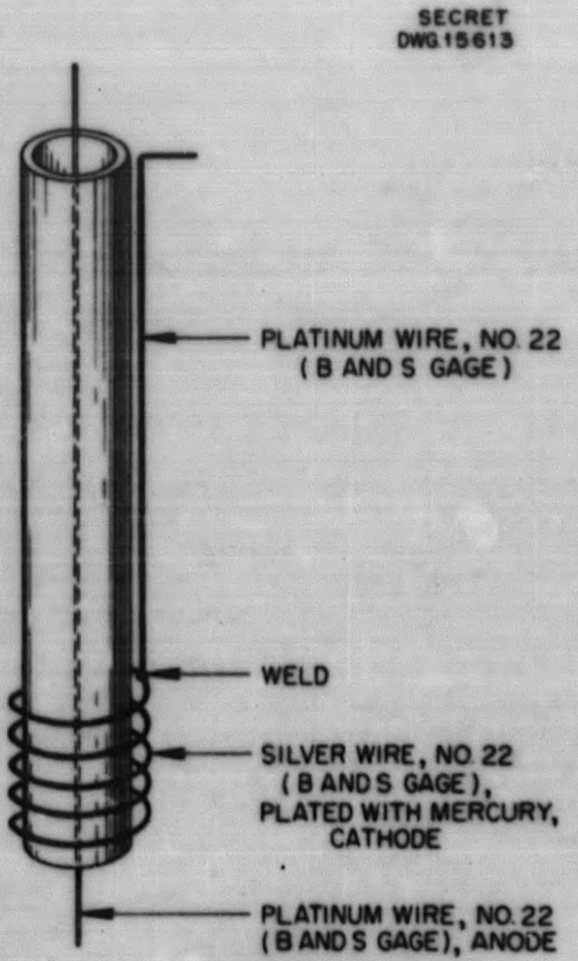

**Fig. 14. Electrode System for the Quantitative Removal of Iron from Plutonium Solutions.**

The electrode is then removed, washed with water, and conditioned by electrolyzing in dilute sulfuric acid for 15 min at a current of 1 ampere.

The electrolysis is carried out for 45 min at a current of 1 amp and 15 min at 0.5 amp in a 5- or 10-ml volumetric flask containing the sample, which should be 0.5 to 1.0 *N* in $H_2SO_4$. The silver electrode should be completely immersed during electrolysis and then withdrawn from the solution with the voltage still on and rinsed with distilled water, which is run into the flask. During electrolysis, the solution will turn from the brown color typical of plutonium(IV) in sulfuric acid to the deep-blue color characteristic of the plutonium(III). Colorimetric tests made on the plutonium solution by using thiocyanate have not shown any iron remaining after electrolysis. Synthetic samples containing 105 μg of iron electrolyzed in the same manner have shown less than 5 μg of iron remaining when tested with orthophenanthroline.

**Colorimetric Determination of Plutonium by Use of Thoron Reagent** (J. M. Chilton). The use of Thoron reagent, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, for the determination of thorium(IV)(15) led to an investigation of the suitability of the reagent for determining plutonium(IV). This possibility was previously considered(16) at Los Alamos, but the reagent was discarded in favor of the more sensitive reagent, sodium alizarin sulfonate. The use of the latter reagent, however, has the disadvantage of requiring the

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(15) P. F. Thomason, M. A. Perry, and W. M. Byerly, "Determination of Microgram Amounts of Thorium," *Anal. Chem.* **21**, 1239 (1949).

(16) G. L. King, *A Spectrophotometric Determination of Multimicrogram Amounts of Plutonium*, LA-1197 (Jan. 26, 1951).

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separation of iron before the development of the chromophore. The results of this investigation will be covered in a topical report.

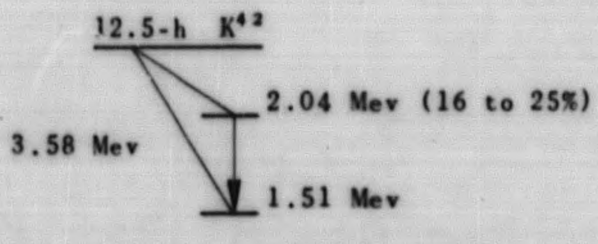
**Plutonium Assay on a Weight Basis.** Apparatus and procedures are being developed to eliminate volumetric procedures in plutonium assaying insofar as is practical. This work will be reported later.

## RADIOCHEMICAL ANALYSES

S. A. Reynolds

### Nuclear Properties

*Decay Scheme of Potassium-42* (W. S. Lyon, B. Kahn[17]). Potassium-42 ($T_{1/2}$ = 12.5 h) is of interest because of the large amount of high-energy beta particles in its decay. Siegbahn and Johansson[18] have indicated the decay to proceed in the following manner:



Recent work by Kahn in the determination of the efficiency of gas-flow proportional counters as a function of beta energy required the use of a hard beta emitter of known disintegration rate, and $K^{42}$ appeared promising. The half life was redetermined, and the branching ratio was measured to within a few per cent.

Reagent-grade potassium carbonate was irradiated in the X-10 graphite reactor for periods averaging 62 hours. The activated material was then passed through a cation-exchange column using either IR-100 or IR-105G resin.[19] The separation method used was similar to that described by Kayas.[20]

The solution containing separated $K^{42}$ and carrier after concentration by evaporation was made to volume in a 10-ml volumetric flask. Suitable aliquots were taken for ionization chamber readings, decay studies, coincidence counting, 4π counting, and scintillation gamma-ray spectroscopy.

Five different runs were made, and in no case was any activity other than $K^{42}$ found in the product. Decay data were obtained by use of a sodium iodide scintillation counter with an automatic traffic counter. The data accumulated over eight half lives indicate the half life to be 12.50 ± 0.20 hours. The gamma-ray spectrum of one such sample is shown in Fig. 15. The gain is such that the pulse-height scale should be multiplied by about 2 to convert to kev. The peak at *A* is the Compton peak and that at *B* is the photoelectron peak from the 1.50-Mev gamma ray. These data were obtained on the new Analytical Chemistry Division sodium iodide scintillation spectrometer that is described in this report (cf., "Sodium Iodide Scintillation Spectrometer").

The absolute disintegration rate of the $K^{42}$ sources was obtained by 4π counting, 4π gamma-ray coincidence

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[17] Health Physics Division.

[18] K. Siegbahn and A. Johansson, "Coincidence Spectrometry for Disintegration Problems," (trans.), *Arkiv Mat., Astron. Fysik* **34A**, No. 10 (1947-48).

[19] This work was performed by G. W. Leddicotte, J. Manning, and J. Oliver, and grateful acknowledgement is hereby made.

[20] G. Keyes, "Complete Separation of Alkali Metals by Ion Exchange" (trans.), *J. chim. phys.* **47**, 408 (1950).

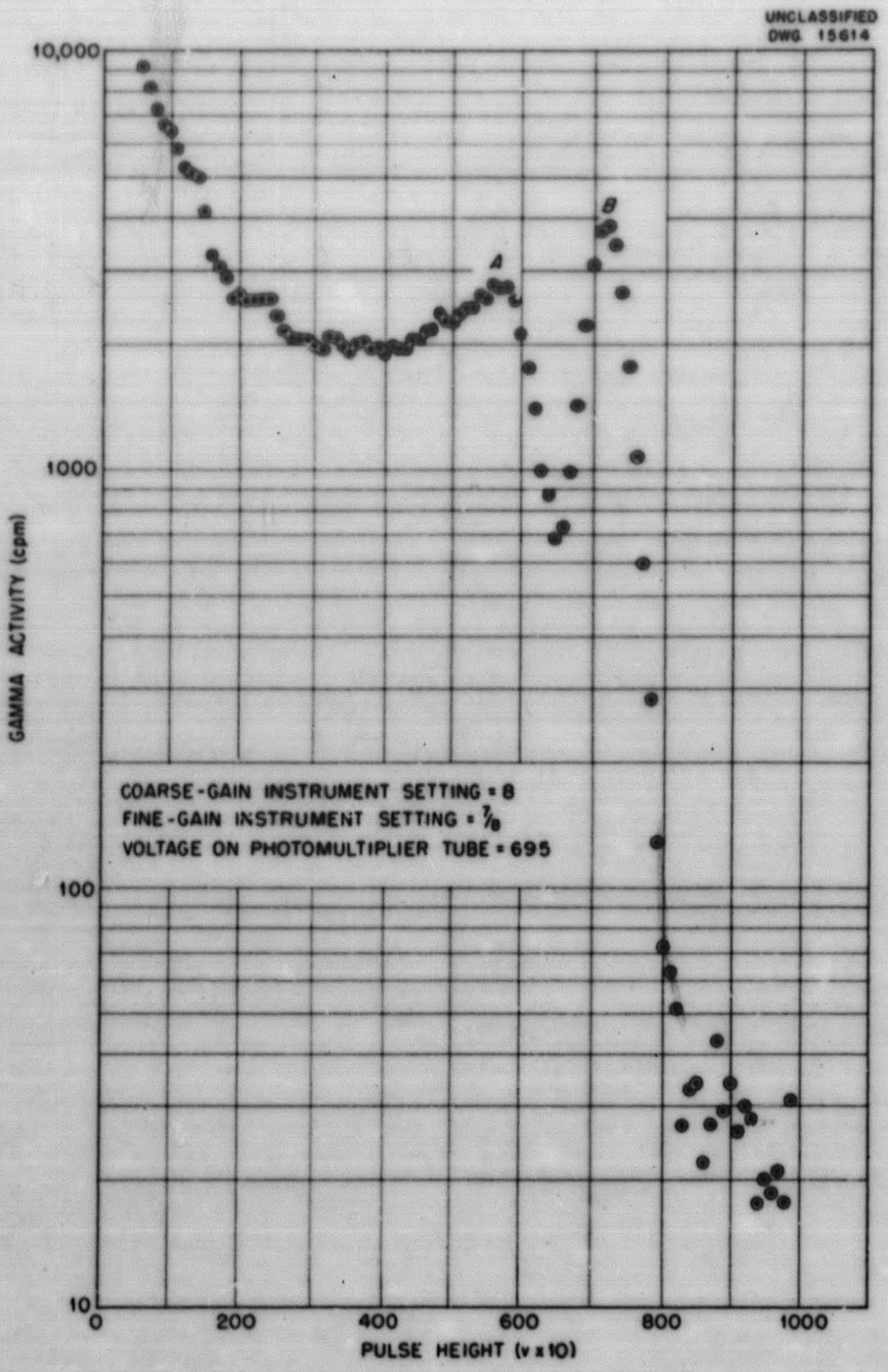

Fig. 15. Gamma-Ray Spectrum of Potassium-42.

counting, and standard beta-gamma coincidence counting. Results by these methods checked to within a few per cent. By use of the Chemistry Division scintillation spectrometer, which was calibrated by Brosi and his co-workers, it has been possible to integrate beneath the photoelectron peak for $K^{42}$ and by comparison with a standard $Co^{60}$ source to arrive at the amount of 1.5-Mev gamma rays present. On the basis of this work the branching has been found to occur 17 ± 1% of the time through the gamma-ray transition.

The data obtained on $K^{42}$ are: $T_{1/2} = 12.50 \pm 0.20$ h, and the fraction decaying through 1.5-Mev gamma rays = $0.17 \pm 0.01$.

*Decay of Thallium-204* (W. S. Lyon, B. Kahn(21)). Thallium-204 is of interest because its beta-ray energy (0.78 Mev) is close to the average energy of the fission products. Lidofsky and Wu(22) have recently reported the presence of x rays associated with this decay. They postulate that the decay of $Tl^{204}$ branches with some fraction decaying by *K*-capture to stable $Hg^{204}$. Their search for gamma radiation by use of a sodium iodide crystal spectrometer revealed no gamma rays. Saxon and Richards(23) used a lens spectrometer and found anomalies in the beta spectrum that might be explained by the presence of a second lower energy beta group. However, no gamma rays or conversion electrons were found, so the possibility of the presence of a second lower energy beta group was eliminated.

A highly pure source of $Tl^{204}$ prepared by W. A. Brooksbank (cf., "Thallium-204 Standard for Liquid-Waste Assay," this report) was obtained, and the gamma-ray spectrum was studied by use of a sodium iodide crystal spectrometer. As expected, *K* x rays of approximately 73 kev were found. With the beryllium-window, krypton-filled, x-ray spectrometer (Chemistry Division), *L* x rays of approximately 10-kev energy were also observed. By comparison with x rays from neighboring nuclides it was hoped that the assignment of the x radiation might be made definitely either to lead (indicating conversion of a gamma ray following beta decay), to thallium (indicating an isomer of thallium), or to mercury (indicating *K*-capture). Thus far resolution has been too poor to allow a fine distinction to be made. Sources of $Ir^{192}$ (Pt x rays), $Au^{198}$ (Hg x rays), $Hg^{203}$ (Tl x rays), and RaDE (Bi x rays) have been examined on both the sodium iodide spectrometer (*K* x rays) and on the beryllium-window, krypton-filled, x-ray spectrometer (*L* x rays), but the data are inconclusive. Integrations beneath the *K* peaks of both a $Tl^{204}$ source and a source of $Hg^{203}$ were made. The $Tl^{204}$ disintegration rate was obtained by absolute beta counting and that of the $Hg^{203}$ by $4\pi$ counting. Comparison of the areas indicated that 2% of the $Tl^{204}$ beta decay was represented in *K* x rays and 0.8% in *L* x rays. A search for harder electromagnetic radiation by use of the sodium iodide crystal revealed no peak above the *K* x ray. However, beta-gamma coincidence data seem to reveal the presence of coincidences between beta particles and some gamma activity. Because of the extremely low gamma-ray counting rate, long counts were necessary to obtain reliable results. The apparent disintegration rate as a function of the type of aluminum absorber before the beta tube was obtained with

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(21) Health Physics Division.

(22) L. Lidofsky and C. S. Wu, "Thallium 204," Sec. VI A, *Progress Report Nuclear Physics Laboratories, April, May and June, 1951*, CU-96, p. 26.

(23) D. Saxon and J. Richards, "The Beta Spectrum of $Tl^{204}$, Magic Numbers, and Neutron Pairing," *Argonne National Laboratory Quarterly Report, April, May and June, 1949. Experimental Nuclear Physics Division and Theoretical Nuclear Physics Division*, ANL-4323, p. 9.

absorbers of either 0, 10, or 20 mg of aluminum per cm$^2$. The apparent disintegration rate rose with addition of absorber, indicating the presence of coincidences between a hard gamma ray and a beta ray of half-thickness of approximately 10 mg/cm$^2$. When extrapolated to true zero (that is, no window or air absorber), the apparent disintegration rate gave reasonable agreement with the rate from absolute beta counting. No x-ray–x-ray coincidences were found.

Because of the small amount of gamma activity present, meaningful results are difficult to obtain. With 2% *K* x rays present it certainly should be possible to see conversion electrons on a lens spectrometer if the x rays arise from conversion of a moderately hard gamma ray.

An attempt to determine the source of these x rays (*K*-capture or gamma-ray conversion) through critical absorption is planned. In addition, comparison of the integral *K* and *L* x-ray counts with $Au^{198}$ and $Hg^{203}$ should establish reliable *K* and *L* x-ray ratios as well as total x-ray amounts. A much stronger $Tl^{204}$ source is being prepared that will provide a more satisfactory sample to use in a search for hard gamma radiation.

*Disintegration of Strontium-85* (W. S. Lyon, S. A. Reynolds). The tentative decay scheme for $Sr^{85}$ reported previously(24) was in error according to Emmerich and Kurbatov's recent report(25) that the 0.51-Mev gamma ray in the decay scheme follows all the *K*-capture processes but comes from a metastable state of half life greater than 1 microsecond. They report no x-ray–gamma-ray coincidences; however, these were observed by Lyon and Coombe,(24) who report that apparently 23% of the disintegration passes through the 0.51-Mev level. If 100% of the disintegration passes through this level, the half life of the metastable state must be approximately 2 μsec, since the revolving time of the coincidence counter is 0.7 microsecond.

## Measurement of Radioactivity

*Sodium Iodide Scintillation Spectrometer* (W. S. Lyon, S. A. Reynolds). The long-awaited sodium iodide gamma-ray spectrometer has been received and assembled. This instrument consists of a sodium iodide crystal mounted on a photomultiplier tube and sealed within a magnesium can. The pulses from the photomultiplier pass through a preamplifier to an A-1 amplifier that has a differential and integral pulse-height selector to a 1024 scaler. The crystal and tube are housed within a lead shield, and there is a standard shelf arrangement for mounting sample cards. The instrument has been set so that on a gain setting of 16 the pulse-height range of 0 to 100 v corresponds to a kev range of 0 to 1000. Thus the energy in kev is approximately equivalent to ten times the pulse height in volts. Two differential standards ($Cs^{137}$ and $Ce^{144}$-$Pr^{144}$) and one integral standard ($Cs^{137}$) are run each day. The $Cs^{137}$ is used to check the 0.66-Mev gamma ray and the $Ce^{144}$-$Pr^{144}$ to check the 0.134-Mev gamma ray.

Figure 16 indicates the complete gamma spectrum of $Cs^{137}$. *A* is the *K* x-ray peak resulting from conversion of the 660-kev gamma ray; *B* is presumably caused by a scattering buildup

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(24) W. S. Lyon and D. J. Coombe, "Disintegration of $Sr^{85}$," *Analytical Chemistry Division Quarterly Progress Report for Period Ending March 26, 1951*, ORNL-1088, p. 44.

(25) W. S. Emmerich and J. D. Kurbatov, "Disintegration of the Ground-State $Sr^{85}$ and Metastable Energy Level of 514 Kev in $Rb^{85}$," *Phys. Rev.* 85, 149 (1952).

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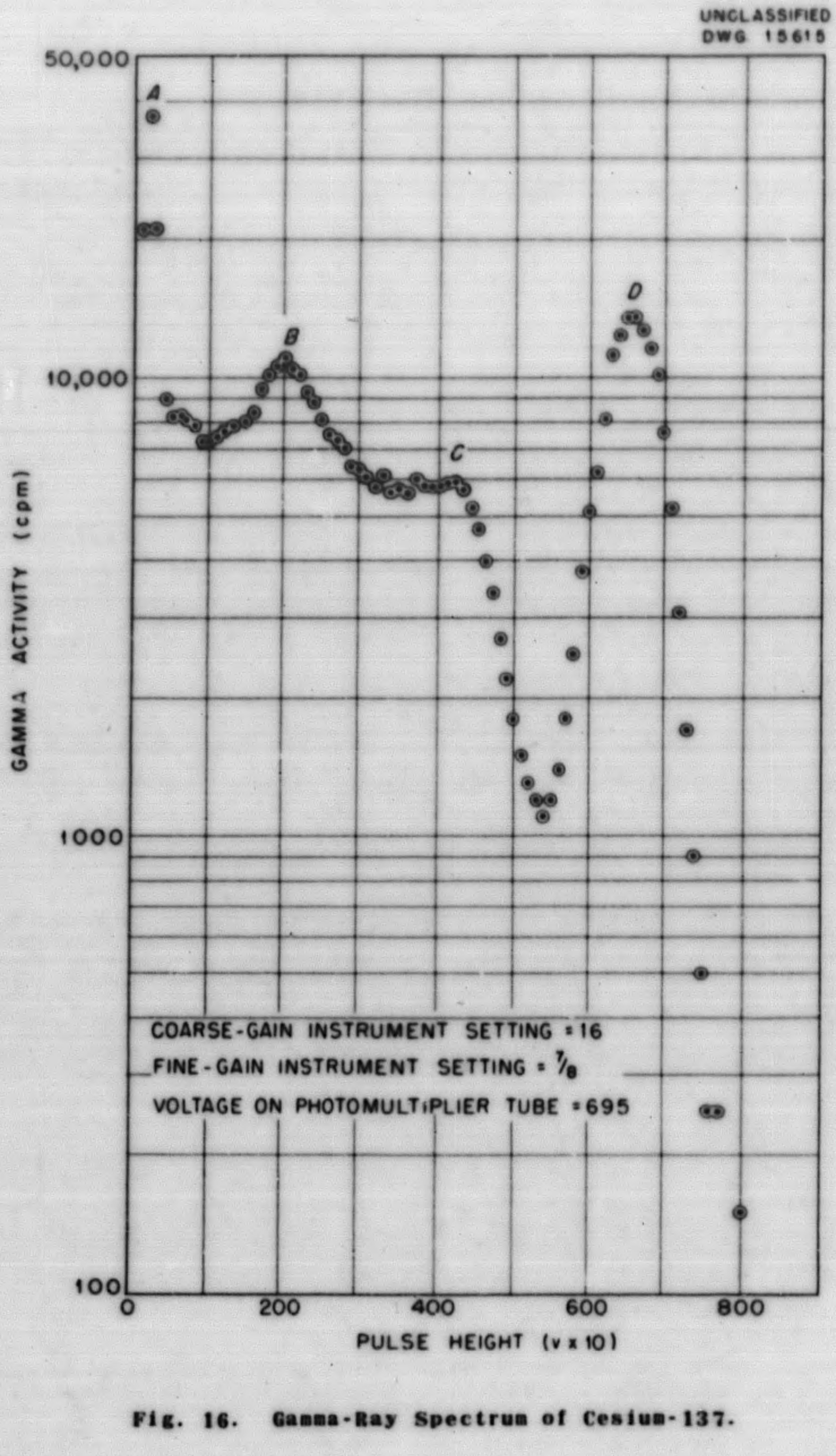

**Fig. 16. Gamma-Ray Spectrum of Cesium-137.**

in the housing; *C* is the Compton peak; and *D* is the photoelectron peak of the 660-kev gamma ray.

Figure 17 shows the low-energy region of $Ce^{144}$-$Pr^{144}$. Photoelectron peaks are evident at 80 and 135 kev.

Figure 18 is the gamma-ray spectrum of $Au^{198}$. A photoelectron peak at 400 kev and the *K* x-ray peak from conversion at 60 kev are discernible.

The spectrometer promises to be a useful tool both for research and for scanning of isotope products to detect contaminating gamma activities.

*Scintillation Counting for Purex Solutions* (D. A. Brown,(26) W. S. Lyon). During recent months workers at KAPL have been attempting to use a scintillation counter to measure gamma-activity decontamination factors in Purex processes and the final Purex product. At a recent meeting of ORNL and KAPL representatives it was decided that the Analytical Chemistry Division would attempt similar studies in an effort to devise some experimental arrangement whereby the scintillation counting might replace ion chamber measurements. As noted in the report of this meeting,(27) the contaminating gamma-activity specification for uranium product is set in terms of ion chamber measurements, since the purpose of the specification is to ensure freedom from harmful radiation in the K-25 fluorinator. Therefore the response of a scintillation counter for use in the Purex process must be similar to that of the ion chamber, that is, the energy vs. efficiency relationship must be similar. It was decided to try a sodium iodide scintillation counter as a detector with a lead absorber to minimize the effect of soft gamma and x radiation for which the sodium iodide crystal is most efficient. It was believed that such an arrangement might meet the requirements.

Gamma activities of solutions of the pure isotopes $Sc^{46}$, $Zn^{65}$, $Nb^{95}$, $Au^{198}$, $Co^{60}$, and $Na^{24}$ were measured with the ion chamber located in Building 3038, and the dpm/ml values of the solutions were calculated in the usual manner.(28) Aliquots of the solutions were placed on watch glasses, evaporated to dryness, mounted, and counted at pulse heights of 20 and 90 kev on the second shelf of the scintillation counter under the following experimental conditions: an integral output, a coarse gain setting of 16, a pulse height of 20 kev, a slit width of 10 kev, and with absorbers (0, 2, 3, and 4 g of lead) on the first shelf. The cpm/ml values were calculated from the data obtained. Efficiencies of the scintillation spectrometer were then calculated by the relationship:

$$\text{Efficiency} = \text{cpm/dpm} .$$

Figures 19 through 22 are plots of efficiencies as observed for the particular isotopes vs. gamma-ray energies in Mev (broken lines) and efficiencies per number of gamma rays per disintegration vs. gamma-ray energies in Mev (solid lines). The solid lines are the significant curves, since they indicate the efficiency per gamma photon. From the curves it is apparent that when enough absorber is present to absorb completely all beta radiation, the curve is essentially a straight line

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(26) DuPont Co.

(27) W. R. Tyson, "Beta and Gamma Specifications – Purex Products Analyses," meeting at Oak Ridge National Laboratory, November 8, 1951.

(28) J. W. Jones and R. T. Overman, *The Use and Calibration of a 100% Geometry Ion Chamber*, AECD-2367 (Mar. 20, 1948).

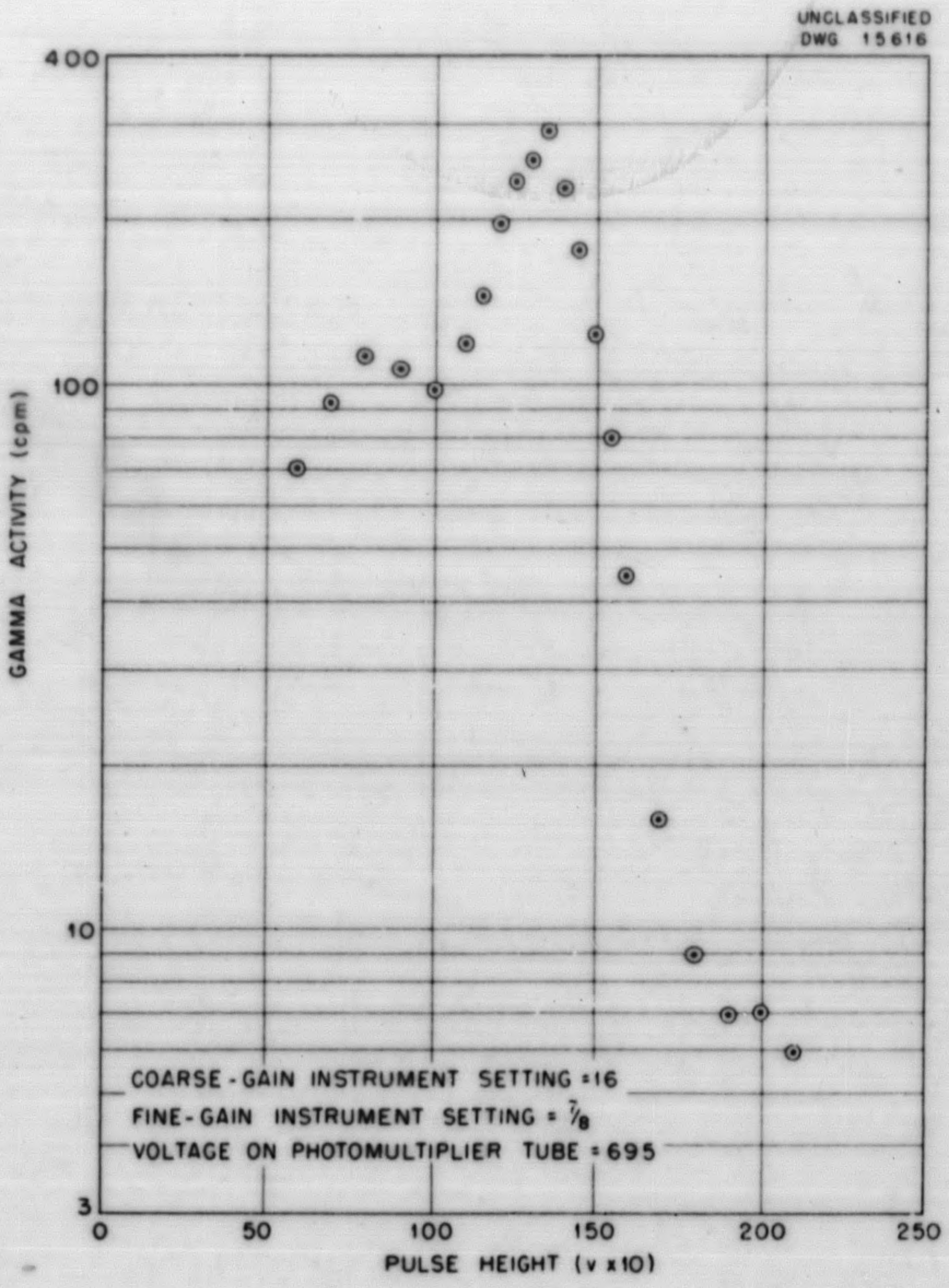

**Fig. 17.** Low-energy Gamma-Ray Spectrum of $Ce^{144}$-$Pr^{144}$.

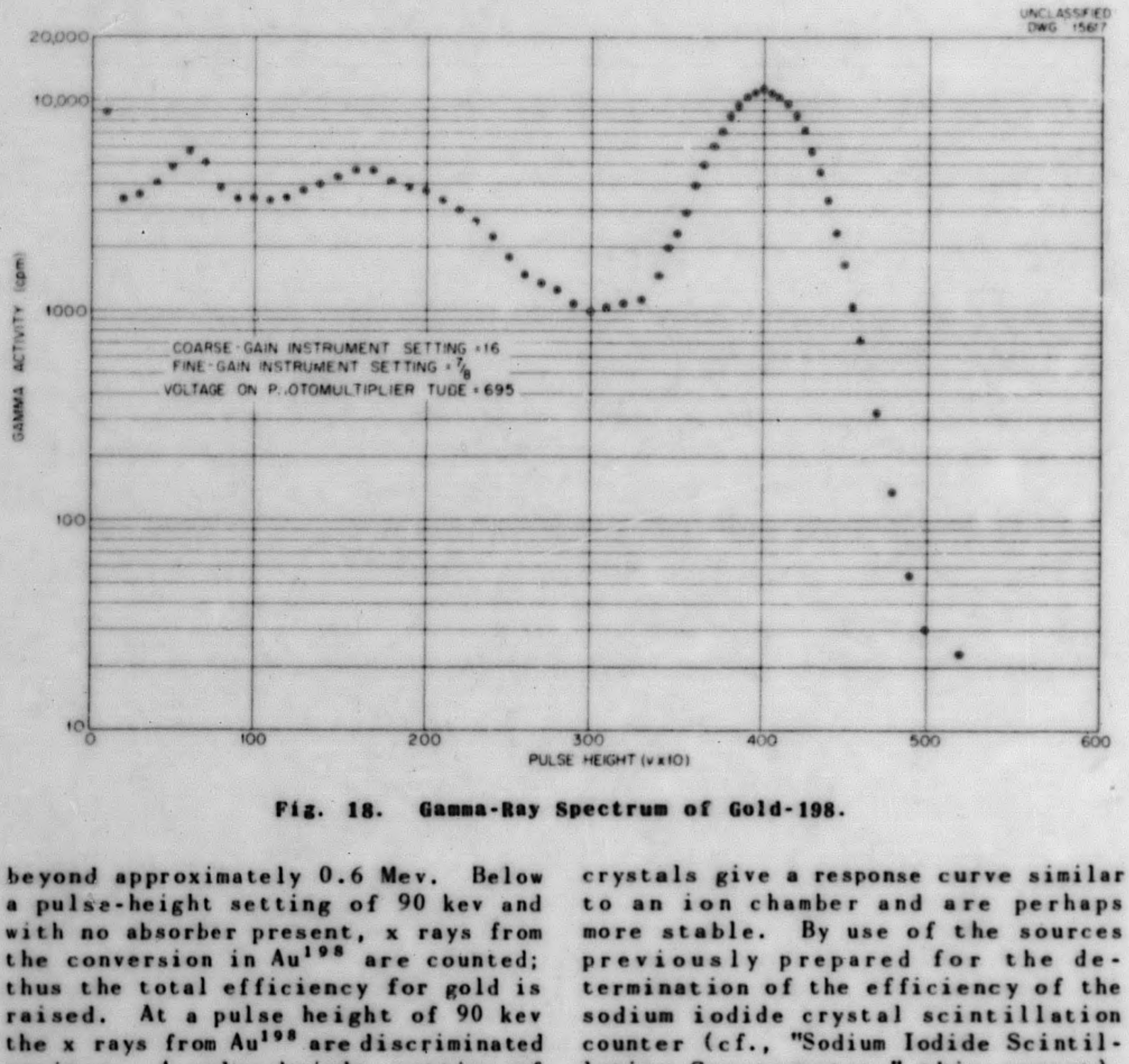

Fig. 18. Gamma-Ray Spectrum of Gold-198.

beyond approximately 0.6 Mev. Below a pulse-height setting of 90 kev and with no absorber present, x rays from the conversion in $Au^{198}$ are counted; thus the total efficiency for gold is raised. At a pulse height of 90 kev the x rays from $Au^{198}$ are discriminated against. A pulse-height setting of 20 kev most nearly corresponds to straight-forward integral counting. At this setting with lead absorber present the response of the sodium iodide crystal scintillation counter, particularly in the low-energy region, is somewhat similar to that of an ion chamber.

Unfortunately sodium iodide counters are extremely sensitive to moisture, and their long-time stability is not well known. It is known that anthracene crystals give a response curve similar to an ion chamber and are perhaps more stable. By use of the sources previously prepared for the determination of the efficiency of the sodium iodide crystal scintillation counter (cf., "Sodium Iodide Scintillation Spectrometer," this report), the efficiency of an anthracene crystal scintillation counter was also determined. In addition, data were obtained by using $Hg^{203}$ and $Na^{22}$. An attempt was made to use a physical geometry similar to that of the sodium iodide crystal counter. Samples were placed approximately 2.0 cm from the crystal, which is enclosed within an aluminum housing (approximately 700 mg of aluminum per cm$^2$). Also, a lead absorber (3.5 g of lead per cm$^2$) was placed before the counter. Figure 23

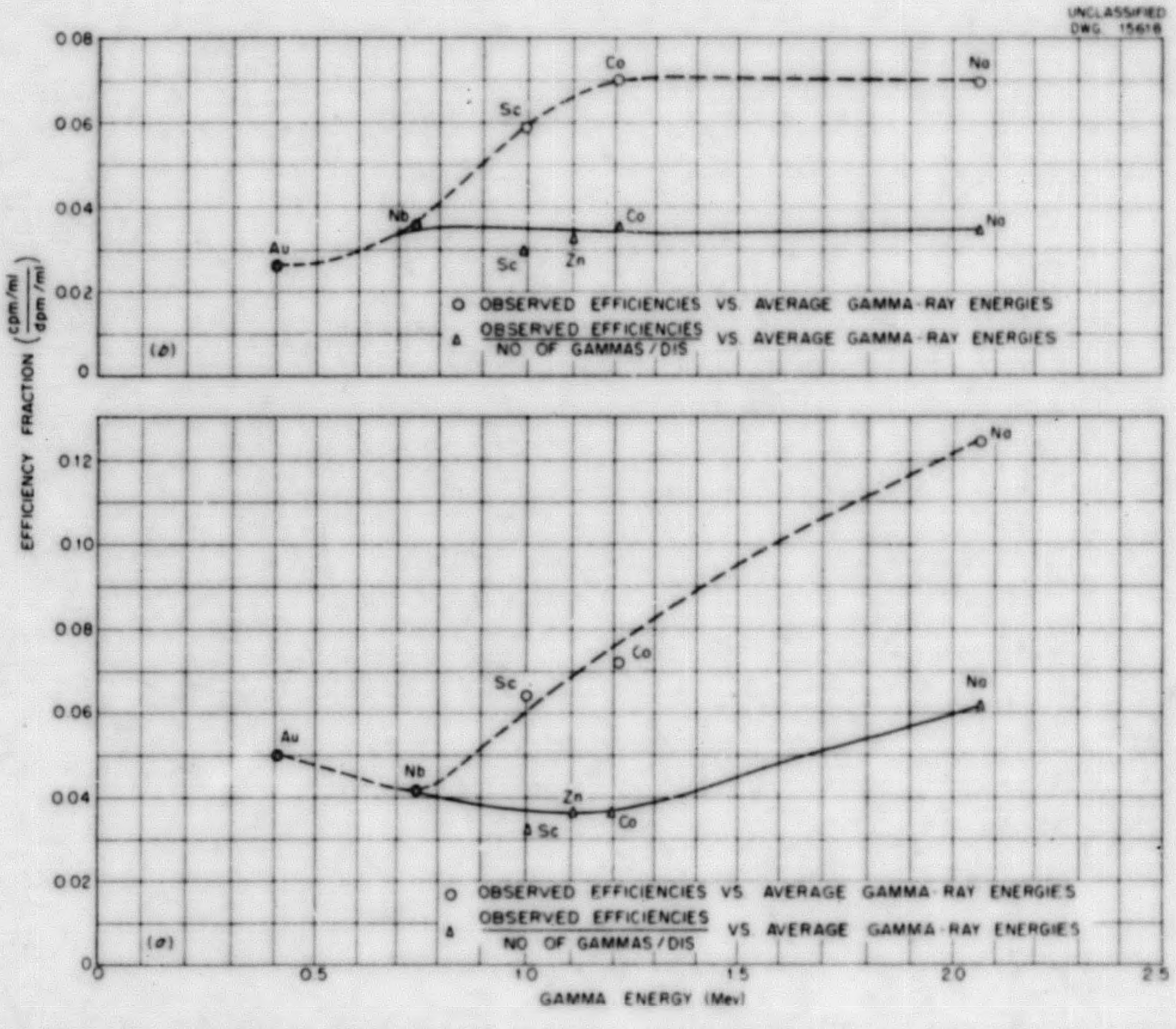

**Fig. 19. Scintillation Counter Gamma Efficiencies.** (*a*) Pulse height, 20 kev; no lead absorber. (*b*) Pulse height, 20 kev; 2 g/cm² of lead absorber.

indicates the energy dependence observed as a function of gamma-ray energy. The data obtained show that the anthracene counter is about one-tenth as efficient as the sodium iodide counter, and the efficiency vs. energy curve obtained with the anthracene counter is more consistent with that obtained with an ion chamber than with a curve obtained with a sodium iodide crystal counter.

*Thallium-204 Standard for Liquid-Waste Assay* (W. A. Brooksbank, S. A. Reynolds). Thallium-204 has been proposed as a standard for use in radioactive liquid-waste disposal studies. The reasons and methods for its use have been discussed previously.[29,30] Seliger of the National Bureau of Standards agreed to standardize a stock solution of $Tl^{204}$ and to

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[29] W. A. Brooksbank and S. A. Reynolds, "Low-Level Waste Activity," *op. cit.*, ORNL-1088, p. 45.

[30] W. A. Brooksbank and S. A. Reynolds, "Assay of Low-Level Beta Activity in Liquid Wastes," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 26, 1951*, ORNL-1113, p. 26.

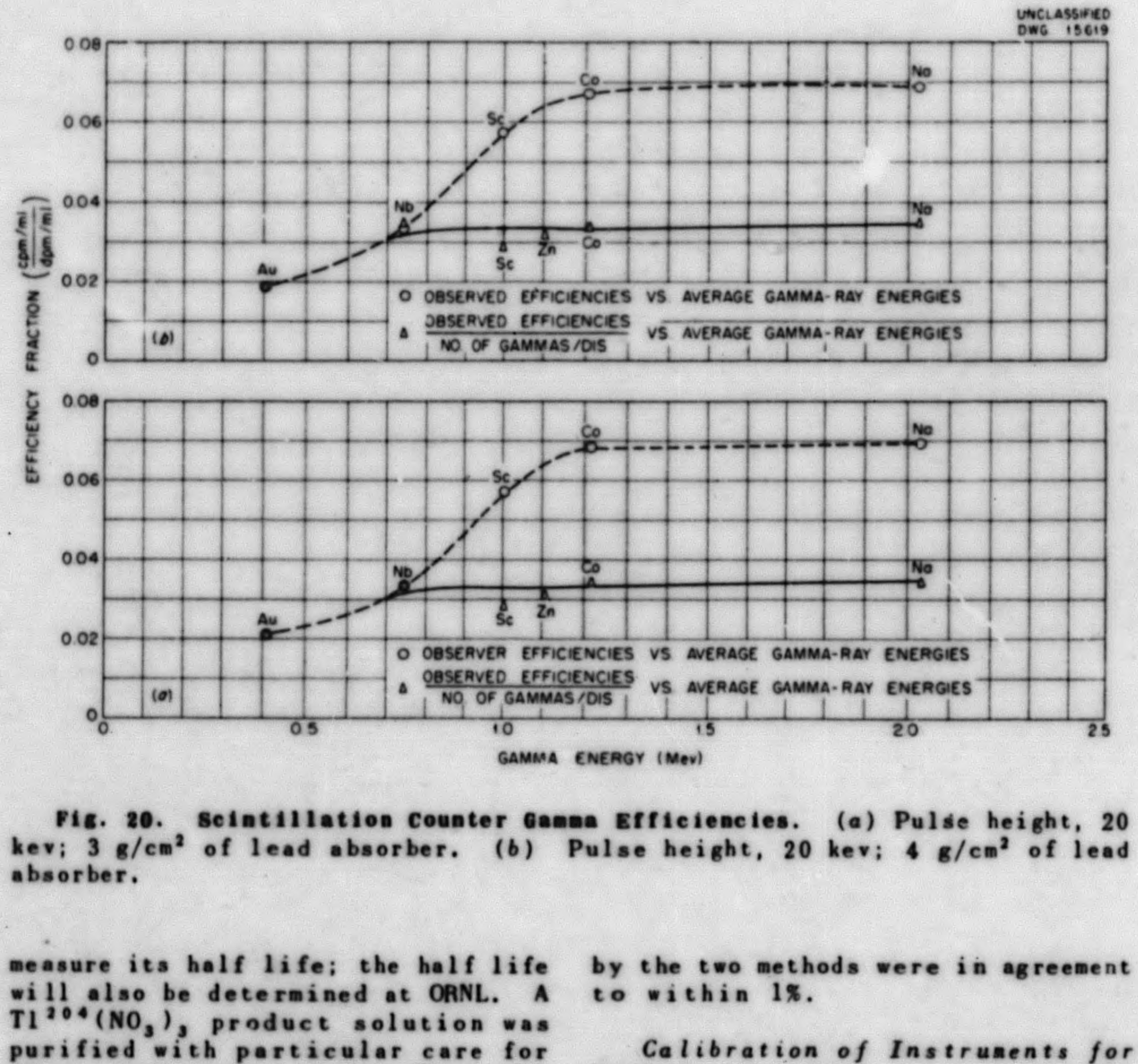

**Fig. 20. Scintillation Counter Gamma Efficiencies.** (*a*) Pulse height, 20 kev; 3 g/cm$^2$ of lead absorber. (*b*) Pulse height, 20 kev; 4 g/cm$^2$ of lead absorber.

measure its half life; the half life will also be determined at ORNL. A $Tl^{204}(NO_3)_3$ product solution was purified with particular care for these determinations. Repeated potassium iodide precipitations and ether extractions from 3 *M* HBr were used in the purification. Silver(I) and iron(III) were used as hold-back carriers. The sample shipped to NBS contained 0.12 mg of $Tl^{204}$ per milliliter of 2 *M* $HNO_3$ and had an activity of 1.55 × 10$^8$ dpm/ml; the activity was determined by Lyon by 4π counting and absolute beta counting. The results by the two methods were in agreement to within 1%.

*Calibration of Instruments for Measurement of Protactinium-233 Disintegration Rate* (S. A. Reynolds). Determination of the disintegration rate of $Pa^{233}$ will be required for various samples from the Thorex and Interim "23" processes. Two high-pressure ionization chambers, two scintillation gamma-ray counters, and several conventional end-window beta counters have been calibrated with known amounts of $Pa^{233}$.

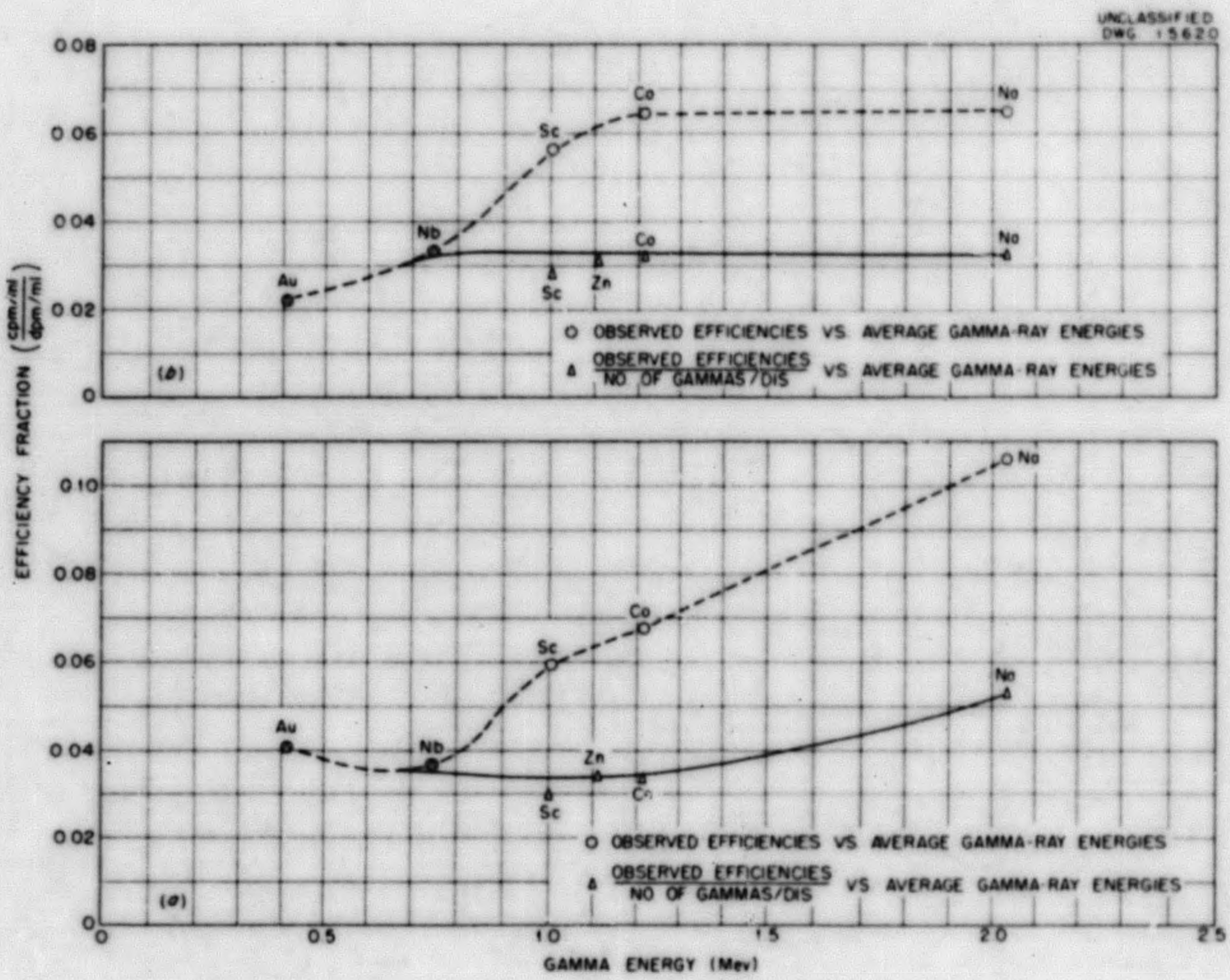

**Fig. 21. Scintillation Counter Gamma Efficiencies.** (*a*) Pulse height, 90 kev; no lead absorber. (*b*) Pulse height, 90 kev; 2 g/cm² of lead absorber.

The decay scheme of Pa$^{233}$ is so complex⁽³¹⁾ that the determination of the disintegration rate of a sample is difficult. Two indirect methods were used. The disintegration rate of Pa$^{233}$ in equilibrium in a sample of Np$^{237}$ was calculated from the alpha counting rate of the Np$^{237}$. In the second method, thorium metal was bombarded at a known thermal-neutron flux, and the disintegration rate of the Pa$^{233}$ produced was calculated from flux, cross-section, and half-life data. The counting instruments were then calibrated with both sources. A difference of 16% was noted in readings, which is within the uncertainty of the methods. The standardization data were weighted toward the bombarded sample, since the alpha count may have been low because of self-absorption. The results should be accurate to ±10%. The calibration data are given in Tables 3 and 4.

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(31) K. Way, L. Fano, M. R. Scott, and K. Thew, *Nuclear Data*, NBS Circular 499, p. 264 (Sept. 1, 1950).

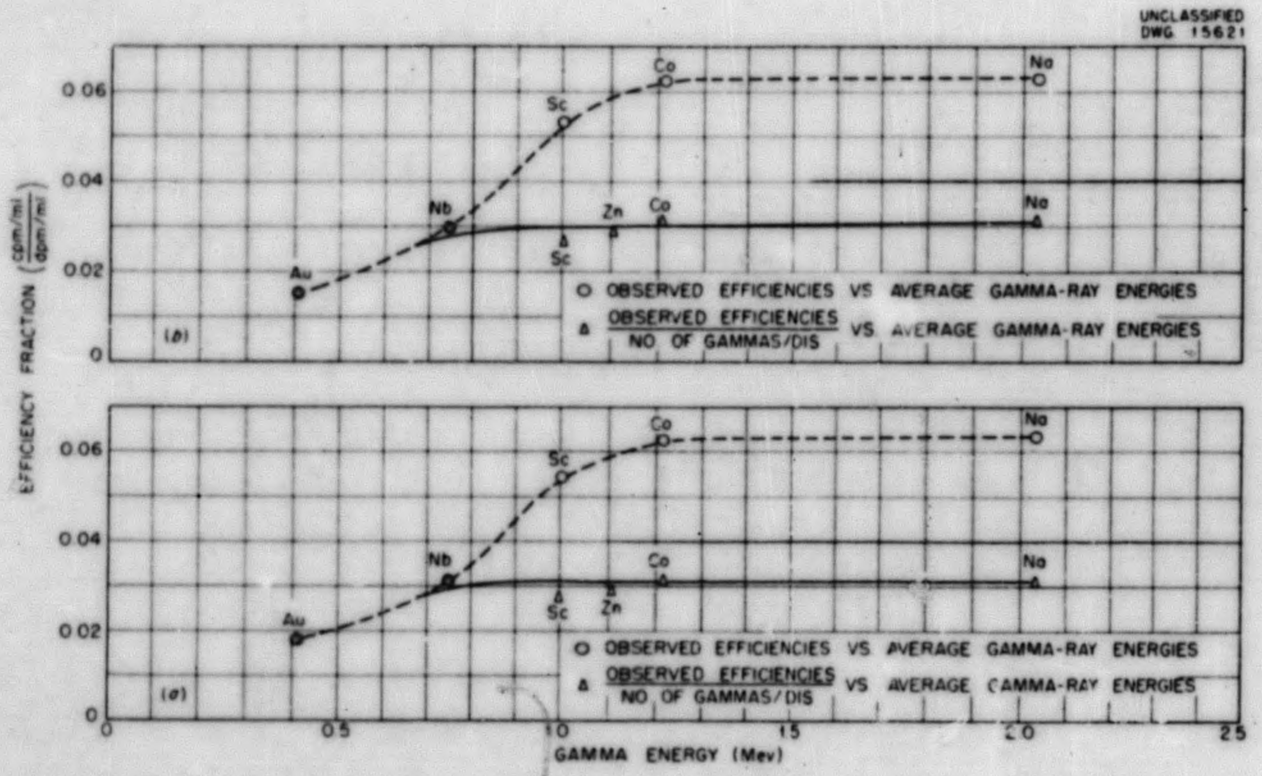

**Fig. 22. Scintillation Counter Gamma Efficiencies.** (*a*) Pulse height, 90 kev; 3 g/cm$^2$ lead absorber. (*b*) Pulse height, 90 kev; 4 g/cm$^2$ of lead absorber.

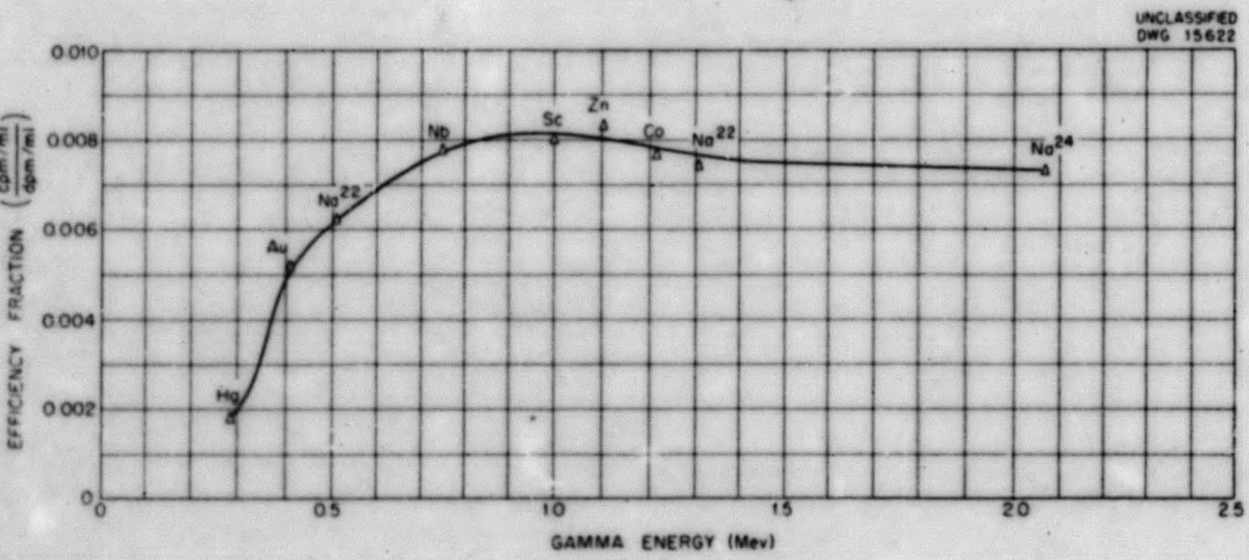

**Fig. 23. Observed Average Efficiencies of Anthracene-Crystal Scintillation Counter.** Approximately second shelf geometry; 3.5 g/cm$^2$ of lead absorber before crystal.

Table 3

HIGH-PRESSURE IONIZATION CHAMBER CALIBRATIONS

| INSTRUMENT LOCATION | SCALE | DISINTEGRATION RATE OF $Pa^{233}$ (dpm/volt) |
|---|---|---|
| Building 3550 (Wilson) | $10^{11}$ | $3.6 \times 10^7$ |
| | $10^{10}$ | $4.1 \times 10^8$ |
| | $10^9$ | $3.7 \times 10^9$ |
| Building 3019 (Lamb) | $10^{11}$ | $1.8 \times 10^7$ |

Table 4

COUNTER CALIBRATIONS

| COUNTER NUMBER | TYPE OF COUNTER | EFFICIENCY (cpm/dpm) |
|---|---|---|
| X45040 | Scintillation | 0.60 |
| [illegible]5066 | Scintillation | 0.58 |
| | G-M[a] | 0.081 |

[a] Samples mounted on 1-in. watch glasses, as usual.

## Analysis of Cyclotron Products

T. H. Handley

An investigation of the rare earths for radionuclides deficient in neutrons has been planned, and a series of ion-exchange columns has been built to prepare the pure rare earths required for the study. The columns will also be used for separating the rare earth activities in the bombarded targets.

The columns, which are similar to those designed by Boyd and Ketelle,(32) are charged with Dowex-50 resin and heated by steam jackets. Two columns (6 mm by 100 cm) are for handling trace quantities and determining the purity of fractions from the larger columns. Another of the columns is 2 by 100 cm and a fourth is 2.5 by 100 cm. The fifth column (5 by 100 cm) is being built to handle gram quantities of the rare earths. Instrumentation for monitoring one column has been assembled and is in operation. At first it was not known whether columns of the larger diameter could be heated uniformly, but tests have shown that this can be done. Since the temperature of the elution solution entering the column is approximately 98°C, only about 40% of the column volume is resin (about 60% being elution solution), and the column is surrounded by a steam jacket, the eluate is at

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(32) B. H. Ketelle and G. E. Boyd, "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. IV. The Separation of the Yttrium Group Rare Earths," *J. Am. Chem. Soc.* **69**, 2800 (1947).

about 98°C when it leaves the column. Trial runs of rare earth oxides with radioactive tracers present have shown that the 2-cm and 2.5-cm columns can easily handle 300-mg quantities without overloading the resin.

Some rare earth concentrates have been furnished by Weaver of the Stable Isotope Research and Production Division. Part of the purified rare earths will be returned to that division for use as raw materials in the separation of various isotopes.

No bombardment work has been done this quarter because the Y-12 cyclotron has been shut down since January 13 for repairs.

No progress has been made on the determination of the fission-yield curves mentioned in an earlier report.(33) This work is at a standstill pending the return of W. H. Jones of Emory University to the division this summer.

## Analysis for HRP

W. A. Brooksbank

*Flux Determinations for the Homogeneous Reactor.* It is possible to calculate the integrated flux of thermal neutrons, $f$, that cause fission of $U^{235}$ by using the following equation in which the value of $A$ is determined experimentally:

$$A = fN\sigma yS$$

where

$A$ = activity of any isotope produced in fission, dps,

$f$ = flux, neutrons/cm$^2$·sec,

$N$ = number of atoms of $U^{235}$,

$\sigma$ = fission cross section for $U^{235}$, barns,

$y$ = fission yield fraction of the nuclide,

$S$ = growth factor $(1 - e^{-\lambda t})$ for the nuclide.

In the homogeneous reactor the solubility of the fission products plays a major role in the choice of nuclides for the flux determination. The isotope used must be completely soluble for the duration of the operating cycle for which the flux determination is desired. On the basis of solubility, the most useful fission products would be the alkalies (cesium and rubidium).(34) Operating conditions of the HRE are such that the noble gases (xenon and krypton) leave the solution rapidly. Since these noble gas nuclides are the parents of the alkalies, most of the cesium isotopes would not be formed in the solution but rather in the traps of the off-gas lines.

Two isotopes that might be used for the flux determinations are $Rb^{86}$ and $Cs^{136}$. Both these nuclides are "shielded-chain" isotopes, which means that they are produced as primary fission fragments without noble gas parents. The fission yields are very low. Table 5 gives the characteristics of these isotopes.

The method for the determination of the activity of the alkalies is simple. Cesium is used as a carrier, and a preliminary separation of $CsClO_4$ decontaminates the $Rb^{86}$ and $Cs^{136}$ from the other fission products. This is followed by several $Fe(OH)_3$ scavengings. The final solution is reduced

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(33) T. H. Handley, "Analysis of Cyclotron Products," *op. cit.*, ORNL 1233, p. 26.

(34) W. L. Marshall, private communication to W. A. Brooksbank, January 1952.

Table 5

NUCLEAR PROPERTIES OF $Rb^{86}$ AND $Cs^{136}$

| NUCLIDE | REPORTED FISSION YIELD (%) | $T_{1/2}$ (d) | RADIATIONS (Mev) | |
|---|---|---|---|---|
| | | | Beta | Gamma |
| $Rb^{86}$ | 0.0001 | 19.5 | 1.8, 0.7 | 1.1 |
| $Cs^{136}$ | 0.01 | 13 | 0.28 | 1.2 |

in volume and the alkalies separated by ion exchange.(35)

Most of this quarter was devoted to shortening the time required for the ion-exchange separation. Instead of the original 140-cm IR-1 resin column,(35) a 15-cm by 1.1-cm-dia column and IR-100-H resin (<125 mesh) has been used with a flow rate of 0.6 ml/min and HCl concentration of 0.118 *N*. Under these conditions $Rb^{86}$ elutes in 275 to 400 min, and the total cesium, including $Cs^{136}$, may be stripped immediately afterward with 9 *N* HCl.

Samples of enriched uranium (10 mg) have been irradiated in the X-10 graphite reactor for 7 hr and the alkalies separated and determined. There was no definite evidence for the formation of $Rb^{86}$.

HRE fuel solutions irradiated in the LITR were next examined. There is some evidence for the existence of $Rb^{86}$ in the samples still being examined by the scintillation spectrometer (cf., "Sodium Iodide Scintillation Spectrometer," this report). If $Rb^{86}$ is formed in fission, the yield is lower than has previously been reported.

Samples of the HRE fuel solutions have been carefully purified of all alkalies by the anion exchange method described elsewhere (cf., "SCRUP Plutonium Determination," this report). Arrangements have been made to irradiate portions (10 mg) of $U^{235}$ in the LITR at fluxes of $1.0 \times 10^{12}$, $5.0 \times 10^{12}$, and $1.0 \times 10^{13}$ neutrons/cm²·sec. Calibration curves will be plotted of the activity of $Rb^{86}$ or $Cs^{136}$ per mg of uranium vs. neutron flux. These curves will be on the basis of a 4-hr irradiation. Samples of HRE fuel will be submitted before and after a 4-hr period at any power level, and the flux will be determined from the calibration curve. Samples of off-gas may also be analyzed for xenon as a further check.

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(35) W. A. Brooksbank, "Alkali Metals Separations," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 52.

### Identification of Radioelements

*Use of the Scintillation Spectrometer* (S. A. Reynolds, W. S. Lyon). The scintillation spectrometer offers promise for identification of gamma emitters by energy measurements. $Nb^{95}$, $Hg^{203}$, and $Pa^{233}$ in mixtures have been identified by this method. Many other qualitative applications will be made.

### Solvent Extraction Methods

*Several Solvent Systems for the Extraction of Uranium from Process Solutions* (F. L. Moore). In the development of a method for the determination of $U^{237}$ in process solutions, it has been necessary to investigate the decontamination possible in several systems. It was found that the gamma rays from 1 mg of $U^{235}$ (99.9%) gave 3374 cpm on a scintillation counter. Since $U^{237}$ may contain appreciable amounts of $U^{235}$, a correction for the $U^{235}$ content must be applied to the gamma-ray count.

It has been found that $UO_2^{++}$ ions readily extract from many acidic solutions, for example, hydrochloric, sulfuric, hydrofluoric, nitric, acetic, oxalic, phosphoric, formic, and maleic acids.

To test the decontamination of uranium from fission products in several solvent systems, a sample of the Purex process dissolver solution containing activity equivalent to 1.86 × $10^6$ cpm of gamma activity was extracted with the solvents indicated in Table 6. The uranium gamma activity of the sample was negligible. In all cases equal volumes of the aqueous and solvent phases were used, and the extractions were made at room temperature. The results in Table 6 indicate

Table 6

EXTRACTION OF FISSION PRODUCTS FROM PUREX SOLUTION IN SEVERAL SOLVENT SYSTEMS

| AQUEOUS PHASE | EXTRACTING SOLVENT | EXTRACTION TIME (min) | FISSION-PRODUCT GAMMA ACTIVITY EXTRACTED (%) |
|---|---|---|---|
| 1.2 *M* $Al(NO_3)_3$<br>2.8 *M* $HNO_3$ | Isopropyl ether | 3 | 0.16 |
| 3 *M* $HNO_3$ | 5% MDOA-xylene[(b)] | 5 | 2.00 |
| 1.5 *M* HCl | 5% MDOA-xylene[(b)] | 5 | 3.54 |
| 1.12 *M* $H_2SO_4$[(a)] | 5% MDOA-xylene[(b)] | 5 | 5.11 |
| 1 *M* HF | 5% MDOA-xylene[(b)] | 5 | 52.63 |
| 0.12 *M* maleic acid | 5% MDOA-xylene[(b)] | 5 | 24.07 |

[(a)] Two clear layers formed in the organic phase; only the top layer was counted.

[(b)] 5 g of MDOA diluted to 100 ml with xylene.

the decontamination achieved in each system. Each value is the average of two separate extractions.

No attempt was made to improve the fission-product decontamination either by washing the organic phase or by the use of reducing agents to prevent possible cerium and ruthenium extractions. It is planned to use the isopropyl ether system in the analysis of process solutions for $U^{237}$.

*Extraction of Anionic Yttrium in Several Systems* (F. L. Moore). The extraction of significant amounts of fission products from hydrofluoric acid and maleic acid, as shown in Table 6, prompted an investigation of the behavior of rare earths in various anionic systems with methyldioctylamine.

Scouting experiments indicated that radioyttrium could be partly extracted from dilute hydrofluoric acid with MDOA-xylene. Although the experiments were not conclusive, it is felt that radioyttrium was present in the dilute hydrofluoric acid as a negatively charged species.

In the study of the extraction of anionic yttrium, $Y^{91}$ tracer in a solution sample containing activity equivalent to $1.6 \times 10^5$ cpm of gamma activity was extracted from various acid systems with 5% methyldioctylamine in xylene or chloroform. Table 7 indicates that radioyttrium may be extracted efficiently from several complexing acids. The aqueous solution was extracted in 5 min with an equal volume of a 5% solution of methyldioctylamine in xylene or chloroform at room temperature.

Table 7

EXTRACTION OF ANIONIC YTTRIUM WITH METHYLDIOCTYLAMINE IN XYLENE AND CHLOROFORM FROM VARIOUS ACIDS

| AQUEOUS PHASE | EXTRACTING SOLVENT[a] | $Y^{91}$ ACTIVITY EXTRACTED (%) |
|---|---|---|
| 9.8 *M* HCl | 5% MDOA-xylene | 0.1 |
| 0.25 *M* $H_2SO_4$ | 5% MDOA-xylene | 0.5 |
| 0.125 *M* maleic acid | 5% MDOA-xylene | 2.1 |
| 0.019 *M* tartaric acid | 5% MDOA-C $HCl_3$ | 64.5 |
| 0.004 *M* tartaric acid | 5% MDOA-C $HCl_3$ | 22.2 |
| 0.017 *M* oxalic acid | 5% MDOA-C $HCl_3$ | 97.9 |
| 0.004 *M* oxalic acid | 5% MDOA-C $HCl_3$ | 93.6 |
| 0.018 *M* citric acid | 5% MDOA-C $HCl_3$ | 94.5 |
| 0.004 *M* citric acid | 5% MDOA-C $HCl_3$ | 47.9 |
| 0.110 *M* acetic acid | 5% MDOA-C $HCl_3$ | 12.6 |
| 0.024 *M* acetic acid | 5% MDOA-C $HCl_3$ | 18.6 |

[a] 5 g of MDOA diluted to 100 ml with xylene or $CHCl_3$.

Methyldioctylamine in xylene produced emulsions at times in the weak acid systems. The substitution of chloroform as the solvent effected a faster phase separation. With both solvents the aqueous phases were cloudy, but they cleared after standing.

In the future it is planned to study the pH-dependence of the extractability of the metal complex in the most promising systems and to study the behavior of americium and curium in those systems.

*Zirconium-Hafnium Separation* (F. L. Moore, G. W. Leddicotte). Work on this problem is described elsewhere (cf., "Extraction of Anionic Species: Zirconium and Hafnium," this report).

*Extraction of Tin and Antimony with Methyldioctylamine in Xylene* (D. J. Coombe). In the examination of extraction methods for separating antimony from tin, both in trace quantities, it was found that methyldioctylamine in xylene will effect a

**Table 8**

**EXTRACTION OF TRACER ANTIMONY WITH METHYLDIOCTYLAMINE IN XYLENE**

| AQUEOUS PHASE | | MDOA IN XYLENE PHASE (vol %) | TOTAL $Sb^{124}$ ACTIVITY EXTRACTED (%) |
|---|---|---|---|
| HCl (*N*) | OXALIC ACID (wt %) | | |
| 8 | | 4 | 99.9 |
| 6 | | 4 | 99.5 |
| 3.5 | | 2 | 83.0 |
| 2.6 | | 2 | 44.7 |
| 1.55 | | 2 | 2.6 |
| 1.25 | | 2 | 0.72 |
| 0.94 | | 2 | 0.35 |
| 1.06 | 2.51 | 2 | 5.5 |
| 0.95 | 0.25 | 2 | 6.9 |
| 0.95 | 0.5 | 6 | 19.9 |
| 0.95 | 0.25 | 6 | 20.8 |
| 0.95 | 1.26 | 5 | 15.6 |
| 0.95 | 0.5 | 5 | 14.8 |
| 0.95 | 0.25 | 5 | 15.0 |
| 0.95 | 0.13 | 5 | 15.6 |
| 0.95 | 0.05 | 5 | 15.2 |
| 0.95 | 1.26 | 2.5 | 7.7 |
| 0.95 | 0.5 | 2.5 | 7.5 |
| 0.95 | 0.25 | 2.5 | 7.3 |
| 0.95 | 0.13 | 2.5 | 8.3 |
| 0.95 | 0.05 | 2.5 | 8.6 |

fast and fairly clean separation. For determining the conditions under which antimony can best be separated from tin, a series of extractions was made from several test solutions containing different hydrochloric and oxalic acid concentrations and known amounts, activity-wise, of radiotin-113 or radioantimony-124. Data from the extractions are shown in Tables 8 and 9 and Fig. 24.

It was found that when a trace quantity of $Sb^{124}$ was contained in approximately 1 *N* HCl (aqueous), less than 0.5% of the total activity present was extracted into the MDOA-xylene phase. When oxalic acid was added to the aqueous phase, the amount of $Sb^{124}$ extracted was in proportion to the MDOA concentration in the xylene rather than to the oxalic acid concentration.

**Table 9**

**EXTRACTION OF TRACER TIN WITH METHYLDIOCTYLAMINE IN XYLENE**

Volume % of MDOA in xylene phase was 2.5% in each case

| AQUEOUS PHASE | | TOTAL $Sn^{113}$ ACTIVITY EXTRACTED (%) |
|---|---|---|
| HCl (*N*) | Oxalic Acid (wt %) | |
| 7 | | 99.6 |
| 6 | | 99.3 |
| 1.7 | | 99.0 |
| 0.85 | | 97.7 |
| 2.2 | 0.075 | 99.8 |
| 2.2 | 0.151 | 99.3 |

Preliminary examination of the extraction data shows that $Sn^{113}$ extracts from 1 *N* HCl both in the presence and absence of oxalic acid in the aqueous phase. The extraction of tin has not yet been studied extensively because of the lack of pure tin tracer of both sufficiently high specific activity and long life. More tests will be made when the tracer is available.

The data obtained so far indicate that a rapid separation of antimony from tin in trace amounts can be effected by extracting the tin from a 1 *N* HCl solution with 2 to 3 vol % methyldioctylamine in xylene.

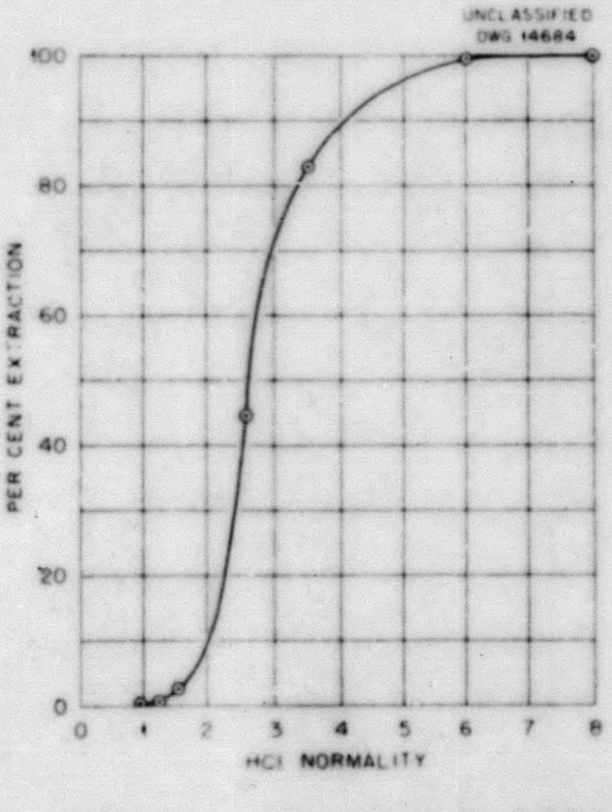

**Fig. 24. Extraction of Tracer Antimony with MDOA-Xylene as a Function of HCl Normality.**

## Applications of Ion Exchange in Radiochemical Analysis

*Separations of Rare Earths* (W. A. Brooksbank, R. R. Rickard(38)). A sample of mixed rare earths from aged fission products was submitted for analysis. An ion-exchange separation with citrate elution at 100°C was used,(32) and the results showed that the sample was mainly Pm$^{147}$. However, Y$^{91}$, Sm$^{151}$, Eu$^{155}$, and Ce$^{144}$-Pr$^{144}$ were isolated and identified. An unidentified activity was eluted between promethium and cerium. There are no known long-lived isotopes of neodymium and praseodymium formed in fission.(31) Praseodymium-144 would not elute as a band because of its short half-life (17 min) and the long time necessary for the column separation. The unknown material is an emitter of pure beta radiation, as shown by scintillation spectrometer study, and was found by range measurements to have a beta energy of about 0.2 to 0.3 Mev. Decay has not been appreciable in two months. Enough of this material will be separated to determine the beta energy accurately with the thin-lens beta-ray spectrometer. Ketelle of the Chemistry Division, has been very helpful in the identification of the activity peaks of the eluate and has expressed a continued interest in this unknown activity.

*Plutonium Determination* (W. A. Brooksbank, H. A. Parker(39)). The anion-exchange plutonium-uranium separation for the analysis of Chalk River dissolver solutions has been completed(40) and the following procedure adopted.

1. Reduce the 0.5- to 1.0-ml sample by heating it with 0.5 ml of 5 *M* $NH_2OH \cdot HCl$ for 1 hr at 80 to 90°C. Add 200 $\mu$l of 1 *M* KI. Make the solution 6.5 *M* in HCl by adding 0.85 to 2.2 ml of concentrated HCl.

2. Transfer the solution quantitatively to the top of the first column with the smallest possible volume of 6.5 *M* HCl. (This column is made of 11-mm-ID, 6-in.-long, glass tubing drawn down at the bottom to retain a glass wool plug. It is filled with 2.5 g of Dowex A-1 resin, 270/325 mesh, conditioned with 6.5 *M* HCl.)

3. Wash the resin with 6.5 *M* HCl at a flow rate of 1 ml/min until 50 ml of eluate has been collected. Add 6 ml of 1 *M* $NaNO_2$ and stir for 5 minutes. Add 90 ml of concentrated HCl and mix well.

4. Pass this feed at a flow rate of 0.2 to 0.5 ml/min over the second column. (This column has an inside diameter of 4 mm and contains 150 mg of Dowex A-1 resin, 270/325 mesh, conditioned with 9.5 *M* HCl.) Discard the effluent. Wash the column with 5 ml of 9.5 *M* HCl.

5. Strip the plutonium from the small column by washing with 7 *N* $H_2SO_4$ until 15 ml has been collected. The sample is then ready for the titration of the plutonium.

The fission-product decontamination obtained with this procedure is adequate, as is shown by the decontamination factors in Table 10.

Losses of plutonium in the course of any method of analysis for Chalk River dissolver solutions must be kept at a minimum, and the over-all accuracy of the plutonium procedure must be 1% or better. Table 11 gives the

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(38) Radioisotope Production Control Group.

(39) General Radiochemical Group.

(40) W. A. Brooksbank, H. A. Parker, and W. T. Mullins, "Plutonium Separation by Ion Exchange," *op. cit.*, ORNL-1233, p. 33-34.

losses in the anion-exchange separation. The losses were determined by dissolving the resin from the columns in a mixture of concentrated $H_2SO_4$ and $HNO_3$ and determining the plutonium by the $LaF_3$ method. The waste stream was analyzed by the same method without pretreatment. The recovery of plutonium as determined by alpha counting was 99.3%. The plutonium losses are also being studied by the use of standard plutonium solutions and potentiometric titration of the plutonium with cerium(IV).

**Table 10**

**DECONTAMINATION FACTORS FOR TYPICAL ORNL DISSOLVER SOLUTION**

| ELEMENT | D.F.* |
|---|---|
| Zirconium | 4 |
| Niobium | 100 |
| Ruthenium | $8.7 \times 10^3$ |
| Total Rare Earths | $1.3 \times 10^5$ |
| Uranium | $10^5$ |

*D.F. – the decontamination factor is the ratio of the activity in the feed to the activity in the product.

The procedure has been issued to the Laboratory and Semi-Works Control group for further testing.

## ACTIVATION ANALYSES

G. W. Leddicotte

**Proposed Price Schedule for Activation Analyses.** Increased interest by industrial organizations in neutron activation analysis as an analytical service has prompted the consideration of a tentative price schedule for such service. A proposed schedule was sent to the ORNL Director's office and to the AEC for evaluation. It is expected that if the price schedule is approved it will be announced in such publications as the quarterly information bulletin of the Isotopes Division, AEC, *Isotopics*, or *Chemical and Engineering News*, and a press release is being considered.

**Analytical Procedures.** Precipitation, ion-exchange, and solvent-extraction methods are being used for determining trace elements in various samples after irradiation in the X-10

**Table 11**

**PLUTONIUM LOSSES OCCURRING IN THE ANION-EXCHANGE SEPARATION STEP IN THE ANALYSIS OF CHALK RIVER DISSOLVER SOLUTION**

| STEP IN THE SEPARATION PROCESS | PLUTONIUM LOSS (% retained on column) |
|---|---|
| Plutonium-uranium separation | 0.0004 |
| Plutonium recovery and fission-product decontamination | 0.05 |
| Waste stream | 0.31 |
| Total | 0.36 |

graphite reactor. Specific precipitation procedures will be reviewed at some future time. Ion-exchange techniques will soon be applied to the analysis of rare earth mixtures. A brief review of the application of solvent extraction techniques to the analytical determination of zirconium and hafnium follows.

**Extraction of Anionic Species: Zirconium and Hafnium** (G. W. Leddicotte, F. L. Moore). Anionic solvent extraction with methyldioctylamine has been studied extensively by Moore.(41) His findings led to the application of this method to specific problems. In cooperation with him, the Activation Analyses group has studied the separation of niobium and tantalum(42) and has also investigated this technique for the separation of zirconium and hafnium from each other. The partition of radioactive traces of these elements in the following systems has been studied:

$H_2O$-HCl, MDOA-xylene,

$H_2O$-$H_2SO_4$, MDOA-xylene,

$H_2O$-HCl-$NH_4SCN$, MDOA-xylene,

$H_2O$-$H_2SO_4$-$NH_4SCN$, MDOA-xylene,

$H_2O$-HCl-oxalic acid, MDOA-xylene.

Equal volumes of aqueous and organic phase were used in each experiment, and the extraction was made by either manual or mechanical shaking in a separatory funnel for 5 minutes. Each phase was checked for zirconium or hafnium gamma activity by use of a scintillation counter.

In the ($H_2O$-HCl, MDOA-xylene) system, it was found that both zirconium and hafnium as radioactive tracers are quantitatively extracted from the aqueous phase into the organic phase when the HCl concentration of the aqueous phase is 8 *M* or greater. The results of the extractions in which the systems ($H_2O$-HCl-$NH_4SCN$, MDOA-xylene) and ($H_2O$-HCl-oxalic acid, MDOA-xylene) were used were inconclusive, and study of these systems is to be continued. The systems ($H_2O$-$H_2SO_4$, MDOA-xylene) and ($H_2O$-$H_2SO_4$-$NH_4SCN$, MDOA-xylene) have shown the most promise. It was found that hafnium radioactive tracer will not extract from the aqueous into the organic phase in the system ($H_2O$–0.05 *M* $H_2SO_4$–0.16 *M* $NH_4SCN$, 5 wt % MDOA-xylene), whereas zirconium radioactive tracer will extract in amounts of 30 to 40% of the radioactivity present. Additional work is to be done on this system as well as the ($H_2O$-$H_2SO_4$, MDOA-xylene) system. The latter system showed that some separation is possible. At present, the effects of MDOA concentration in the xylene and of concentration (mg/ml) of inactive zirconium and hafnium are being studied.

**Applications of Activation Analysis.** Sodium, calcium, and gallium in aluminum have been determined routinely. Activation analysis is now being used for the nonroutine determination of traces of As, Ni, Fe, Cr, V, Hg, and Cu in petroleum hydrocarbons. After neutron irradiation of the sample, inactive isotopic carrier as the metallo-organic compound is added to a portion of the irradiated sample contained in the sample dish of a Parr oxygen bomb. After destruction of the organic material by ignition of the bomb, the contents of the bomb were washed into a beaker, "holdback" carriers were added, and the specific chemical separations were made.

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(41) F. L. Moore, "Extraction of Anion Complexes," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, p. 54.

(42) F. L. Moore, "Extraction of Anionic Species (Niobium and Tantalum)," *op. cit.*, ORNL-1129, p. 35; "Extraction of Anionic Species – Protactinium, Thorium, Zirconium, and Hafnium," *op. cit.*, ORNL-1233, p. 35.

Additional work is to be done on these separation procedures.

A steam-jacketed ion-exchange column of the type used by Ketelle and Boyd(32) is being set up for the separation of trace samarium from $Nd_2O_3$.

Application of activation analysis to the determination of the following is being considered: lithium in metals, arsenic in feeding materials, trace quantities of Toxaphene(43) in milk, trace elements in chlorinated hydrocarbons, and selenium in animal tissue.

## SPECTROCHEMICAL ANALYSES

C. Feldman
A. Estepp M. Murray
M. Wittels

**Determination of Boron in $Fe_2O_3$.** The cross sections of several $Fe_2^{58}O_3$ preparations were found to be unexpectedly high, and since the samples involved were suspected of being contaminated with boron, a quantitative spectrochemical analysis for boron was requested. The spectrochemical determination of traces of boron in the presence of large amounts of iron involves two serious difficulties. First, the chemical form of the boron in the sample is not known, and it is therefore difficult to prepare synthetic standards that can be depended on to give the same volatilization and excitation behavior as the sample. Second, the most sensitive boron line, B 2496.78, is only 0.25 Å away from a fairly strong iron line. When the boron-to-iron ratio is low and the spectrograph has only moderate dispersion (5 to 7 Å/mm), it is difficult to resolve these lines under conditions conducive to accurate photometry.

The first difficulty can be circumvented by dissolving the sample, preparing synthetic standard solutions, and subsequently treating standards and sample alike. If an instrument of higher dispersion cannot be used, the other difficulty must be overcome by separating the boron from the iron. The separation cannot be made by precipitating the iron because of the danger of coprecipitating boron. The use of ion exchange was adopted because it offered the possibility of effecting a quick and complete separation while keeping the sample volume low enough (that is, the boron concentration high enough) to permit subsequent spectrographic determination of the boron.

Test runs showed that boron at the 5 ppm level in 0.1 *N* HCl solution is not retained on a 3-ml column of Dowex-50 resin contained in a 7-mm-ID buret, whereas 40 mg of iron in the same solution is quantitatively adsorbed. It was found that evaporation of the acid eluate caused loss of boron; however, this loss was prevented if the solution was alkalized before evaporation. The data given in Table 12 were obtained by the following procedure.

Dissolve $Fe_2O_3$ by adding two to three times the stoichiometric amount of approximately 4 *N* HCl. If the $Fe_2O_3$ does not dissolve, warm the mixture in a reflux flask made by inserting a vertical tube with a standard tapered end into the neck of a 25-ml Erlenmeyer flask. Wrap the upper end of the tube in moist filter paper to prevent the escape of boron vapors. When dissolution is complete, dilute the solution with distilled water until it is 0.1 to

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(43) An insecticide of high chlorine content manufactured by Hercules Powder Co.

Table 12

RECOVERY OF BORON AND IRON FROM 0.1 *N* HCl SOLUTION

| ANALYTICAL PROCEDURE | BORON (μg) | | IRON (μg) | |
|---|---|---|---|---|
| | Taken | Recovered | Taken | Recovered |
| Run through column and evaporate almost to dryness | 44.0 | 37.5 | 40,000 | <3 |
| Run through column, make alkaline to phenol red with $NH_4OH$, and evaporate almost to dryness | 44.0 | 43.2 | 40,000 | <3 |

0.2 *N* in HCl and pass it through a 3-ml column of Dowex-50 resin contained in a 7-mm-ID buret at a rate of approximately 0.5 ml/min. Wash the column with at least 3 ml of 0.1 *N* HCl at the same rate. Collect the eluate in a volumetric flask of such volume that the final boron concentration will be 0.5 to 10.0 ppm, add 75 μg of cobalt in solution and 0.05 ml of concentrated $H_2SO_4$ for each milliliter of final volume, and make to volume. Measure the intensity ratio, B 2497.73/Co 2424, and read the boron concentration from a previously prepared working curve. The lower limit of detection can be lowered by a factor of 2 by adding 2.5 mg of Ca per milliliter of solution to be exposed spectrographically.

**Determination of Beryllium in Thorium Metal.** The slowness of the usual method for dissolving thorium (dilute $HNO_3$ plus trace of HF) prompted a search for a faster method. It was found possible to dissolve 100 mg of thorium in less than 5 min by the following method. Place a weighed sample in a 30-ml platinum dish or crucible and add 1 to 2 ml of concentrated HCl. When the reaction has subsided and all the undissolved thorium is in the form of a finely suspended powder, add 10 ml of distilled water and stir. Add 1 drop of (1 + 10) HF and stir. Warm until dissolution is complete and add more concentrated HCl if necessary.

The thorium samples received usually contain beryllium in concentrations of 0.005 to 0.100%. It is impossible to use the Be 3131 line for this determination if it is done in solution, since this line has a thorium interference. The following procedure was therefore adopted. Weigh 30 to 50 mg of thorium metal into a 30-ml platinum dish or crucible, dissolve the metal in the manner described above, add 1875 ± 30 μg of cobalt as the nitrate, and make to a 25-ml volume. Expose the solution by the porous-cup method, read the intensity ratio Be 2348/Co 2424 and/or Be 2348/Co 2521, and obtain the beryllium concentration from an appropriate working curve.

**Determination of Traces of Cesium in $Rb_2CO_3$ and in $H_2O$.** Because of the extremely low excitation potential and strong self-reversal of Cs 8521, it is desirable to use an alkali metal as the internal standard for determining traces of cesium. However, since the rubidium salts received for analysis contain varying amounts of these alkalies, accurate adjustment of the internal standard concentration is often difficult. Other elements used as internal standards could not be expected to follow the self-reversal behavior of Cs 8521 and would therefore be unsatisfactory.

This problem has been investigated by a modification of the line-width method. As ordinarily applied to trace analysis, this method involves measuring the width of the internal standard line at the transmittance level of the peak of the trace element line. However, any self-reversal on the part of the latter directly affects the result obtained, which is thus in no way superior in reproducibility to the intensity ratio of a self-reversed line to that of a non-self-reversed line determined by orthodox photometry. The inverse process, that is, measurement of the width of the trace element line at the transmittance of the peak of the internal standard line, is, in effect, inapplicable to trace lines in the moderate density, since the internal standard line in this case must always be weaker than the trace line. Use of sufficiently low concentration of internal standard would lead to very poorly defined photometric conditions.

This difficulty could be circumvented, however, by using an internal standard concentration high enough to give an accurately measurable line but making the trace line-width measurement at a transmittance level correspond to some empirically fixed fraction of the internal standard intensity. The transmittance level (and thus the aforementioned fraction) selected should be as high as possible above background but low enough to avoid the central or more self-reversed portions of the trace line.

Preliminary tests of this method by using Cs I 8521 as the trace line and Ca II 8542 as the internal standard line show that a continuous working curve running from 7 to 750 ppm of cesium in a 0.5% rubidium solution can be obtained. Ca II 8542 is one of the few sensitive lines in this region but has proved poorly suited for this use because of the wide difference in excitation potentials between it and Cs I 8521. Good precision is obtained by using K I 7664.9 as the internal standard, but variation of the potassium content of rubidium samples makes its use for this purpose impractical. The search for a suitable internal standard line is continuing.

## INORGANIC PREPARATIONS

D. LaValle R. H. Sampley

**Aluminum Phosphide** (D. LaValle). The work on the preparation of aluminum phosphide was continued. The preparation is essentially a problem of bringing about a reaction between aluminum powder and red phosphorus (in excess) at approximately 400°C either in vacuum or an atmosphere inert to this reaction (hydrogen or argon) and subliming off the excess phosphorus.

Previous preparations employed porcelain boats in argon atmospheres, sealed and evacuated quartz tubes, and metal bombs completely filled with the aluminum-phosphorus mixture. One successful preparation was made in a porcelain boat, but the yield was too small to be of use and the preparation could not be duplicated. All other attempted preparations were failures. Segregation of materials occurred in the metal bombs and quartz tubes. The aluminum-phosphorus mixture is supposed to ignite when heated locally, but this exothermic reaction occurred in only

3 of the 15 or more experiments made under the various conditions noted above.

Moisture was probably present in experiments in which ignition occurred. The resulting $Al_2O_3$ plus the original oxide in the aluminum was in an amount intolerably large for the proposed use of the compound. Further experiments showed that with completely dried materials the reaction proceeded only to about 85% completion, and the metallic aluminum remaining was not undesirable if it could be reduced to 10% of the total product.

Two successful preparations were made by using aluminum dust of high purity, a 400-mesh screen, and a double-chambered quartz tube for carrying out the reaction. The products differed widely in chemical reactivity but had identical x-ray patterns.

The aluminum powder used was screened to 400 mesh and dried by vacuum desiccation for several days. The red phosphorus was purified with $CS_2$ and HCl and dried in a stream of hydrogen at 200°C. Without exposure to air, the materials were transferred to a dry-box and ground together in a mortar.

A quartz tube with two 20-mm-ID chambers connected by a 2-in. length of 8-mm-ID tubing was used for the first successful preparation. One of the chambers opened to the atmosphere through a 3-in. length of 8-mm tubing. The reaction mixture was placed in the lower chamber, and the tube was evacuated and sealed off above the upper chamber. The tube was completely enclosed in a furnace and the temperatures brought up to 500°C and maintained for 24 hours. The tube was then pulled far enough out of the furnace to expose the empty chamber, and the phosphorus was allowed to sublime and condense into this chamber. The tube was then sealed off at the constriction to isolate the excess phosphorus from the AlP. The remaining product, which yielded 85% AlP, was then ground in a mortar with additional dry phosphorus, and the mixture was treated again in the same type of double-chambered quartz tube at 500°C. The AlP yield increased to 90%.

The materials for the second successful preparation were treated in the same way except that the dry phosphorus was also screened to 400 mesh before being mixed with the 400-mesh aluminum. A double-chambered quartz tube in the shape of a V, with the constriction at the point of the V, was used. This V-tube was inverted and held in a clamp on a ring stand. The material was firmly packed into one chamber by tapping, and a burner was used to heat around the tube at the surface of the mixture. Ignition started and proceeded downward with only a slight application of the flame to keep it going. The excess phosphorus was sublimed over into the other leg of the tube and sealed off. The remaining product yielded 91% AlP and was not reprocessed.

The products of both successful preparations were analyzed for AlP, metallic aluminum, total aluminum, and total phosphorus, and directly for $Al_2O_3$ by the sublimation of aluminum and phosphorus with dry HCl gas at 500°C.(44) In the reprocessed material the $Al_2O_3$ content was less than 3% and in the other product less than 1%. Both materials were accepted and used by the Chemical Physics group of the Chemistry Division.

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(44) W. E. White and A. H. Bushey, Aluminum Phosphide - Preparation and Composition," *J. Am. Chem. Soc.* **66**, 1666 (1944).

**Phosphors and Other Compounds** (R. H. Sampley). The preparation of phosphors and other compounds for the Physics Division continues. The following were prepared in various quantities: LiI, LiBr, $Li_2CO_3$, HI, $SnBr_2$, neodymium ethyl sulfate $[Nd^{142}(C_2H_5SO_4)_3 \cdot XH_2O]$, $Mn(OH)_2$, $CdI_2$, $In_2O_3$, cerous ethyl sulfate $[Ce(C_2H_5SO_4)_3]$. The following compounds were purified: HBr, 6 lb; LiI; and LiCl, 16 pounds.

Phosphors were prepared as indicated in Table 13. The most promising phosphors found thus far are LiI and LiBr.

Table 13

PHOSPHORS PREPARED FOR THE PHYSICS DIVISION

| PHOSPHOR | ACTIVATORS |
|---|---|
| LiBr | Sb, Bi, Ce, Cr, Cs, Cu, Dy, Eu, Ho, In, Pb, Mn, Nb, Os, Ru, Se, Ag, Ta, Te, Tl, Sn, Y, Zr |
| LiI | Same as for LiBr |
| LiF | Same as for LiBr |
| LiCl | Same as for LiBr |
| $Li_2BeF_4$ (Lithium fluoroberyllate) | Eu |

## ANALYTICAL CHEMICAL CONTROL OF THE HRE SOLUTION

R. H. Powell

**Princo Densitrol.** The following inventory list of the Princo Densitrol units and auxiliary equipment on hand is presented as a preface to the status report on the development of the Princo Densitrol.

Two low-temperature (50°C) Densitrol units with pyrex glass plummets calibrated for the specific gravity range of 1.0330 to 1.5300 (20°C/4°C)

One high-temperature (250°C) Densitrol unit without a plummet, which must be developed for use at this temperature since a pyrex plummet is not satisfactory

One type-347 stainless steel plummet pressurized internally with $N_2$ for the low-temperature Densitrol unit

One calibrated pyrex glass plummet for the low-temperature Densitrol unit

A soft-iron core tube for use in construction of the high-temperature metal plummet

Two Lavite-base, glass-insulated, copper-wire-wound microformers for the low-temperature Densitrol unit

One Lavite-base, glass-insulated, silver-wire-wound microformer for the high-temperature Densitrol unit

One manual-type, self-regulating, type-347 stainless steel, Kates flow regulator with a variable flow range of 0.1 to 0.5 gpm

One fixed-flow-type, self-regulating, type-347 stainless steel, Kates flow regulator for 0.25 gpm flow

One low-temperature Densitrol unit, together with its Brown recorder for automatically recording the specific gravity of the HRE uranyl sulfate fuel solution over a specific gravity range of 1.0330 to 1.0530 (20°C/4°C), was installed in the HRE mockup at Y-12 in December 1951. A pyrex plummet, calibrated for the Densitrol unit that has an average operating temperature of 50°C, and a Bakelite-base microformer(45) have been installed as part

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(45) W. H. Davenport, Jr. and R. H. Powell, "Chemical Control," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending November 15, 1951*, ORNL-1221, p. 53, esp. p. 54.

of the unit. At the time these installations were made the Lavite-base, glass-insulated, wire-wound microformer had not been received nor had the metal plummets been developed to a satisfactory stage where their use could be recommended.

The mockup unit has not yet been tested because of higher priority testing of pumps with water instead of fuel. It cannot now be stated when the Densitrol will get its first testing and evaluation at the 70°C temperature that is expected in the mockup. The 70°C temperature instead of a 50°C temperature is a concession to present operational requirements of the mockup. It is hoped that a metal plummet and a Lavite-base, glass-insulated, wire-wound microformer may be substituted in the Densitrol prior to the mockup testing.

The second low-temperature Densitrol unit has been utilized in a laboratory test loop with solution circulated by a small centrifugal pump. A reservoir designed to permit change and dilution of solution and heated by a spherical mantle is included in the system. Studies are being made of the effect of flow rate, solute concentration, temperature, and bubble content of the liquid, and of the microformer-setting position on the performance of the Densitrol when pressurized metal plummets are used.

An internally pressurized plummet constructed of types-347 and -316 stainless steel is shown in Fig. 25. The central section of the plummet was made of type-347 stainless steel tubing with 0.015-in. wall thickness. The design and fabrication of the plummet were a joint effort of the Precision Thermometer and Instrument Co., Philadelphia, Pa., and ORNL. This plummet is currently being tested in $Na_2SO_4$ solutions of varying specific gravity and from 20 to 70°C with atmospheric pressure external to the plummet. The plummet has internal nitrogen gas pressures and other properties as indicated in the following tabulation. The original attempt to fill the plummet to an internal pressure of 920 psi at 30°C was unsuccessful.

Weight, g:

Ring = 5.6
Chains plus ring = 9.6
Sinker = 16.0
Total = 100.0

Volume, cc:

Float body plus pressure tube = 85.0
Chains = 0.19
Sinker = 1.9

Nitrogen-filled with 4.4 g of $N_2$, giving internal pressures as follows:

745 psi at 27°C
802 psi at 50°C
850 psi at 70°C

*Technique for Internally Pressurizing Metal Plummets.* The technique for filling stainless steel plummets with nitrogen and titanium plummets with argon under pressure was developed mainly by Fox of the ORNL Research Shops. It consists of the following operations:

1. Weigh the plummet prior to the filling operation.

2. Set up an adequate explosion shield.

3. Screw a small, brass T-union onto the fill point of the plummet. (Pressure valves are threaded into opposite ends of the arms of the T.)

4. Bleed a cylinder of nitrogen gas, with pressure gage attached, to within a few pounds more than the desired fill pressure. Attach the cylinder to one arm of the T with the T valve open.

5. Attach an evacuation line to the other arm of the T. Evacuate the entire system up to the main nitrogen-cylinder regulator valve, and then flush small amounts of nitrogen through the plummet, T connections, and T valves. Repeat the evacuation of nitrogen and the remaining air. At this point of the procedure introduce several pounds of helium gas for future leak detection and to maintain a *slight, positive*, internal helium pressure during the future welding operation. (This is best accomplished by use of a small balloon filled with helium.) Introduce the helium gas through a second T connection (with suitable valve) on the line from the nitrogen cylinder to the plummet.

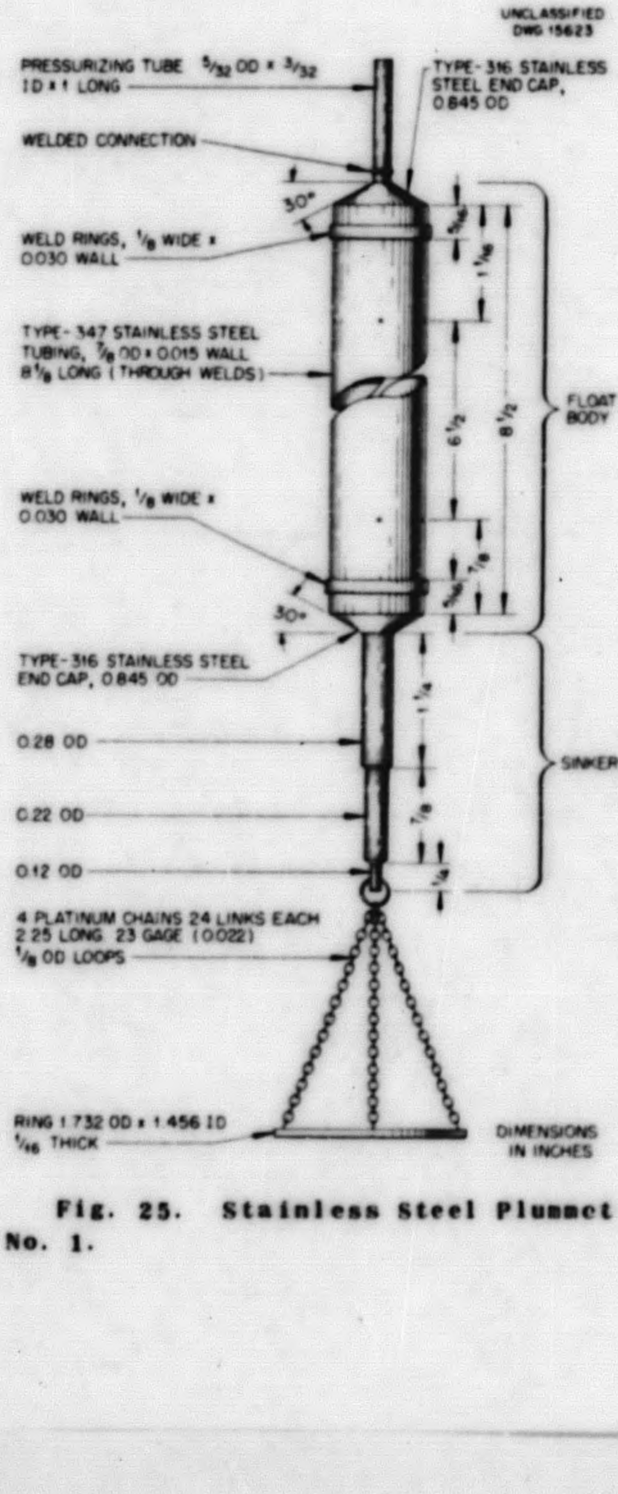

**Fig. 25. Stainless Steel Plummet No. 1.**

6. Close the valves that isolate the helium-filled balloon and the valve that isolates the evacuation system. Keep the valve connecting the plummet to the nitrogen transfer line open, and then open the main nitrogen-cylinder valve for filling the system at the complete pressure of the nitrogen tank.

7. Close all valves that are open.

8. Raise a Dewar flask containing liquid nitrogen into position so that the plummet is cooled when it is immersed up to its fill point. After sufficient time (5 min) has elapsed for the plummet and the gas it contains to reach temperature equilibrium with the liquid nitrogen, lower and remove the Dewar flask, unscrew the plummet from its attachment, and immediately weld the plummet by the heliarc technique. Quickly insert the plummet into an explosion-proof case and allow it to warm to room temperature, at which temperature it will be pressurized.

9. For safety test the plummet for flaws by submitting it to elevated temperature by use of a carefully controlled heat radiator inside an explosion case and preferably inside a bomb shelter.

10. Cool and weigh the pressurized plummet.

11. Utilize the residual helium for leak detection.

The same general technique is used in pressurizing a titanium plummet with argon. However, the flushing of the apparatus is conducted with helium instead of nitrogen.

In the case of the titanium plummet, a second and successful attempt was made to fill it with argon. It had been originally filled at too low a pressure and gas escaped during the freezing of the argon or during the welding process. The weld was leakproof. The argon within the plummet was refrozen by immersing the entire plummet in liquid nitrogen, and then the end of the welded tip was ground off, allowing the argon in the plummet to escape as the plummet approached room temperature. Thus the titanium plummet was pressurized to 1009 psi at 20°C with 8.7061 g of argon. The very small weight and/or pressure of helium added from the balloon was neglected.

*Problems Encountered in Pressurizing Titanium Plummet with Argon.* The titanium plummet, fabricated and developed at ORNL,(46) was successfully pressurized after a second attempt. The rim welds were strength-tested by dead-weight testing before the plummet was pressurized with argon, and it was found that the welds could withstand an internal pressure of up to 2500 psi at room temperature. After the titanium plummet was filled with argon to 1009 psi at room temperature (20°C) and after it was subjected to liquid nitrogen for freezing the argon, there was concern over the strength of the final weld made by the heliarc process at the fill point. An arbitrary safety factor of 1000 psi over and above the fill pressure of 1009 psi (a total of 2009 psi) was decided upon to protect personnel handling the unshielded plummet.

Precaution was taken against the action of heated nitrogen, hydrogen, and oxygen when the titanium plummet was subjected to a temperature of 313°C, at which temperature the internal argon pressure was 2000 psi.

A 0.25-in. quartz tube was inserted in each end of the explosion case, which was made of 2-in., sch. 80 steel pipe equipped with perforated, screw-cap ends. Temperature was determined by use of an iron vs. constantan thermocouple and a Leeds & Northrup potentiometer. The temperature-sensitive end of the thermocouple was placed against the titanium plummet within a quartz radiator. The heating elements were wound around the radiator, and the entire assembly was within the explosion case.

In pressure testing, the temperature of the titanium plummet was slowly increased to 313°C over a 65-min period. At 313°C the plummet exploded at a total pressure of 2000 psi, which was the upper limit of pressure set for the test. Figure 26 shows the nature of the rupture. Note that the plummet did not fragment and especially that all welds remained intact.

Since the titanium plummet was weakened at high temperatures, for example, 313°C, its performance might be unsatisfactory under certain high-temperature HRE conditions such as a "scram" or a failure of a cooling unit for reducing the fuel temperature in the Densitrol line from 250°C to the 50 to 70°C range, which would cause the plummet to rupture if it had been filled to 1000 psi at 50 or 70°C to counterbalance the external pressure.

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(46)*Ibid.*, p. 53, esp. p. 56, Figs. 13 and 14.

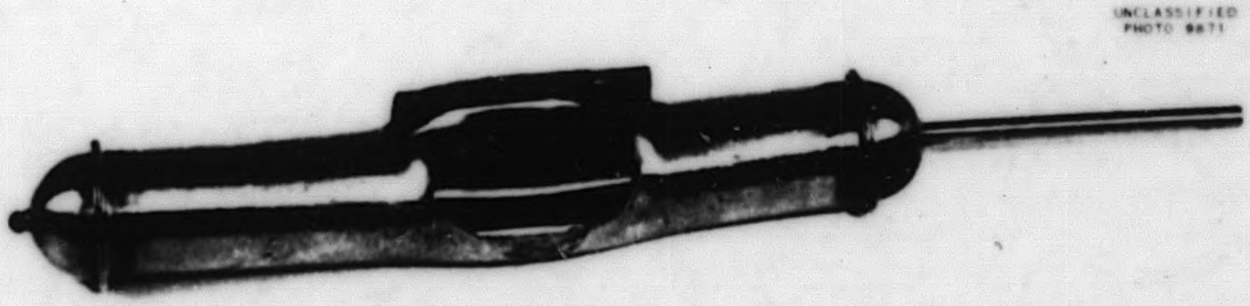

**Fig. 26. Ruptured Titanium Plummet No. 1.** Wall thickness, 0.025 inch.

A 0.025-in. titanium plummet (with 1000-psi internal pressure) used in the 250°C Densitrol unit could be unsatisfactory if warping or volume-change developed at 250°C. It is recognized that a titanium plummet operating at 250°C would be *designed* for use with 1000 psi of argon at 250°C. The titanium plummet (Fig. 26) was designed for low-temperature service; consequently, approximately 1000 psi of pressure was required.

The problem of gas attachment to external surfaces of metal plummets is being investigated over the temperature range of 50 to 70°C where the effect of bubble attachment is not so critical as at the lower temperatures (20°C).

In general, the design of the titanium plummet (Fig. 26) caused less bubble retention than the design of the stainless steel plummet (Fig. 25) when both plummets were tested in (and viewed through) a glass cylinder incorporated in a laboratory test loop. Air and oxygen were used to create bubbles on the plummets. An increase in temperature (70°C) aids in the over-all removal of bubbles from the plummets.

**Radiation-Resistant Glasses.** Neutron-absorbing, cadmium borosilicate, optical glasses(47) have been examined for changes in their optical spectrum after exposure in in the X-10 graphite reactor at 250°C, at an average flux of $7.3 \times 10^{11}$, for $5.4 \times 10^{18}$ nvt. The chemical compositions of the glasses identified as 1M, 2M, 3M, and 4M are given in Table 7 of ORNL-1221(48) and by Melnick.(49) Their conditions after the first radiation exposure have been reported.(50) Measurement of further changes in their optical spectra after irradiation under similar temperature conditions, in hole 60, were made 30 hr after reactor shutdown, which was 17.5 hr after removal of the glass samples from the reactor (as contrasted to a similar seven-day period *after* removal from the reactor at the end of the first irradiation exposure). Certain differences in optical spectra may be attributed to a seven-day delay at room temperature

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(47) W. H. Davenport, Jr. and R. H. Powell, "Analytical Chemical Control of the Homogeneous Reactor Solution," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950*, ORNL-925, p. 260, esp. p. 275.

(48) Davenport and Powell, *op. cit.*, ORNL-1221, p. 60.

(49) L. M. Melnick, H. W. Safford, K. H. Sun, and A. Silverman, "Neutron-Absorbing Glass: $CdO$-$SiO_2$-$B_2O_3$ System," *J. Am. Ceram. Soc.* **34**, 84 (1951).

(50) W. H. Davenport and R. H. Powell, "Radiation-Resistant Glasses," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 81.

in measuring the spectra. The seven-day delay was occasioned by inability to remove the glasses from a radiation shield where similarly irradiated bombs were being stored for radiation cooling. At the end of the irradiation period each glass had more than 20 r/hr total activity, as measured at contact by a cutie pie. After the second irradiation the glasses had a somewhat higher activity: 10 r/hr at 2 in.

It is to be emphasized that the damage to glasses, coded ORNL-1M, -3M, and -4M, observed at the end of $5.4 \times 10^{18}$ nvt was only slightly different from that observed at the end of a second irradiation period of $9.23 \times 10^{18}$ nvt at 250°C. The total exposure was $1.46 \times 10^{19}$ nvt. All glasses remained in the dark while they were in the reactor and after removal, except as indicated on Figs. 27, 28, 29, and 30. The damage is indicated by absorbance curves for these glasses (Figs. 27, 28, 29, and 30). It is recognized that some damage occurred in each glass from its self-radiation *at room temperature* during the period between the end of the first irradiation exposure (July 2, 1951) and the beginning of the second exposure (July 23, 1951) and during a seven-day waiting period after the first irradiation.

An early steady-state equilibrium may have been closely approached at 250°C; however, this possibility cannot be proved by this experiment. Reference to the figures indicates the following:

1. The most stable glass *after initial irradiation* is the one with highest boron content.

2. The least stable glass *after initial irradiation* is the one without any "added" boron.

3. Self-induced damage sets in soon when the glasses are removed from the 250°C inpile temperature to room temperature out of the reactor.

4. The net damage is related to the opposite effects of self-damage from induced activity and of the change in the rate of annealing of the glass at 250°C to room temperature, at which temperature the annealing rate is much slower.

5. Exposure of the irradiated glasses to ordinary light from a 150-w tungsten light bulb can temporarily cure, at room temperature, the major net damage; but once the light source is removed, the drastic self-damaging effect predominates.

6. The possibility exists that certain glasses and naturally transparent inorganic materials and certain fused materials can be made useful for inpile service or for low-pressure reactor service, when a high annealing temperature (250°C is not considered a true annealing temperature) and a light source are concurrently applied to these optical materials. Further, there is a suggestion that a steady state of radiation damage may be achieved early if temperature and light exposure are likewise controlled. Further study of this subject is recommended.

Certain materials such as fused spinel, fused sapphire, and fused titania possess remarkable corrosion resistance to 0.17 *M* uranyl sulfate at 250°C, and because of this feature alone should be carefully examined for resistance to radiation damage and for possible reactor service such as optical windows, reactor liners, and electrical insulating materials in contact with uranyl sulfate. No uranyl sulfate concentrations higher than 40 g of uranium per liter have been studied.

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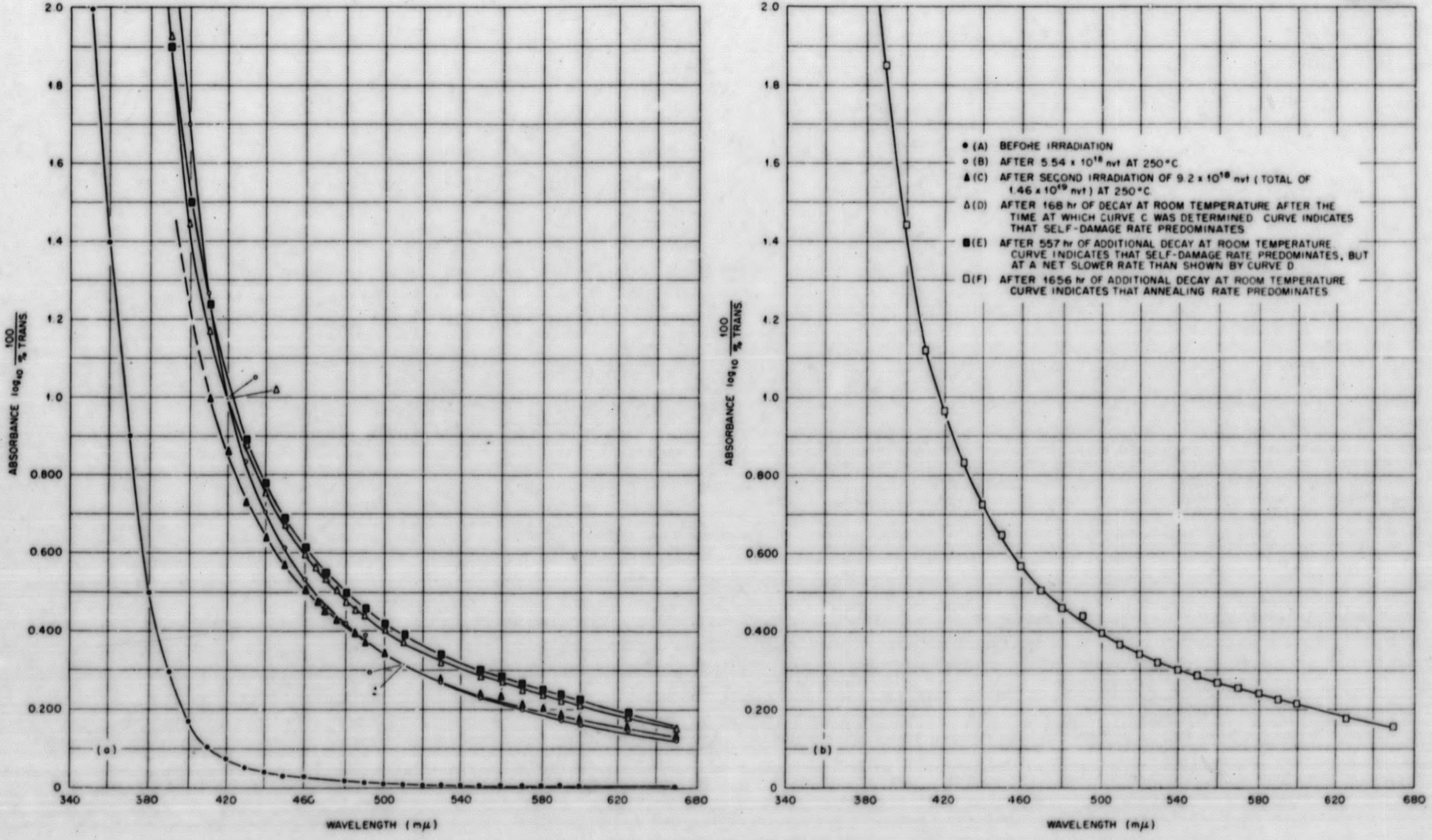

**Fig. 27. Absorbance Curves for Radiation-Resistant Glass, ORNL-1M.** Boron, very strong; cadmium, weak.

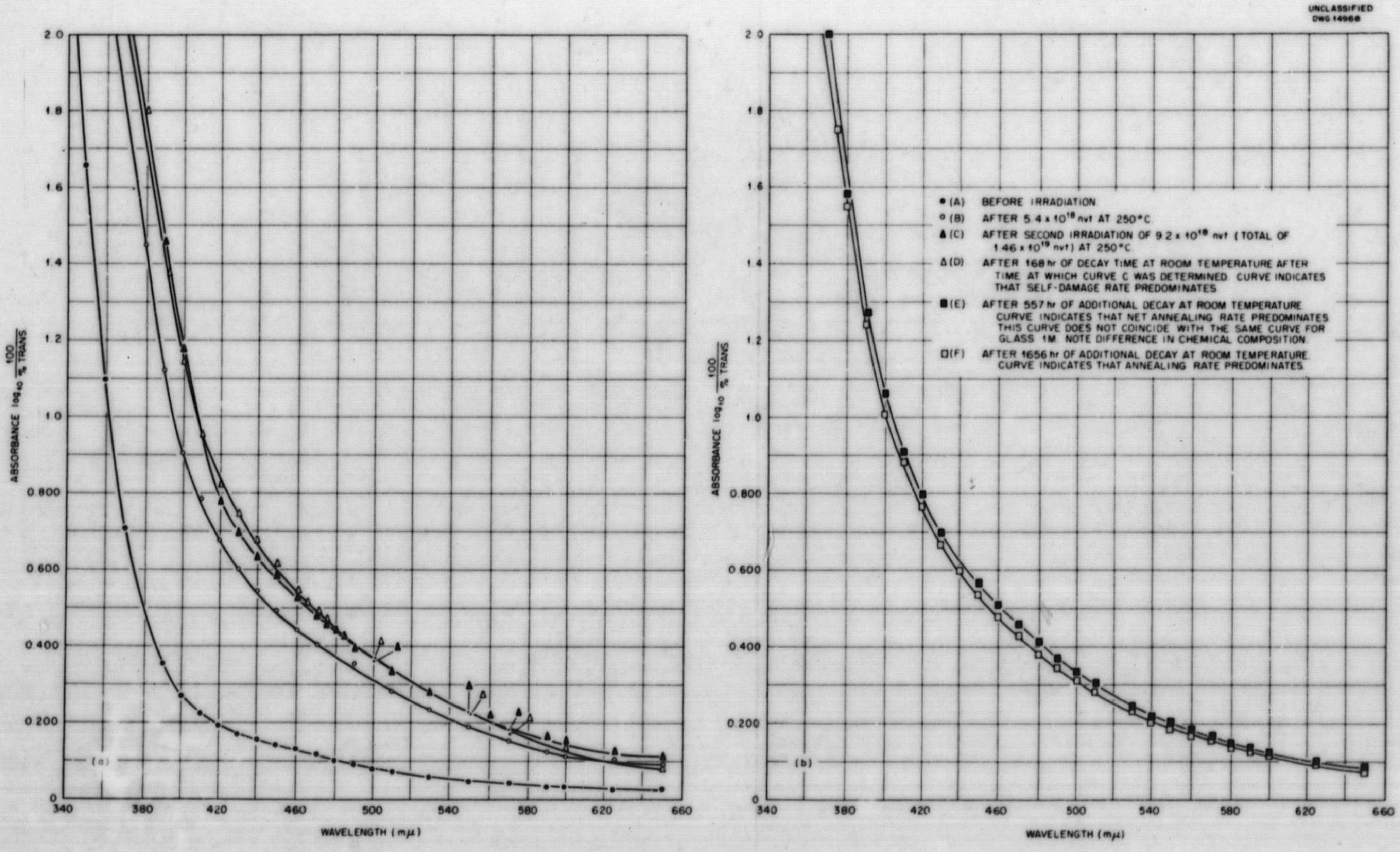

**Fig. 28. Absorbance Curves for Radiation-Resistant Glass, ORNL-2M.** Boron, trace; cadmium, strong.

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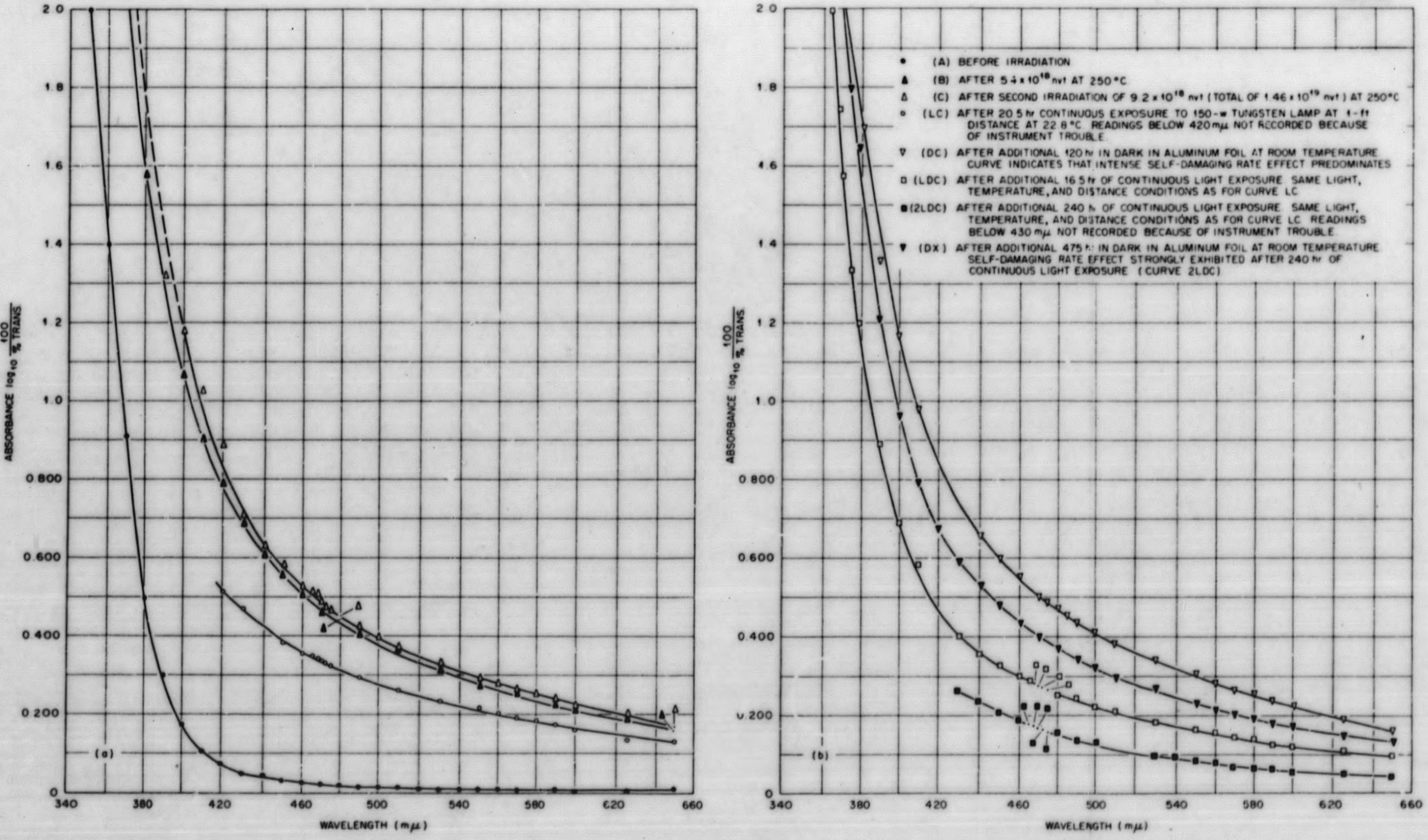

**Fig. 29. Absorbance Curves for Radiation-Resistant Glass, ORNL-3M.** Boron, moderate; cadmium, moderate.

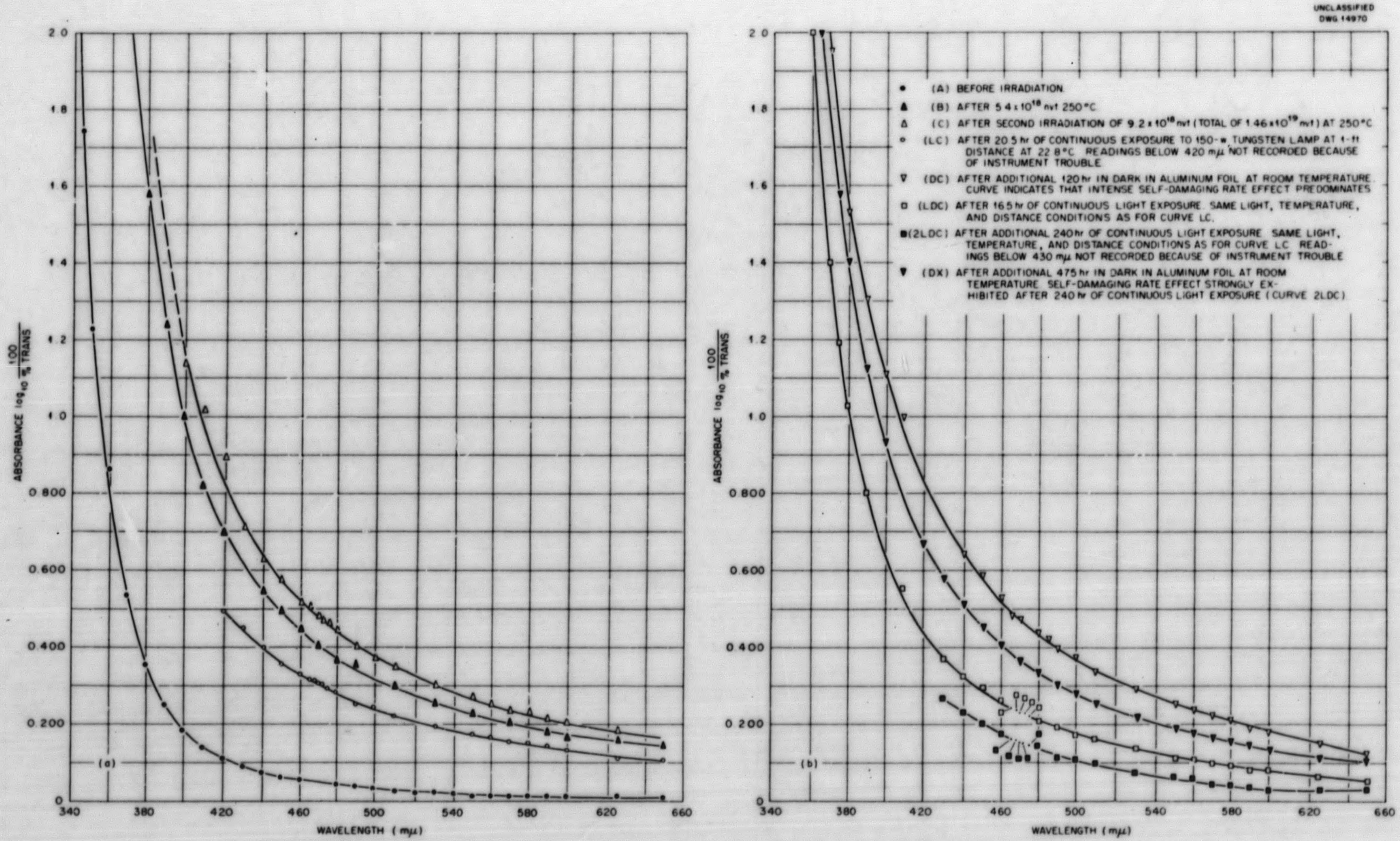

**Fig. 30. Absorbance Curves for Radiation-Resistant Glass, ORNL-4H.** Boron, weak; cadmium, moderate.

**Search for Corrosion-Resistant Inorganic Materials.**(51) Samples of fused titania ($TiO_2$) and fused sapphire ($Al_2O_3$) were submitted to the Engineering Materials Corrosion Testing Laboratory for evaluation of their corrosion resistance in uranyl sulfate solutions at 250°C. The evaluation of these materials is part of a continued search for a corrosion-resistant electrical insulator for use in a Q-coil system that is being considered for determining the uranium concentration of high-temperature HRE fuel solutions.

A few of the initially observed physical properties of the titania and sapphire samples are given in Table 14.

*Experimental Conditions and Corrosion Data.* The corrosion studies were made under static conditions in approximately 0.17 *M* uranyl sulfate solutions at 250°C. The solutions and samples were contained in type-347 stainless steel autoclaves designed to contain 150 ml of liquid. The autoclaves were cleaned and then pretreated for 24 hr at 250°C in nitric acid (1 wt %). No attempt was made to support the samples in the test solutions; instead they were placed carefully in the bottom of the autoclaves prior to the start of each test run. The uranyl sulfate solutions were removed, sampled, and returned to the autoclave at weekly intervals. During the corrosion tests the solutions were maintained under a partial pressure of oxygen of 150 psia by the weekly addition of calculated quantities of 35 wt % hydrogen peroxide. The uranium concentrations and pH values of the uranyl sulfate solutions were determined also. Corrosion data and the results of solution analyses are reported in Tables 15 and 16. The corrosion data represent cumulative results. Uranium analyses are reported in duplicate.

*Discussion.* The cumulative weight loss of the titania increased slightly, but steadily, from 0.05 mg/cm$^2$ at the end of the first week to 0.48 mg/cm$^2$ after eight weeks. The corrosion rates, based on cumulative weight losses, were fairly constant during the total test period, except that a slight increase of 0.18 mpy was observed starting with the fifth week. The total increase in rate was 0.10 mpy during the following three-week period. Little change in the appearance of the sample occurred except for the development of a slight, brown discoloration after two weeks. No other physical changes were observed.

**Table 14**

**SOME PHYSICAL PROPERTIES OF TITANIA AND SAPPHIRE**

| | INITIAL WEIGHT (g) | APPROXIMATE DENSITY (g/cm$^3$) | SURFACE AREA (cm$^2$) | APPEARANCE |
|---|---|---|---|---|
| Fused titania | 4.3075 | 4.43 | 6.2 | Irregular-shaped bottom, orange color, semi-opaque, nonpolished |
| Synthetic sapphire | | | | |
| White | 3.7736 | 4.2 | 6.6 | Transparent |
| Golden | 2.3886 | 4.2 | 6.3 | Transparent |

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(51) J. L. English, personal communication to R. H. Powell, March 28, 1952.

## Table 15

### CORROSION OF SYNTHETIC SAPPHIRE IN 0.17 *M* URANYL SULFATE WITH A PARTIAL PRESSURE OF OXYGEN OF 150 psia AT 250°C

| EXPOSURE (hr) | SOLUTION pH | URANIUM CONTENT OF $UO_2SO_4$ SOLUTION (g/l) | WEIGHT LOSS OF SAPPHIRE SAMPLES (mg/cm$^2$) | | CORROSION RATE (mpy) | |
|---|---|---|---|---|---|---|
| | | | White | Golden | White | Golden |
| 0 | 2.35 | 40.1 | | | | |
| 168 | 2.50 | 39.6, 39.6 | 0.21 | 0.25 | 1.04 | 1.24 |
| 336 | 2.00 | 38.2, 38.3* | 0.21 | 0.41 | 0.52 | 1.01 |
| 504 | 2.60 | 40.3, 40.3 | 0.39 | 0.62 | 0.62 | 1.01 |
| 672 | 2.40 | 38.1, 38.3 | 0.52 | 0.73 | 0.63 | 0.89 |
| 840 | 2.40 | 38.1, 38.3 | 0.68 | 0.89 | 0.67 | 0.87 |
| 1008 | 2.40 | 34.1, 34.1 | 0.94 | 1.05 | 0.77 | 0.85 |
| 1176 | 2.35 | 38.8, 38.9 | 1.20 | 1.44 | 0.84 | 1.01 |
| 1344 | 2.40 | 39.1, 39.2 | 1.50 | 1.70 | 0.92 | 1.04 |

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[*] Original uranyl sulfate solution was replaced with one containing 39.5 g of uranium per liter.

## Table 16

### CORROSION OF A SYNTHETIC FUSED TITANIA SAMPLE IN 0.17 *M* URANYL SULFATE WITH A PARTIAL PRESSURE OF OXYGEN OF 150 psia AT 250°C

| EXPOSURE (hr) | SOLUTION pH | URANIUM CONTENT OF $UO_2SO_4$ SOLUTION (g/l) | WEIGHT LOSS OF TITANIA SAMPLE (mg/cm$^2$) | CORROSION RATE (mpy) |
|---|---|---|---|---|
| 0 | 2.35 | 40.1 | | |
| 168 | 2.30 | 37.5, 37.6 | 0.05 | 0.23 |
| 336 | 2.20 | 37.9, 38.0* | 0.03 | 0.07 |
| 504 | 2.50 | 40.0, 40.2 | 0.15 | 0.22 |
| 672 | 2.20 | 38.1, 38.4 | 0.16 | 0.19 |
| 840 | 2.10 | 39.0, 39.0 | 0.19 | 0.18 |
| 1008 | 2.30 | 37.2, 37.3 | 0.26 | 0.20 |
| 1176 | 2.30 | 38.7, 38.7 | 0.40 | 0.27 |
| 1344 | 2.40 | 38.7, 38.9 | 0.48 | 0.28 |

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[*] Original uranyl sulfate solution was replaced with one containing 39.5 g of uranium per liter.

Weight losses of the synthetic sapphires were greater by a factor of 3 to 4 than those of the titania for a comparable exposure period of eight weeks. The corrosion rates, calculated from the corrosion occurring during the first week, were 1.04 and 1.24 mpy on the white and yellow sapphires, respectively. Final rates for 1344 hr were 0.92 and 1.04 mpy. The two specimens did not show any decrease in transparency or other physical evidences of corrosion attack.

Of approximately 20 ceramics and related materials tested in uranyl sulfate solutions, the titania and synthetic sapphires have shown the most promising corrosion resistance by far. However, before any definite recommendations can be made, the titania, sapphires, and spinels should be subjected to a more thorough study.

## OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth
F. D. McNeer B. I. Gary

**Microscopy of Oxide Films and Crystallographic Studies for HRP.** Chromium steel (Carpenter 443) containing approximately 1.25% copper is of interest in the HRE. A study of oxide films produced on unpretreated samples of this steel in 0.17 *M* $UO_2SO_4$ at 250°C for 2016 hr indicated that a very thin spinel-type of film formed at the metal substrate and was covered by a succession of layers of the metallic oxides of chromium and iron, or combinations of both. The calculated lattice spacings and lattice constant of this spinel oxide were determined from electron diffraction patterns but did not agree with those of the more common spinels found on steels. Based on Mott's theory(52) of the formation of oxide films on metals, the assumption was made that the thin film could well be a copper spinel with the possible formula $Cu \cdot Cr_2O_4$. In experiments made by the Corrosion group of the HRP, samples of chromium steel containing copper displayed very good corrosion resistance, 0.02 mpy, under the test conditions described above. This would suggest that the spinel oxide film has good protective qualities. Based on corrosion data collected from unpretreated samples that were exposed for shorter periods (1008 hr) and had considerably higher corrosion rates (0.06 to 0.09 mpy), the protective nature of these films appears to be, at least partly, a function of the time of exposure to the $UO_2SO_4$ solution. The diffraction patterns of films taken from the samples exposed for the shorter period exhibited weaker spinel lines and stronger lines for the hexagonal and rhombohedral metallic oxides of chromium and iron. Electron diffraction of oxide films from metal samples pretreated in 1% $HNO_3$ or 2% $CrO_3$ indicated the absence of the spinel oxide in the former and a very weak spinel line pattern in the latter.

Studies are now being made of the oxide films formed on type-347 stainless steels that were (1) pretreated in 1% $HNO_3$ and contained varying amounts of $MoO_4^{=}$, (2) exposed in 0.17 *M* $UO_2SO_4$ to which copper sulfate was added, and (3) exposed in 0.17 *M* $UO_2SO_4$ in which fission products were included.

Other work for the HRP included a microscopic examination of graphite-bearing materials containing silver or Babbitt metal that have been proposed for HRE pumps. Observations indicated that extensive corrosion attack had taken place in the metal regions of the graphite-bearing samples after exposure to $UO_2SO_4$ solutions.

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(52) N. F. Mott, "The Theory of the Formation of Protective Oxide Films on Metals, II.," *Trans. Faraday Soc.* **36**, 472 (1940).

Crystallites that had formed on the surface of type-347 stainless steel, Stellite, and Inconel after they had been immersed in a solution of 300 g of uranium (as $UO_2F_2$) per liter of water for two to three days were identified as silver by crystallographic methods. These results were verified by x-ray diffraction and spectrographic analyses. The silver was apparently an impurity introduced during the production of the $UO_2F_2$.

**Electron Microscopy of Metals.** An electron microscopic study of electropolished thorium of interest to the Metallurgy Division was made by use of the polyvinyl alcohol-formvar replica technique to determine whether the spotty effect on the metal surface noted with the optical microscope was a precipitate or a texture introduced by polishing. Electron micrographs (Fig. 31) indicate the existence of a precipitate rather than a polishing effect.

The surfaces of a copper crystal grown by Smith of the Metallurgy Division are being studied with the electron microscope to learn more about the nature of the terrace growth observed with the optical microscope and to verify, if possible, the existence of a spiral terrace formation that has been reported by various observers who used interferometric methods.

**Microscopic Evaluation of Radiation Damage to Metals and Thin Metal Films.** At the suggestion of Snell of the Physics Division a study of the effect of irradiation with neutrons on thin, sputtered metal films has been undertaken. Films of aluminum approximately 600 A thick were deposited on electron microscope screens and observed, and micrographs were taken. The screens were then exposed to a beam of neutrons

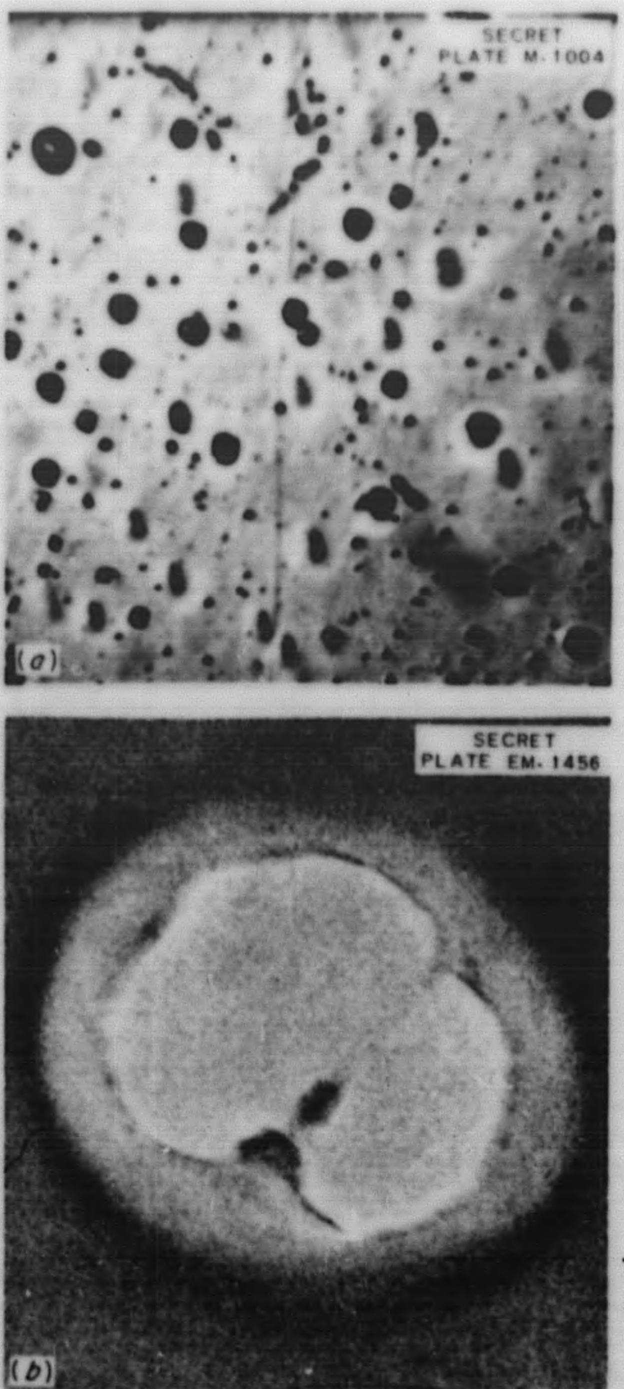

**Fig. 31. Surface of Electropolished Thorium.** (*a*) Optical micrograph showing either a precipitate or a polishing effect. 3000X. (*b*) Electron micrograph identifying the surface effect as a crystalline precipitate. 45,000X.

from the X-10 graphite reactor for varying periods of time and reobserved in the electron microscope. Results to date fail to show any change in the films observable within the resolving power of the microscope (50 to 100 Å). Further work under altered exposure conditions is contemplated.

Assistance has been given to the Solid State Division in developing a remote-control technique for making replicas of the surfaces of irradiated metals for optical and electron microscope studies of radiation damage. Initial replicas made by the Faxfilm(53) method, in which remotely controlled manipulators are used to lay down the replica film, give promise of being satisfactory for optical microscopy. The polyvinyl alcohol-formvar replica technique has been suggested as a possible method for electron microscopic study of submicro changes.

**Other Work.** Use has been made of the traveling stage accessory to the Welch Densitometer(54) to determine the uniformity of radioactive sources deposited in drop form and dried on thin, plastic films. Radioautographs of the radioactive sources of radiation were taken on 2- by 2-in. lantern slide plates, and densitometer traces were made with the established apparatus.(54)

Particle size studies have been made of various exchange resins, nickel powders, and $BeF_2$-$UF_4$-NaF eutectic. Microscopy, including measurements, has been done of various nickel-wire screens. Photomicrographs were taken of $U^{235}O_3 \cdot H_2O$, irradiated $UO_3 \cdot H_2O$, enriched $UO_3$, and $TeO_2 \cdot 2H_2O$.

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(53) A commerical product of the Faxfilm Co., Cleveland, Ohio.

(54) T. E. Willmarth, F. D. McNeer, and B. I. Gary, "Traveling Stage for Welch Densitometer," *op. cit.*, ORNL-1233, p. 47-48.

## SERVICE ANALYSES

A summary of the analytical service work of the X-10 Analytical Chemistry Division laboratories is given in Table 19. A brief discussion of it follows.

### IONIC ANALYSES

P. F. Thomason

The service work of the Ionic Research and Development group has continued at a normal rate the past quarter. The analyses of irradiated fuel samples from the corrosion studies of $UO_2SO_4$ solutions, solid eutectics of $UF_4$, and $UO_3$ slurries constituted the bulk of the service work of this group. The methods used for these analyses have been reported previously.(1)

### RADIOCHEMICAL ANALYSES

S. A. Reynolds

Relatively little service work was done this quarter by members of the Radiochemical Analyses group. Identifications and nonroutine protactinium analyses were made for the Chemical Technology Division. The work for the Operations Division included special radioisotope analyses.

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(1) P. F. Thomason, "Ionic Analyses - Development Group," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, p. 65.

## ACTIVATION ANALYSES

G. W. Leddicotte

Activation analysis techniques were applied routinely to the determination of sodium, calcium, and gallium in aluminum. Additional work is being done on the determination of trace elements in petroleum hydrocarbons.

## GENERAL RADIOCHEMICAL ANALYSES

C. L. Burros

Assistance was given to the Chemical Technology Division in their studies of the valence states of plutonium in the HRE fuel, of adsorption and desorption of fission products on metal surfaces, and of the solvent-extraction separation of fission products from uranium in Purex process samples.

Silica is often present in samples from the Purex process. The silica causes high yields (sometimes above 100%) in the determination of the UX activity[2] of the samples. A modification to the UX procedure has been developed whereby the silica interference may be removed by scavenging with $BaSO_4$ and $SrSO_4$ precipitation after the initial $K_2ThF_6$ precipitate is dissolved.

## GENERAL ANALYSIS LABORATORY

J. H. Edgerton

The high-temperature brazing alloy evaluation program of the Metallurgy Division necessitated the analysis of alloy samples of silver, palladium, manganese, magnesium, nickel, zirconium, and boron. Samples were dissolved by prolonged boiling with concentrated $HNO_3$. It was found that the silver could not be separated satisfactorily from the palladium by precipitation as the chloride because of strong coprecipitation of palladium unless the palladium was first converted into a tetramine salt. This was done by treating the hot nitrate solutions of the samples with $NH_4OH$ until the precipitated silver had redissolved. The silver was then reprecipitated with HCl and the precipitate filtered off and weighed as $AgCl_2$. The acid filtrate, which contained the palladium complex, was treated with a 1% dimethylglyoxime solution that precipitated the palladium as $Pd(C_4H_7O_2N_2)_2$, palladium dimethylglyoxime. The precipitate was then collected by filtration through a Gooch Crucible, dried at 110°C, and weighed. An ion exchange column was used for the determination of the boron content of the sample. After $CO_2$ had been removed from the neutral or slightly acid solutions of the sample by boiling, the solutions were passed through a strong-acid type of cation exchanger (Dowex-50, 12% cross linked).[3] The boron was then determined by the mannitol method.[4] Although invert sugar is usually recommended for the titration, mannitol was found to be very satisfactory for the alloys analyzed. By this method Martin and Hayes[3] have separated boron as boric acid from 60 times its weight of iron and 10 times its weight of beryllium, magnesium, aluminum, zinc, cadmium, cobalt, copper(II), mercury(II), nickel, thorium, tin(IV), zirconium, uranium, and titanium. Nickel,

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[2] N. E. Ballou and D. N. Hume, "Determination of UX Activity in Process Solutions," *Development of Methods for the Determination of Fission Product Activities in Plant Process Solutions*, CN-1312, p. 97 (May 15, 1945).

[3] J. R. Martin and J. R. Hayes, "Application of Ion Exchange to Determination of Boron," *Anal. Chem.* **24**, 182 (1952).

[4] J. H. Edgerton, "Determination of Boron," *Analytical Chemistry Division Quarterly Progress Report for Period Ending September 10, 1951*, ORNL-1129, p. 49.

zirconium, magnesium, and manganese in the alloys were determined colorimetrically.

The solubility of alloy components in liquid hydroxide and fluoride and other liquid fuels at 800°C is being studied by the Metallurgy Division. Samples of these liquid fuels were submitted for the determination of corrosion products. Analyses were made on the high-temperature oxide products for nickel, carbon, boron, and sodium. In this same study it was also necessary to test for the presence of inhibitors in the bath material. The bath samples were analyzed for zirconium and magnesium.

The determination of the fluoride content of eutectics was required by the Solid State Division in their study of radiation damage to fuel eutectics ($UF_4$-NaF-BeF). The general pyrohydrolysis procedure described previously was used. However, three changes were made in the procedure. The use of $Al_2O_3$ rather than $U_3O_8$ as a catalyst was found to give equally satisfactory results, even in the presence of the beryllium eutectics, and at the same time eliminated the necessity of separating the $U^{235}$ from the $U^{238}$, both of which are present following the use of $U_3O_8$ as a catalyst in the pyrohydrolysis. Thymol blue proved to be superior as an indicator to phenolphthalein, which was previously used in the titration. An S B-1 syringe microburet was purchased for more accurate titration of the HF solution. The microburet may be used with a 5- or a 1-ml syringe. The 1-ml syringe is calibrated to deliver an amount as small as 0.001 ml. The use of the microburet gave much more accurate results than were obtained with the ordinary pipet.

The determination of the neutron-scattering cross section of vanadium and nitrogen by the Chemistry Division necessitated the determination of the percentage of vanadium and nitrogen in vanadium nitride samples. The nitrogen was determined by the Kjeldahl procedure; however, a large excess of $K_2SO_4$ (20 g of $K_2SO_4$ per g of sample) was necessary to prevent loss of nitrogen during decomposition of the sample. A 50-ml volume of concentrated $H_2SO_4$ was then added and the decomposition allowed to continue at boiling temperature for 6 to 8 hr;(6) the exact length of time depended upon the temperature at which the sample was prepared. The vanadium was determined by using potassium permanganate(7) in the volumetric oxidation-reduction method.

The recovery of plutonium from metallurgical waste by the Chemical Technology Division necessitated the study of the salt residues resulting from dissolution of slag and crucible materials. Samples of the slag in acid solutions were submitted for iodine determination; the iodine in the slag was in the form of $I_2$ and $IO_3^-$. Several analytical methods for iodine were tried. Carbon tetrachloride extraction of the $I_2$ was most satisfactory. The extraction was made with urea and the reducing agent, hydroxylamine hydrochloride, in the presence of interference from Fe(III), Cr(III), Ni(II), Mg(II), Ca(II), Na(I), Al(III), $F^-$, Si, NO, $NO_2$, and $HNO_3$. Following extraction, the solutions were titrated with 0.1 *N*

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(6) V. A. Epel'baum and B. F. Ormont, "Analysis of Vanadium Nitride" (trans.), *Zavodskaya Lab.* **14**, 104 (1948); *C. A.* **43**, 971 (194[illegible].

(7) C. J. Rodden (Editor-in-chief), *Analytical Chemistry of the Manhattan Project*, p. 460-461, McGraw-Hill, New York, 1950.

$Na_2S_2O_3$ and the $CCl_4$ acted as its own indicator. A different procedure was found to be more satisfactory for the analysis of alkaline samples of iodine that contained $NO_2^-$, $NO_3^-$, $F^-$, $Cl^-$, and Si as interference. The sample was distilled with an excess of ferric ammonium alum in an $H_2SO_4$ solution to liberate the iodine as $I_2$. The distillate was caught in a solution of $CCl_4$ contained in an ice bath. The titration was then made with 0.01 *N* $Na_2S_2O_3$, and the $CCl_4$ again acted as its own indicator.

In the Chemical Technology Division's study of the dehydration of $UO_2SO_4 \cdot 3H_2O$ in connection with the recovery of $D_2O$ from HRE fuel solutions, the $UO_2SO_4 \cdot 3H_2O$ was dehydrated in a dry air stream at a temperature range of 150 to 400°C. When as much water had been driven off as was possible at this temperature, the $UO_2SO_4 \cdot 3H_2O$ was heated to 800°C to check for any water that might not have been driven off at the lower temperatures. Samples of the $UO_2SO_4 \cdot 3H_2O$ that had been heated at 150 to 800°C were submitted for uranium, sulfate, and water determinations. The method applied for the determination of the uranium content of the $UO_2SO_4 \cdot 3H_2O$ was hydrolysis at 1000°C in the presence of superheated steam. Details of the apparatus have been given in a previous report.[5] A catalyst was not necessary since the $U_3O_8$ that was formed acted as its own catalyst. After an ignition period of 45 min, the residue in the boat was cooled and weighed as $U_3O_8$. Gravimetric determinations of uranium were also made on separate portions of the sample by precipitating the uranium as $U_3O_8$ with $NH_4OH$. The results obtained checked satisfactorily with the hydrolysis method. Comparative data obtained by the two methods on a variety of samples are given in Table 17.

The sulfate content of the sample was determined on another portion by separating the uranium out on an

Table 17

COMPARISON OF THE HYDROLYSIS AND THE GRAVIMETRIC METHODS FOR URANIUM IN $UO_2SO_4 \cdot XH_2O$ SAMPLES

| SAMPLE NO. | TEMPERATURE TO WHICH $UO_2SO_4 \cdot XH_2O$ WAS HEATED BEFORE SAMPLING (°C) | URANIUM (%) | |
|---|---|---|---|
| | | $NH_4OH$ Precipitation | Hydrolysis |
| 1 | Room (25) | 57.56 | 58.12 |
| 2 | Room (25) | 58.75 | 57.85 |
| 3 | 150 | 64.29 | 64.20 |
| 4 | 200 | 64.18 | 63.88 |
| 5 | 250 | 64.26 | 64.21 |
| 6 | 300 | 64.68 | 64.76 |
| 7 | 350 | 65.08 | 65.19 |
| 8 | 400 | 64.92 | 65.07 |
| 9 | 800 | 84.68 | 84.63 |

ion-exchange column of Dowex-50, 12% cross-linked, and titrating the resulting $H_2SO_4$ with standard alkali. Also, a gravimetric sulfate determination was made by precipitation with $BaCl_2$ in an HCl solution. Results by the two methods are compared in Table 18.

A study of the stability of Dowex-50 resin, 12% cross-linked, in 6 to 12 *N* nitric acid, which is being conducted by the Chemical Technology Division, is of interest in the RaLa process. Polarographic determinations of microgram amounts of residual sulfate were made on samples of the eluate submitted from the study. The sulfate was reduced to hydrogen sulfide and precipitated as cadmium sulfate.(8) The cadmium sulfate was then dissolved in HCl and the cadmium determined polarographically. The sulfate was calculated from the total cadmium. Since any $HNO_3$ present in the sample would react with the $H_2S$ just as the reducing mixture would, it was necessary to use formic acid to destroy any $HNO_3$ present. Sulfates in distilled, demineralized, filtered, and steam condensate water were also determined by this method. The results were in agreement with data obtained by gravimetric methods.

Oil samples were submitted by the Engineering and Maintanence Division and the HRE for determination of density, flash point, ash, sediment, water, distillation temperature, heat of combustion, and viscosity. Apparatus for all the determinations is available, and standard ASTM methods will be used.

## LABORATORY AND SEMI-WORKS CONTROL

G. R. Wilson

Forty-one per cent of the total work for the quarter was for the

Table 18

COMPARISON OF VOLUMETRIC (ION EXCHANGE) AND GRAVIMETRIC ($BaCl_2$) METHODS FOR $SO_4$ IN $UO_2SO_4 \cdot XH_2O$ SAMPLES

| SAMPLE NO. | TEMPERATURE TO WHICH $UO_2SO_4 \cdot XH_2O$ WAS HEATED BEFORE SAMPLING (°C) | SULFATE (%) | |
|---|---|---|---|
| | | $BaCl_2$ Precipitation | Volumetric (Ion Exchange) |
| 1 | Room (25) | 22.65 | 22.54 |
| 2 | Room (25) | 22.70 | 23.18 |
| 3 | 150 | 25.50 | 25.55 |
| 4 | 200 | 25.52 | 25.35 |
| 5 | 250 | 25.52 | 25.53 |
| 6 | 300 | 25.38 | 24.80 |
| 7 | 350 | 25.76 | 25.83 |
| 8 | 400 | 25.36 | 25.72 |
| 9 | 800 | 0.36 | 0.16 |

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(8) A. D. Horton and P. F. Thomason, "Polarographic Determination of Sulfate," *Anal. Chem.* 23, 1059 (1951).

DECLASSIFIED

Thorex and Interim "23" groups of the Chemical Technology Division. The methods used in this work have all been reported except those for free acid and aluminum in the presence of thorium.

The Beckman, Model K, automatic titrator is being used to determine free acid in samples that contain thorium and aluminum, for example, Thorex feed samples and Thorex countercurrent run samples. The thorium and aluminum are complexed with $K_2C_2O_4$. By a potentiometric titration and plot of pH against volume(ml) of base added, it was found that the end point of the titration occurred at pH 7. The samples are then titrated by setting the pH dial of the automatic titrator at pH 7; titrating with standard base and reading the volume(ml) of the base is required to titrate the acid in the sample directly from the buret when pH 7 is reached.

After the sample has been analyzed for free acid by the above method and for thorium by the Thoron colorimetric method, the aluminum is determined by the method reported by Thomason (cf., "Indirect Determination of Aluminum in '23' Process Feed Solutions," this report).

The development of a method for the polarographic determination of uranium in the presence of orthophosphate[9] was completed. Variation in the height of the uranium polarographic wave with varying acid concentrations was studied by use of $HClO_4$, HCl, $HNO_3$, $H_2SO_4$, $H_3PO_4$, and HF. Since the chief interest was in $H_3PO_4$, a concentration of 0.7 *N* $H_3PO_4$ was chosen, which was on the plateau region of the plot of *N* $H_3PO_4$ vs. uranium wave height, and polarograms of solutions of various uranium concentrations were made. The height of the polarographic wave for uranium was found to be proportional to the uranium concentration over the range of 1 to 100 $\mu$g of uranium per milliliter of 0.7 *N* $H_3PO_4$. A report will be written on this work.

## PILOT PLANT CONTROL

C. E. Lamb

Accelerated operations by the Pilot Plant on the Purex program resulted in 90% of the total analyses for this quarter being made for that group. A higher percentage of analyses is anticipated for this group as their program progresses.

A revision of the fluoride procedure[10] to give increased sensitivity and more reproducible results was necessary for the analysis of aqueous samples submitted by the Chemical Technology Division in connection with their study of irradiated Teflon. Reduction of the Thoron concentration increased the sensitivity in color development.

In addition to samples from the Pilot Plant several highly concentrated plutonium solutions were submitted from the Isolation Process for determination of plutonium, uranium, acid, and gamma activity.

The use of zinc bromide solution as a shielding agent for the storage

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[9] F. L. Conover and G. R. Wilson, "Polarographic Determination of Uranium in the Presence of Orthophosphate," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-788, p. 17.

[10] M. T. Kelley, P. F. Thomason, L. T. Corbin, S. A. Reynolds, C. L. Burros, and E. J. Frederick, "Inorganic Fluorides - Spectrophotometric Method with 'Thoron' Reagent (Method No. 7)," *Manual of Analytical Procedures for the $U^{235}$ Recovery Process*, ORNL-983 (Aug. 20, 1951).

of highly radioactive samples proved unsatisfactory because of the development of turbidity in the solution. Lead silicate glass (type GS), produced by Penberthy Instrument Co., is being installed to eliminate the necessity of periodic filterings encountered in the use of zinc bromide solution.

## HRE ANALYSES

U. Koskela

The analytical laboratory in the 7500 area has been in operation since November 19, 1951, during which time some 2600 determinations have been performed.

The new filter photometer, model Q-1201, has been tested and found satisfactory for the colorimetric determinations of chromium, fluoride, iron, nickel, and uranium. Additional filters have been ordered so that elements whose chromophores have their maximum absorptions between 380 and 500 mμ and above 525 mμ may also be determined.

The determination of the $D_2O/H_2O$ ratio in the reflector is being studied. A survey of the literature(11) indicated that this ratio might be determined by a specific gravity measurement using the falling-drop method. McKown(12) recommended ethyl anisate as the water-immiscible medium. Equipment has been assembled and tests are being run with this medium with $NH_4NO_3$ solutions of known specific gravity used as standards (sp. gr. $D_2O$, 25°C/25°C = 1.10775 ± 0.00003, as reported by Kirshenbaum, Graff, and Forstat(13)). Further work is still needed to obtain reproducibility of drop size and a $D_2O$ sample free from impurities.

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(11) I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water*, NNES, Div. 3, Vol. 4A, McGraw-Hill, New York, 1951.

(12) H. S. McKown, Trail Report (SAM Report 100XR-5156), April 25, 1944.

(13) I. Kirshenbaum, J. Graff, and H. Forstat, SAM Report A-2193, 1945.

## Table 19

### SUMMARY OF ANALYTICAL SERVICE WORK AT X-10 SITE FOR PERIOD DECEMBER 27, 1951 THROUGH MARCH 26, 1952

| | NO. OF PERSONNEL | | ORNL DIVISIONS REQUESTING ANALYSES | | | | | | | | | | | | OTHERS REQUESTING ANALYSES | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TECHNICAL | NONTECHNICAL | | CHEMICAL TECH. | CHEMISTRY | ENGR. & MAINT. | HEALTH | HEALTH-PHYSICS | LAB. PROTECTION | METALLURGY | OPERATIONS | PHYSICS | REACTOR EXPER. ENGR. | SOLID STATE | | ARGONNE NAT'L. LAB. | HRP | K-25 | ORSORT | TOTAL DETERMINATIONS |
| GROUP MAKING ANALYSES | | | Number of Determinations | | | | | | | | | | | | | | | | | |
| Activation Analyses | 3* | 3 | | 11 | 18 | | 4 | 3 | | | 228 | 3 | | | 26 | | | | | 293 |
| General Analyses | 5 | 4 | | 775 | 63 | 27 | | | | 300 | 44 | 16 | | 6 | | 48 | | | | 1,279 |
| General Radiochemical | 4 | 6 | | 6,014 | 74 | | | | | | | | | | | | | | | 6,088 |
| HRE | 3 | 3 | | | | | | | | | | | 2,262 | | | | | | | 2,262 |
| Ionic Analyses | 7 | 1 | 40 | 150 | 181 | | 2 | | | | | | | | | | | | | 373 |
| Laboratory and Semi-Works Control | 2 | 11 | | 13,101 | 504 | | | | | 134 | 601 | | | | | | | | | 14,340 |
| Optical and Electron Microscopy | 4 | 0 | | 20 | 101 | | | 27 | | 30 | 45 | | 186 | | | | | | | 409 |
| Pilot Plant Control | 7 | 14 | | 19,060 | | | | | | | | | | | | | | | | 19,060 |
| Radiochemical Analyses | 5 | 0 | | 24 | | | | 5 | | | 30 | | | | | | | | 3 | 62 |
| Radioisotope Production Control | 4 | 18 | | 5,021 | 1,226 | | | | | | 7,286 | | | | | 22 | | | | 13.555 |
| Spectrochemical Analyses | 4 | 0 | | 264 | 101 | 13 | 3 | 5 | 10 | 230 | 28 | 10 | | | | | 11 | 1 | | 676 |
| TOTALS | 48 | 60 | 40 | 44,440 | 2,268 | 40 | 9 | 40 | 10 | 694 | 8,262 | 29 | 2,448 | 6 | 26 | 70 | 11 | 1 | 3 | 58,397 |

*One began March 21, 1952.

# ANALYTICAL CHEMISTRY DIVISION– Y-12 SITE

## RESEARCH AND DEVELOPMENT

R. Rowan, Jr.

### DETERMINATION OF IMPURITIES IN LITHIUM HYDROXIDE

W. K. Miller D. L. Manning
J. E. Lee, Jr.

The development of methods for the analysis of lithium hydroxide has been continued.

**Vanadium.** The extraction of the cupferrate of vanadium with ether has been proposed as a means of separating vanadium from large quantities of lithium hydroxide. Vanadium can be determined colorimetrically by the phosphotungstate method(1) after evaporation of the extract and destruction of the organic material with nitric and perchloric acids. It was shown experimentally that this method is not quantitative in the presence of large amounts of lithium unless a carrier (Fe(III)) is added before the cupferron precipitation, although complete recovery of vanadium was obtained without a carrier in the absence of lithium. Samples of $LiOH \cdot H_2O$ containing 1 to 2 ppm of vanadium were successfully analyzed for vanadium by adding 0.1 mg of Fe(III) per milliliter to the aqueous solutions of the samples before extraction.

The analysis of lithium hydroxide for vanadium in concentrations below 1 ppm by the above method would require extremely large samples. The search for a more sensitive method revealed that 0.1 to 0.05 $\mu g$ of vanadium per milliliter can be detected by means of the ORNL high-sensitivity polarograph. A supporting electrolyte of $NH_4OH$ and $NH_4Cl$ proved satisfactory.

Tests have indicated that vanadium as vanadate can be completely separated from alkali hydroxides on a strong-base anion-exchange resin. This method will be discussed more fully in connection with the determination of chromium.

At present the procedure that appears most promising as a practical solution of the problem is to separate vanadium from lithium hydroxide by ion exchange, evaporate the eluate containing vanadium to a small volume, and determine the element polarographically. Chromium is eluted from the ion-exchange column simultaneously with vanadium, and both elements can be determined polarographically.

**Chromium.** Repeated attempts to separate chromium from a lithium salt solution by extraction as peroxychromic acid have been unsuccessful. Peroxychromic acid appears to be highly unstable.

Deposition of microgram quantities of chromium from 0.5 *M* $H_2SO_4$ solutions by electrolysis in a mercury cathode resulted in incomplete removal of chromium from the electrolyte. A survey of the literature(2) confirmed the fact that the last traces of chromium cannot be removed by electrolysis. It had been proposed to collect the chromium in a mercury cathode pool and leach it from the pool by prolonged shaking of the mercury with sulfuric acid.

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(1) E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d ed., p. 607, Interscience, New York, 1950.

(2) T. D. Parks, H. O. Johnson, and L. Lykken, "Removal of Metals at the Mercury Cathode," *Anal. Chem.* **20**, 148 (1948).

The distillation of chromium as chromyl chloride was tested as a means of separating chromium from the lithium hydroxide matrix. Attempts to distill chromium by addition of hydrochloric acid to a perchloric acid solution of the element at 200 to 210°C in an all-glass apparatus(3) resulted in incomplete recovery of chromium in the distillate.

The failure of all these methods to separate chromium from the lithium hydroxide matrix prompted the testing of ion-exchange resins as a means of separation. It appeared possible to elute chromium as chromate from an acid-washed column of a cation-exchange resin (Dowex-50); lithium would remain in the column as a cation. Repeated attempts to effect the separation by this procedure resulted in only partial recovery of 50 $\mu g$ of chromium by acid elution. Since there was a possibility of the reduction of chromate in the column in acid solution to the cationic species, chromium(III), the tests were repeated with ammoniacal solutions to elute the chromate. Although the recovery of chromium in the eluate was better under these conditions, it was too low to be satisfactory. Even if the method were found to be satisfactory, a large volume of resin would be required to retain the lithium.

A test was made of a small volume of the same cation-exchange resin as a means of retaining micro amounts of chromium(III) while macro quantities of the lithium ion were being preferentially eluted. All of a 100-$\mu g$ sample of chromium was retained on a 20-ml column but none could be eluted with 200 ml of 1 *M* sulfuric acid, so this approach was abandoned.

The use of an anion-exchange column in which chromium is retained as the chromate would theoretically require only a small volume of resin. Experiments were performed in which 25 $\mu g$ of chromium as chromate was introduced into a small column containing the chloride form of a strong-base anion-exchange resin (Dowex-1). The column was eluted with both 7 *M* $NH_4OH$ and 1 *M* $HClO_4$, but no chromium was recovered in the eluate. The chloride form of a weak-base anion-exchange resin (Amberlite-IR-4b) was employed unsuccessfully in a similar experiment.

Approximately complete recovery of 25 $\mu g$ of chromium was obtained by retention of the chromate in an acid-washed alumina column and elution with aqueous ammonia. Repeated attempts, however, to separate 2 $\mu g$ of chromium as chromate from 3 g of sodium chloride in aqueous solution by anion exchange in the alumina column proved unsuccessful.

A satisfactory procedure for the separation of chromium from lithium hydroxide makes use of the hydroxide form of Dowex-1. Chromium as chromate in alkaline solution (1 *N* LiOH) is introduced into a 5-ml column of the resin. The column is washed with water prior to the elution of chromate with ammonium carbonate solution. Since ammonium carbonate is decomposed on heating, the eluate can be evaporated to any desired volume. Chromium(III) is oxidized quantitatively to chromate with hydrogen peroxide in a basic medium, and the excess hydrogen peroxide is decomposed by boiling the solution. A peroxide treatment of the lithium hydroxide prior to passing the material through the column will assure that chromium is present only in the hexavalent state. In a test, 2 $\mu g$ of chromium was quantitatively recovered from 500 ml of 1 *M* NaOH by this procedure.

Further experiments have shown that vanadium can be separated from lithium hydroxide by exactly the same procedure

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(3) G. F. Smith, *Mixed Perchloric, Sulphuric, and Phosphoric Acids and Their Applications in Analysis*, 2d ed., p. 60, G. Frederick Smith Chemical Co., Columbus, Ohio, 1942.

as that described above. This indicates that chromium and vanadium can probably be determined on a single sample. Chromium can be determined either colorimetrically or polarographically in the presence of vanadium. However, the second polarographic wave of chromium, which represents the reduction of chromium(III) to chromium(II), interferes with the polarographic determination of vanadium. It will be necessary therefore to correct the vanadium wave for the quantity of chromium present, unless a complexing agent is found that will separate the two waves. A shift of the pH of the electrolyte has not remedied the interference.

**Sodium, Potassium, Calcium, and Magnesium.** No new work has been done on the determination of sodium, potassium, calcium, and magnesium.

## DETERMINATION OF TRACE AMOUNTS OF THORIUM IN ORES

W. K. Miller C. M. Boyd

A method was presented in the last quarterly progress report(4) for the chromatographic extraction of thorium from ores prior to the colorimetric estimation with Thoron reagent.(5) Results on synthetic solutions were promising. Two samples of ores, Haygood Rock and Superior Rock, were analyzed for thorium by this procedure. Less than 1 ppm was found in Haygood Rock, whereas the values obtained for the Superior Rock sample ranged from 9 to 28 ppm. Despite the precision of the results for the second sample being rather poor, it is believed that the method can be applied to a variety of ores containing thorium.

## REPLACEMENT OF SULFATE BY CHLORIDE IN ALKALI SULFATES

W. K. Miller

The flame photometric determination of the alkali metals is rendered less sensitive by the presence of sulfate. It is especially desirable to replace the sulfate of lithium sulfate by chloride for the flame photometeric determination of sodium and potassium in this material, since sodium and potassium chlorides can be separated from the bulk of lithium chloride by an extraction with 2-ethylhexanol. The replacement can be made by precipitation with barium chloride, but alkali metal impurities in the reagent must be taken into consideration.

The use of an acid-washed alumina column has been investigated as a means of replacing the sulfate ion by the chloride ion. A column of activated alumina was washed with 1 *M* HCl prior to introduction of the sample of alkali sulfate. The alkali metal ion was then eluted with 1 *M* $NH_4OH$ and the eluate was evaporated to dryness. The residue was ignited to 500°C to volatilize ammonium chloride and finally weighed as alkali chloride. The weight of the ignited residue indicated complete recovery of the alkali metal. The addition of barium chloride to the dissolved residue failed to produce a precipitate, which indicated complete retention of sulfate by the column. Although these experiments showed that alkali sulfates can be quantitatively replaced by the chloride, it has not been possible to wash the columns completely free of sodium ion prior to the introduction of the sample. The results of a determination of sodium in a lithium sulfate sample that had been passed through

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(4) W. K. Miller and C. M. Boyd, "Determination of Trace Amounts of Thorium," *Analytical Chemistry Division Quarterly Progress Report for Period Ending December 26, 1951*, ORNL 1233, p. 68.

(5) P. F. Thomason, M. A. Perry, and W. M. Byerly, *A Colorimetric Method for the Determination of Microgram Amounts of Thorium*, ORNL-90 (July 9, 1948).

the column would therefore be questionable. Replacement of sulfate by chloride could not be effected by the chloride form of Dowex-1, which is a strong-base anion-exchange resin.

One attempt was made to destroy sulfate by reduction to $H_2S$ with HI. The presence of a yellow residue indicated that some of the sulfate had been only partly reduced. It has been reported,(6) however, that successful replacement of the sulfate of lithium sulfate by the iodide has been accomplished by successive additions of preservative-free HI to solid $Li_2SO_4$ at approximately 500°C. By the passage of chlorine through a solution of the salt, iodide could be converted to chloride. This method will be tested.

Sodium and potassium in concentrations above 0.01% in lithium sulfate have been determined successfully by the flame photometric method in a 1 *N* HCl solution of the sulfate. If lower concentrations of sodium and potassium are to be determined, however, the sulfate must be removed.

## ELECTRODEPOSITION OF BISMUTH ON ALUMINUM

W. K. Miller D. L. Manning

Work has been initiated on the development of a satisfactory procedure for the electrodeposition of bismuth on aluminum. If the direct deposition of bismuth on aluminum is found to be impractical, a thin coat of copper will be plated on the base metal prior to the deposition of bismuth.

Most attempts in this laboratory to plate bismuth on aluminum or copper-coated aluminum have resulted in unsatisfactory coatings of black, spongy material that can be removed merely by rubbing. One experimental electrolysis that employed a bismuth anode and an aluminum cathode in a warm (40 to 50°C) nitrate-tartrate bath at 0.5 v, produced a thin plate of bismuth of a firm, uniform nature, but repeated tests under the same conditions on the following day produced the black, spongy coating. The explanation for these results is being sought. Prior to all electrolytic experiments, the aluminum test strips have been pretreated according to a recommended procedure.(7)

## ANALYTICAL STUDIES OF FLUORIDE EUTECTICS

J. C. White C. K. Talbott
W. J. Ross C. M. Boyd

The progress of the analytical work related to the program has been discussed.

The analysis of ternary and quaternary eutectics composed of fluorides of alkali metals, beryllium, and uranium, which had been subjected to corrosion tests in stainless steel and nickel alloy containers, has comprised a large portion of the work during the past quarter. Determinations of uranium, beryllium, total alkali metals, and fluoride are required to follow possible changes in composition of the eutectics. Iron, nickel, chromium, manganese, and molybdenum are determined to ascertain the extent of corrosion of metal containers. In addition, studies of the contaminants found in the starting materials have been made and are still

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(6) W. D. Harman, private communication to W. K. Miller, February 1952.

(7) E. E. Halls, "Electroplating Aluminum and Aluminum Alloy Components. I. Study of Pretreatments and Dipping Processes," *Metal Treatment and Drop Forging* 18, 125 (1951).

in progress. The contaminants include silicon, chloride, nitrate, sulfide, and sulfate in all fluorides and $UO_2$ and $UO_2F_2$ in $UF_4$. Since methods already exist for the determination of the elements mentioned the principal problem has been the adaptation of these methods to the starting materials of interest and the improvement of the speed and accuracy of the methods.

**Composition of the Eutectics.** The work on methods for determining the composition of the eutectics is discussed in the following.

*Uranium.* The determination of uranium has been reported previously.(8)

*Beryllium.* The titrimetric method developed by McClure and Banks(9) for the determination of beryllium has been studied. In this method, the pH of the solution containing beryllium is adjusted to 11.2 with sodium hydroxide solution and then to 8.5 with hydrochloric acid. Solid sodium fluoride is added to complex beryllium and liberate hydroxyl ions, and the solution is titrated to a pH of 7.0 with standard hydrochloric acid solution. By use of hydrochloric acid that has been standardized against National Bureau of Standards beryllium oxide, essentially 100% recovery of beryllium is obtained, in contrast to the 94 to 97% recovery obtained with an acid that has been standardized against sodium carbonate. This departure from exact equivalence in the titration might be traced to the slight solubility of beryllium hydroxide at pH 8.5.

A promising method that has been developed for the separation of beryllium from uranium, which is a step required before the titrimetric procedure, is based upon the use of anion-exchange resins. If a sulfate solution of uranium and beryllium at a pH of 0.5 to 1 is passed through a column of Dowex-1 in the basic form, uranium is retained in the anionic form, probably as a complex sulfate, whereas beryllium is passed through unadsorbed. Emphasis has been placed on batch tests in which the solution is stirred in a beaker with the resin. For beryllium-to-uranium ratios of more than 1:1, separation is complete within 15 to 30 minutes. Results indicate that a fivefold excess of uranium may be removed in a slightly longer period. The behavior of higher concentrations of uranium will be studied, and columns of rather high flow rates (5 to 10 ml/min) will be tested.

*Total Alkali Metals.* The determination of sodium, potassium, and lithium as total alkali sulfates has proved to be excessively time-consuming. A tentative procedure receiving current attention is based upon the sulfate determination that employs a cation-exchange resin, as reported by Day *et al.*(10) It is planned to separate uranium by an anion-exchange resin similar to that used in the beryllium-uranium separation. The eluate from the uranium separation, which contains alkali sulfates and free sulfuric acid, is titrated for free acid. A total sulfate determination is then made as outlined by Day *et al.*,(10) and the sulfate equivalent to alkali metals is calculated from these data. This method will be rapid and much more accurate than the present procedure.(11)

*Fluoride.* A newly developed procedure for the determination of total

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(9) J. H. McClure and C. V. Banks, *An Empirical Titrimetric Method for the Determination of Beryllium*, AECU-812 (Nov. 24, 1950).

(10) H. O. Day, J. S. Gill, E. V. Jones, and W. L. Marshall, *A Search for a Reliable Sulfate Analysis of Uranyl Sulfate: The Ion Exchange Method*, ORNL CF-52-2-50 (Feb. 7, 1952).

(11) J. C. White, "Determination of the Major Components," *op. cit.*, ORNL-1233, p. 60.

fluoride in fluoride eutectics involves fusion of the eutectic with sodium carbonate in a reducing atmosphere. Fluoride is extracted from the melt by water and determined in the extract. This method has been described previously in greater detail.(8)

**Impurities.** Methods for determination of the impurities in fluoride eutectics are described in the following.

*Iron and Molybdenum.* The colorimetric methods for the determination of iron and molybdenum in fluoride eutectics have been reported elsewhere.(8)

*Nickel.* The effects of pH and of concentration of ammonium persulfate(12) in the determination of nickel in sulfate solutions were studied in an effort to correct certain difficulties in oxidation of the nickel ion. Recommendations resulting from this study were used to eliminate these difficulties.

*Chromium.* The latest changes in the colorimetric determination of chromium have been reported elsewhere.(8)

*Manganese.* The advantages of the periodate method of oxidation of manganese in the presence of large amounts of chromium have been reviewed and reported elsewhere.(8)

**Analysis of Components of Fluoride Eutectics.** In order to determine the possible effects of traces of impurities in the separate components of the eutectics of fluoride mixtures, that is, alkali metals, beryllium, and uranium(IV), upon the extent of corrosion of metal containers, determinations of traces of silicon, nitrate, chloride, sulfate, and sulfide in these materials are being made. In addition, $UF_4$ is being analyzed for $UO_2$ and $UO_2F_2$. The progress of this work is reported in the following.

*Silicon.*(8) The sample for the determination of traces of silicon in fluorides was prepared by fusing the sample with sodium carbonate and extracting the melt with water, as recommended by Hoffman and Lundell.(13) The actual determination was made by Straub and Grabowski's method(14) that was modified to eliminate the interference of fluoride. The results of duplicate determinations made on starting materials and on a eutectic sample by this method are shown in Table 20.

*Chloride.* The use of a silver-silver chloride indicator electrode in the potentiometric titration of chloride with silver nitrate was studied. This technique is impractical for the determination of chloride in the range 0.010 to 0.001% in a fluoride medium, because the high ionic strength of the system makes it extremely difficult to identify the potential break. Kolthoff and Kuroda(15) reported the potentiometric determination of traces of chloride in a medium of known nitrate concentration by titration to a predetermined apparent-equivalence potential. In the present work, this same idea was followed for titration in a fluoride medium. Preliminary results showed that the concentration of chloride in 1 g of sodium fluoride was so small that the required volume of 0.001 *N* silver nitrate was only

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(12) From J. C. White to L. J. Brady, *Effect of pH and Concentration of Ammonium Persulfate on Colorimetric Determination of Nickel by the Dimethylglyoxime Method*, Y-B31-324 (Jan. 17, 1952).

(13) J. I. Hoffman and G. E. F. Lundell, "Determination of Fluorine and Silicon in Glasses and Enamels Containing Fluorine," RP110, *J. Research Nat. Bur. Standards* **3**, 581 (1929).

(14) F. G. Straub and H. A. Grabowski, "Photometric Determination of Silica in Condensed Steam in Presence of Phosphates," *Ind. Eng. Chem., Anal. Ed.* **16**, 574 (1944).

(15) I. M. Kolthoff and P. K. Kuroda, "Determination of Traces of Chloride," *Anal. Chem.* **23**, 1304 (1951).

Table 20

IMPURITIES IN FLUORIDES OF ALKALI METALS, BERYLLIUM, AND URANIUM(IV) AND IN THEIR EUTECTICS

| FLUORIDE | LOT NO. | IMPURITIES | | | |
|---|---|---|---|---|---|
| | | Silicon (ppm) | Nitrate (ppm) | Chloride (ppm) | $UO_2F_2$ (%) |
| KF | 6272 | 58 | 23 | | |
| NaF | 3293 | 27 | 5 | 20 | |
| LiF | 117B | 41 | 2 | | |
| $BeF_2$ | | 370 | 12 | | |
| $UF_4$ | 2244 | 5 | | | 1.12 |
| NaF-KF-LiF-$UF_4$ | 52A36 | 560 | | | |
| | 52A47 | 367 | | | |

about 1 ml at the equivalence potential. This volume of titrant is equivalent to approximately 20 ppm of chloride. Further work on this method is planned.

A colorimetric method developed by Kuroda and Sandell(16) for the determination of traces of chloride is also being studied. This method is indirect in that chloride is precipitated as silver chloride, and the silver is determined photometrically as a colloidal suspension of silver sulfide. The authors reported excellent precision.

*Sulfide and Sulfate.* The adaptation of existing methods for the determination of sulfide and sulfate in starting materials and eutectics is planned but has not been started.

*Uranium Dioxide.* The separation of $UO_2$ as the insoluble residue from the ammonium oxalate extraction of $UF_4$ is an established method.(17) The presence of sparingly soluble fluorides and of metal oxide impurities rules out the usual technique of weighing the residue for final determination of $UO_2$. The residue must be analyzed for uranium. A study is under way to determine the optimum time required for the eutectic to dissolve in ammonium oxalate. Optimum conditions for the determination of $UO_2$ in reagent-grade $UF_4$ are being established.

*Uranyl Fluoride.* It has been reported(18) that $UO_2F_2$, unlike $UF_4$, is soluble in alcohol. A separation based on this dissimilarity was made to determine the amount of $UO_2F_2$ in $UF_4$. Two grams of $UF_4$ was refluxed with absolute alcohol for 2 hr; the $UO_2F_2$ in the filtered alcohol extract was determined gravimetrically. Fluoride was detected in the alcohol extract. The results are given in Table 20.

## STUDIES OF DIATOMACEOUS EARTH

J. C. White W. J. Ross

The work on diatomaceous earth has been reported elsewhere.(8)

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(16) P. K. Kuroda and E. B. Sandell, "Determination of Chlorine in Silicate Rocks," *Anal. Chem.* **22**, 1144 (1950).

(17) "Determination of $UO_2$ in $UF_4$ by the 'Ammonium Oxalate Insoluble' Separation," *TEC-CEW Manual of Standard Analytical Methods*, December 1945, CD-3801 Rev., p. 112.

(18) S. K. Allison, "Analyses of $UF_4$," *Metallurgical Project Report for Month Ending November 15, 1942*, p. 7, esp. p. 8, CC-342.

## ANALYSIS OF URANYL SULFATE SOLUTIONS

O. Menis

**Zirconium.** The study of the determination of zirconium by the chloranilic acid method(19) has continued. Because of the strong interference of the sulfate ion with the formation of the zirconium chloranilic acid complex, a search has been made for a substitute for sulfate as a complexing agent to hold back zirconium when uranium is extracted with tributyl phosphate (TBP). The sodium salt of ethylenediamine tetracetic acid (Versene) did not interfere with the extraction of uranium but failed to form a sufficiently stable complex with zirconium to prevent extraction of the element into the organic phase.

It is now planned to attempt a separation of uranium and zirconium by use of an anion-exchange resin. The work of Brooksbank(20) indicates that a quantitative separation is possible by passing the materials, in a hydrochloric acid medium, through a column of Dowex-1. Uranium forms a strong anionic complex in hydrochloric acid solution and is retained on the column, whereas zirconium, which is not so strongly complexed, passes through. After uranium is removed, zirconium can be determined in the hydrochloric acid medium by means of the chloranilic acid reagent.

**Nitrate.** In the last quarterly progress report,(21) a method was described for the determination of microgram quantities of nitrogen (primarily nitrate) in uranyl solutions and uranium oxide slurries by a modified Kjeldahl procedure in which the reducing agent was chromous ion. Further studies have resulted in the adaptation of a rapid and more sensitive method for the determination of nitrate.

A colorimetric procedure for the determination of nitrate by measurement of the absorbancy of the ferrous-nitroso complex was described by Staple, Marshall, and Simon.(22) These investigators determined 1 to 3 mg of nitrate after a separation in which the nitrate was distilled from a solution of the uranium oxides. It was stated that when the nitrate is present in a 65 to 70% (*v*/*v*) sulfuric acid solution, the color is almost fully developed in 10 min and is stable for 8 hours.

The present investigation involved a study of both the sensitivity of the method and its applicability to the analysis of uranyl solutions without distillation. The complex was developed in 30-ml volumes of 70% (*v*/*v*) sulfuric acid in water. Two series of solutions of 112 and of 224 mg of ferrous sulfate heptahydrate per 30 ml of volume were tested. Each solution contained 54 mg of uranium(VI) and nitrate in the range of 100 to 400 μg. The absorbancies were measured at 525 mμ by means of a Beckman DU spectrophotometer.

In the presence of the lower concentration of ferrous salt, the color of the sample containing only 100 μg of nitrate was not fully developed, as indicated by comparison with optical densities of solutions containing more ferrous sulfate, and faded rapidly, although this was not true for more than 100 μg of nitrate. In a series of eight tests on standard samples that contained 112 mg of

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(19) O. Menis, "Zirconium," *op. cit.*, ORNL-1233, p. 79.

(20) W. A. Brooksbank, private communication to O. Menis, February 1952.

(21) O. Menis and C. K. Talbott, "Nitrogen," *op. cit.*, ORNL-1233, p. 76.

(22) E. Staple, E. Marshall, and W. Simon, *The Determination of Small Amounts of Nitrate in* $U_3O_8$ *and Other Uranium Oxides*, MDDC-1564 (July 23, 1946).

ferrous sulfate, the relative error was 6%. In solutions containing 224 mg of ferrous salt, the color developed fully over the entire range of concentrations, and the relative error was only 1.5%. After standing for 1 hr, however, the solutions became turbid. Therefore it is necessary to measure the absorbancy within 30 min after color development, during which period the factor remains constant. The turbidity that develops on longer standing is probably caused by the precipitation of ferrous sulfate from a solution that was initially supersaturated with respect to the salt. By adherence to the optimum conditions and use of 10-cm absorption cells, as little as 5 $\mu$g of nitrate per milliliter can be determined in a 5-ml sample of uranyl sulfate solution by this method.

**Carbon.** Since it is suspected that volatile carbon compounds are present in uranyl sulfate solutions, a method for the determination of microgram quantities of carbon has been adapted for use on these solutions. A wet combustion method, in which carbon is collected as $CO_2$ and the $CO_2$ weighed, has been described previously(23) in connection with the determination of carbon in chlorinated silanes. The train was simplified for use with uranyl sulfate solution by eliminating scrubbers for the halides.

In order to condition and test the train, several samples of ethyl alcohol were decomposed by the wet combustion mixture prior to the analysis of standard samples. The determination of carbon in ethyl alcohol by this procedure produced results that averaged approximately 92% of the theoretical value. It is possible that with further work the slightly low values could be traced to a loss of volatile intermediate products, but the method is sufficiently accurate in its present form for the purpose intended. In order to improve the accuracy of the determination, it would probably be necessary to include a heated tube filled with copper oxide for the purpose of converting molecular fragments to $CO_2$.

The results of determinations of carbon in ethyl alcohol and in samples of uranyl sulfate solution are shown in Table 21.

**Free Acid.** Preliminary tests have been made of the method of determining free acid in uranyl sulfate and fluoride solutions by potentiometric titration with standard sodium hydroxide solution and a glass indicator electrode. The method depends on the detection of the first inflection point in the titration curve. The break occurs at a pH between 3.0 and 7.0; the exact pH depends on the ratio of uranyl ion to free acid.(24)

A Precision-Dow Recordomatic titrometer was used for the titrations. The limit of detection when the titration was made with 0.1 *N* NaOH was 0.02 milliequivalents of free acid in a solution containing 30 to 60 mg of uranium(VI) in a final volume of 50 ml. The first inflection point becomes indistinct in solutions of higher uranium concentration. In fluoride solutions, however, the end point is sharp even in solutions of a high $UO_2^{++}$ to free-acid concentration ratio. The results of some of these titrations are shown in Table 22.

The preliminary data (Table 22) indicate that in solutions containing 30 to 60 mg of uranium in a 50-ml volume, 0.02 to 0.2 milliequivalents of acid can be determined by this rapid method with a relative error of ±1 to 4%.

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(23) O. Menis and C. K. Talbott, "Determination of Carbon in Chlorinated Silanes," *Analytical Chemistry Division Quarterly Progress Report for Period Ending March 26, 1951*, ORNL-1088, p. 88.

(24) C. J. Rodden (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*, p. 74, 584-585, McGraw-Hill, New York, 1950.

### Table 21

### DETERMINATION OF CARBON BY A WET COMBUSTION METHOD

| SAMPLE | TEST | CARBON (mg) | | ERROR (mg) | ERROR (%) |
|---|---|---|---|---|---|
| | | Present | Found* | | |
| Ethyl alcohol | 1 | 1.31 | 1.17 | −0.14 | −11 |
| | 2 | 1.31 | 1.20 | −0.11 | −8 |
| | 3 | 1.31 | 1.20 | −0.11 | −8 |
| | 4 | 1.20 | 1.12 | −0.08 | −7 |
| | | | | Average | −9 |
| Uranyl sulfate solution, 40 mg of U(VI) per ml | 1 | | 0.253 | | |
| | 2 | | 0.256 | | |
| | Average | | 0.255 | | |
| | 1 | | 0.183 | | |
| | 2 | | 0.179 | | |
| | Average | | 0.181 | | |

*The carbon found in uranyl sulfate solution is reported in mg/ml.

### Table 22

### DETERMINATION OF FREE ACID IN URANYL SOLUTIONS

| URANYL SOLUTE | URANIUM, (mg) | ACID (milliequivalents per 50 ml of test solution) | | |
|---|---|---|---|---|
| | | Present, $Y$ | Found, $X$ | Difference, $Y - X$ |
| None(a) | | 0.197 | 0.197 | 0.000 |
| | | 0.197 | 0.199 | +0.002 |
| | | 0.197 | 0.197 | 0.000 |
| $UO_2SO_4$(b) | 39.7 | 0.197 | 0.197 | 0.000 |
| | 39.7 | 0.197 | 0.190 | −0.007 |
| | 39.7 | 0.197 | 0.195 | −0.002 |
| | 39.7 | 0.0197 | 0.0192 | −0.0005 |
| $UO_2F_2$(c) | 60.0 | 0.197 | 0.187 | −0.010 |
| | 60.0 | 0.0197 | 0.0192 | −0.0005 |

(a) Standard acid solution.

(b) Standard acid solution to which $UO_2SO_4$ was added.

(c) Standard acid solution to which $UO_2F_2$ was added.

The preponderance of negative errors that occurs when uranium is present emphasizes the fact that standardization of the method should be carried out with uranium present. Future work will include titrations with a more dilute base, as well as a test of the separation of uranium by a ferrocyanide(25) precipitation prior to acid titration.

## DETERMINATION OF URANIUM BY DIRECT TITRATION WITH CHROMOUS SULFATE

O. Menis    F. E. Jenkins

The method for the determination of uranium by direct titration with chromous sulfate(26) has been investigated for applicability in the presence of ferric and molybdate ions.

In the titration of uranium with chromous sulfate by means of the Precision-Dow Recordomatic titrometer, the equivalence point is indicated by a sharp, nearly right-angle break in the potential curve. When molybdate is present, however, the potential change occurs more gradually. In the determination of uranium in a series of standard solutions containing varying amounts of molybdate, the equivalence point was determined empirically to be that at which the slope of the potential curve initially changes. The results of these tests (Table 23) indicate that the average standard deviation for the titration of uranium in the presence of molybdate is approximately 0.4%.

The potentiometric titration curve of uranium(VI) in the presence of iron exhibits two distinct inflection points, the first of which is the equivalence point for the iron(III), whereas the second represents the complete titration of both iron(III) and uranium(VI). In the presence of certain reagents that complex iron, the first break in the curve is more distinct, which tends to improve the results for both iron(III) and uranium(VI). The sodium salt of ethylenediamine tetracetic acid (Versene) and $\alpha,\alpha'$-bipyridyl both improve the end point, but a more effective complexing agent is the thiocyanate ion. The results of the titration of uranyl solutions containing up to 2 mg of iron(III), in the presence of thiocyanate, are shown in Table 24. These data indicate that uranium can be determined in the presence of iron with satisfactory precision. Considering the range of concentration of iron in these samples, the precision for iron determination is also satisfactory. Study of the accuracy of the method with standard uranium solutions is planned.

Work is now in progress on the determination of uranium(VI) and iron(III) in solutions containing 50 to 100 μg of iron. It is also planned to investigate the titration of uranium in the presence of copper(II).

## DETERMINATION OF FLUORIDE IN AQUEOUS SOLUTIONS

O. Menis    F. E. Jenkins

Several methods for determining microgram quantities of fluoride in aqueous wash solutions from HRE corrosion tests, which also contain traces of chloride and nitrate, have been investigated. The colorimetric alizarin sodium sulfonate with zirconium nitrate(27) and the titanium peroxide(28) methods were found to be too insensitive.

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(25) *Ibid.*, p. 214.

(26) O. Menis and C. K. Talbott, "Determination of Uranium by Direct Titration with Chromous Solution," *op. cit.*, ORNL-1233, p. 73.

(27) F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 2d. ed. *I*, 580, Van Nostrand, New York, 1936.

(28) *Ibid.*, p. 571.

### Table 23

### DETERMINATION OF URANIUM IN THE PRESENCE OF MOLYBDATE BY THE CHROMOUS SULFATE TITRATION METHOD

Composition of test solution:
- 7.5 ml of concentrated $H_2SO_4$
- 52.4 mg of U as $UO_2SO_4$
- Molybdate as indicated
- $H_2O$ to make 75.0-ml total volume

Titrant:
- Approximately 0.1 *M* $CrSO_4$ solution

Temperature:
- 88 to 93°C

Conditions of test:
- Air excluded from $CrSO_4$ and sample solutions
- Helium gas bubbled through solution 5 min before titration
- Helium gas swept over surface of solution during titration
- Precision-Dow Recordomatic titrometer used

| MOLYBDATE (mg of Mo) | VOLUME OF TITRANT (ml), $X$ | AVERAGE, $\overline{X}$ | DIFFERENCE, $X - \overline{X}$ |
|---|---|---|---|
| | 5.45 | | 0 |
| | 5.45 | | 0 |
| | 5.45 | 5.45 | 0 |
| 0.216 | 5.47 | | 0 |
| 0.216 | 5.47 | | 0 |
| 0.540 | 5.45 | | -0.02 |
| 0.540 | 5.45 | | -0.02 |
| 1.08 | 5.49 | | +0.02 |
| 1.08 | 5.45 | 5.47 | -0.02 |
| | Standard deviation ($MoO_4^=$ present) = 0.02. | | |

The method that depends on an amperometric titration with thorium nitrate(29) and employes the ORNL high-sensitivity polarograph(30) and a dropping-mercury cathode has been investigated. The titration was carried out at room temperature (28 to 29°C) in 5 ml of solution that was 0.5 *M* with KCl. The mercury drop time was 3.0 sec, and the sensitivity (current range) was 1.69 μa for full chart scale. The diffusion current was measured at 1.35 v vs. S.C.E. This potential was selected after determination of the diffusion current of a thorium nitrate solution in 0.1 *N* KCl. An approximately 0.05 *N*

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(29) A. Langer, "Amperometric Titration of Fluorine with Thorium Nitrate," *Ind. Eng. Chem., Anal. Ed.* **12**, 511 (1940).

(30) M. T. Kelley, P. F. Thomason, L. T. Corbin, S. A. Reynolds, C. L. Burros, and E. J. Frederick, "ORNL High-Sensitivity Recording Polarograph (Method No. 8)," *Manual of Analytical Procedures for the $U^{235}$ Recovery Process*, ORNL-983, (Aug. 20, 1951).

### Table 24

### DETERMINATION OF URANIUM(VI) AND IRON(III) IN THE PRESENCE OF $NH_4SCN$ BY TITRATION WITH CHROMOUS SULFATE

Composition of test solution:

10 mg of $NH_4SCN$
$UO_2SO_4$ as indicated
$Fe_2SO_4$ as indicated
Other components and final volume as given in Table 23

Conditions of test:

Same as given in Table 23

| $UO_2SO_4$ (as mg of U) | $Fe_2(SO_4)_3$ (as mg of Fe) | FACTOR | |
|---|---|---|---|
| | | Uranium[a] | Iron[b] |
| 60.6 | | 1.045 | |
| 60.6 | | 1.045 | |
| 60.6 | 2.180 | 1.037 | 5.22 |
| 60.6 | 1.090 | 1.037 | 5.41 |
| 60.6 | 0.218 | 1.045 | |
| 60.6 | 0.043 | 1.045 | |
| 60.6 | 2.180 | 1.045 | 5.08 |
| 60.6 | 2.180 | 1.045 | |
| 60.6 | 2.180 | 1.054 | 5.36 |
| 60.6 | 2.180 | 1.054 | 5.08 |
| 60.6 | 2.180 | 1.045 | 5.08 |
| 60.6 | 2.180 | 1.045 | 5.05 |
| 60.6 | 1.526 | 1.045 | 5.41 |
| 60.6 | 1.029 | 1.045 | |
| | Average | 1.045 | 5.21 |
| | Standard Deviation = | 0.006 | 0.16 |
| | = | 0.6% | 3.1% |

[a] Milligrams of uranium per milliliter of $CrSO_4$ solution.

[b] Milligrams of iron per milliliter of $CrSO_4$ solution.

thorium nitrate solution was standardized amperometrically against fluoride prior to titration of the samples. Comparison of the results with those on samples to which standard additions of fluoride had been made indicated that the relative error was ± 1 to 7% on solutions containing 9 to 18 $\mu g$ of fluoride.

## SOLUBILITY OF HRE CORROSION AND FISSION PRODUCTS IN URANYL FLUORIDE SOLUTIONS

O. Menis M. L. Druschel

In order to facilitate the collection of relevant analytical data in HRE corrosion studies, it is planned to determine the solubilities of some corrosion and fission products in uranyl fluoride solutions. At present, the determination of the solubility of anhydrous nickel fluoride in uranyl fluoride solutions containing 100 mg of uranium per milliliter at 25 and 250°C is in progress, but no data are available.

## PREPARATION OF RUTHENIUM HYDROXIDE

O. Menis M. L. Druschel

In connection with studies of the solubility of fission products in the uranyl fluoride system, ruthenium hydroxide has been prepared from ruthenium trichloride by a modification of a procedure described by Mellor.(31) The recommended procedure in which the hydroxide is precipitated at pH 3.0 to 5.0 gave very low yields (10 to 20%). Better results were obtained by a rapid addition of potassium hydroxide solution (10%) until a pH of 6.0 was reached; potassium hydroxide solution was then added dropwise until a heavy flocculant precipitate was obtained. The precipitate was washed free of chloride by decantation and finally filtered. A yield of 99% was obtained by this method.

## COLORIMETRIC DETERMINATION OF RUTHENIUM

O. Menis F. E. Jenkins

The use of a new colorimetric reagent, $\beta$-nitroso-$\alpha$-naphthol, for the determination of ruthenium was described in a previous progress report.(32) The study of this method has recently been completed.

The visible and ultraviolet absorption spectra of the complex between ruthenium and the reagent are shown in Fig. 32. It is evident that a relatively broad maximum exists at approximately 600 mμ. The reagent, however, exhibits no absorption at this wavelength (Fig. 32).

A factor of 1.64 ± 0.02 μg of ruthenium per milliliter per optical density unit was calculated from absorption measurements at 600 mμ on a series of standard solutions of ruthenium that had been treated according to the colorimetric procedure. The stock solution of ruthenium from which the aliquots were taken had been standardized gravimetrically. In the presence of excess reagent the complex was found to be very stable – the absorbancy decreased only 3% in 24 hr.

Efforts to determine the nature of the complex have been unsuccessful, because the reagent is slowly decomposed in the HCl-$SO_2$ solution required to maintain ruthenium in a single, reduced, valence state, and a large excess of reagent is essential for the development of the colored complex. The method is presently being used to determine the solubility of ruthenium in uranyl solutions.

## ABSORPTION SPECTRA OF URANYL SULFATE SOLUTIONS

O. Menis

In compliance with a request by a staff member of the HRP, a study has been made of the ultraviolet and visible absorption spectra of uranyl sulfate solutions of several concentrations. A brief survey of the literature indicated that very little work had been published on this subject. Pringsheim(33) used a quartz spectrograph to make absorption measurements

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(31) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, XV, 514, Longmans, Green and Co., New York, 1936.

(32) O. Menis and F. E. Jenkins, "Ruthenium," *op. cit.*, ORNL-1233, p. 77.

(33) P. Pringsheim, "Das Absorptionsspektrum und die Photochemisch Sensibilisierende Wirkung des Uranylsulfats in Wässeriger Lösung," *Physica* 4, 733 (1937).

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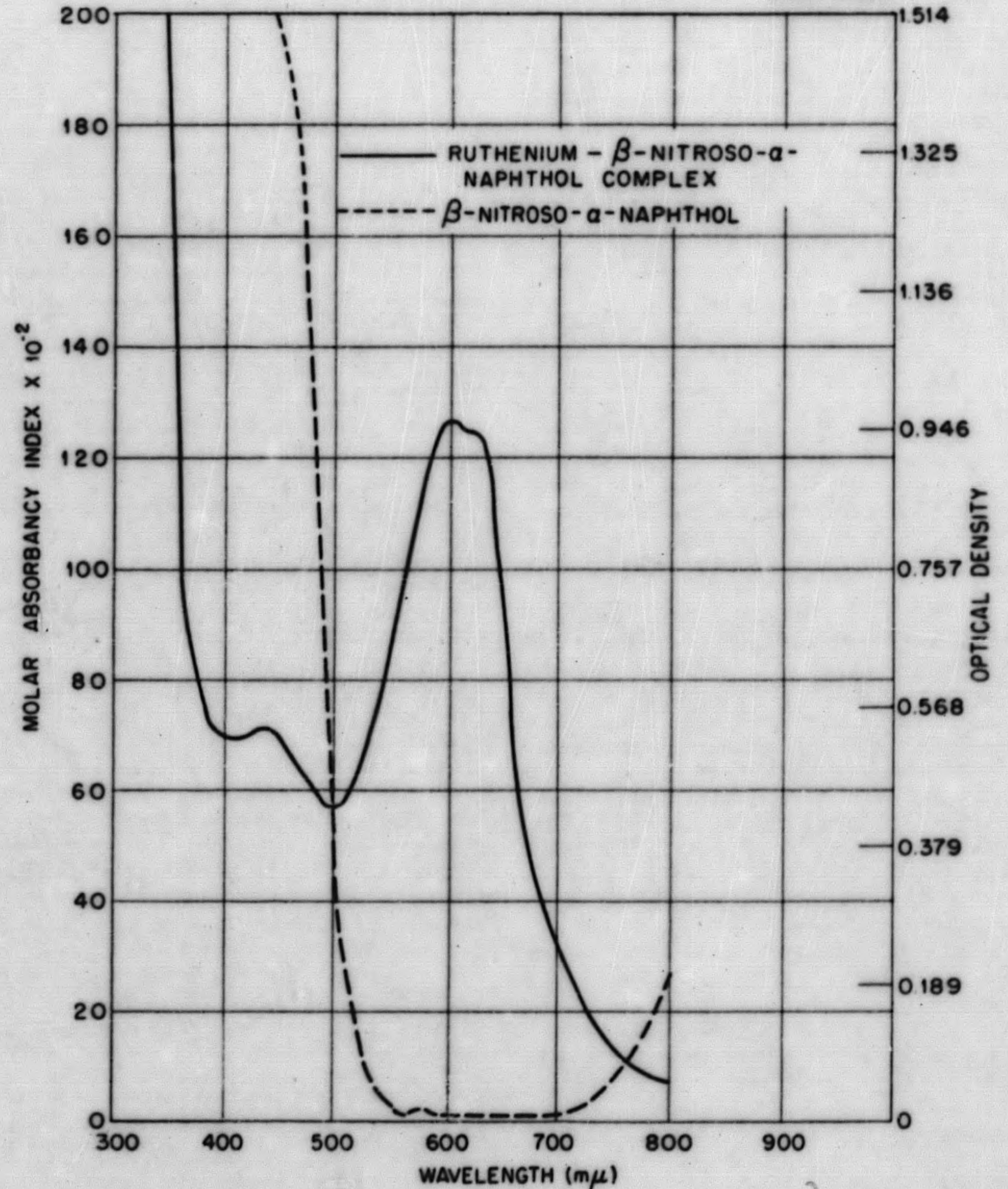

**Fig. 32. Absorption Spectra of Ruthenium-β-Nitroso-α-Napthol Complex and β-Nitroso-α-Napthol Reagent.**

from 365 to 436 mμ, but his data are difficult to interpret. In connection with a study of ionic association in aqueous solution, Betts and Michels[34] published an absorption spectrum in the range of 340 to 500 mμ of a solution that was 0.1 *M* in uranyl ions and 0.082 *M* with respect to bisulfate.

Absorbancy measurements for the present study were made by means of a Beckman DU spectrophotometer equipped with a tungsten lamp for measurements in the visible region and with a hydrogen-discharge lamp for those in the ultraviolet region of the spectrum. The solutions were maintained at constant temperature (25.2 ± 0.1°C) in matched quartz cuvettes by means of an attachment (Thermospacer) for the Beckman spectrophotometer. The sensitivity control knob of the instrument remained constant between measurements and zero adjustments against water were made by varying the slit width.

A series of standard solutions was prepared from a stock solution that had been found by analysis to be free of impurities and excess sulfuric acid. Plots of the absorbancy measurements at the various concentrations of uranyl sulfate are shown in Fig. 33. The calculated molar absorbancy indexes at the maximum (418 mμ) are 13.50, 13.48, and 13.44 for the solutions containing 2.168, 5.42, and 10.84 mg of uranium per milliliter, respectively.

In Fig. 34 the molar absorbancy index of uranyl sulfate is plotted as a function of the wavelength in both the visible and ultraviolet regions of the spectrum. The measurements were made on a solution whose uranium concentration allowed optimum spectrophotometric accuracy of absorbancy measurements in the region of the maximum. The wavelength of the maximum and the fine structure of the spectrum conform closely to those reported by Betts and Michels.[34]

## DETERMINATION OF COPPER

O. Menis

Microgram quantities of copper can be determined colorimetrically by use of sodium diethyldithiocarbamate.[35] The cupric diethyldithiocarbamate complex can be extracted with carbon tetrachloride or butyl acetate, and its absorbancy can be measured at 440 mμ or at 560 to 600 mμ. Since the shorter wavelength is at the absorption peak, it offers maximum sensitivity and is useful in the range of 1 to 60 μg of copper. The longer wavelength range represents a plateau in the absorption spectrum and renders the method less sensitive. The longer wavelength is, however, convenient to use when copper is present in the range of 60 to 1000 μg. Furthermore, because of the appreciable width of the absorption plateau, measurements can be carried out by means of a simple filter photometer. The interference of nickel can be eliminated by complexing the element with the sodium salt of ethylenediamine tetracetic acid (Versene).[36] Iron, cobalt, manganese, and zinc interferences are also eliminated by this reagent. The complexes of silver and bismuth with diethyldithiocarbamate are formed in the presence of Versene, but their interference is negligible if the absorption is measured at 560 to 600 mμ.

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[34] R. H. Betts and R. K. Michels, "Ionic Association in Aqueous Solutions of Uranyl Sulfate and Uranyl Nitrate," *J. Chem. Soc.* **S286** (1949).

[35] J. L. Hague, E. D. Brown, and H. A. Bright, "Photometric Determination of Copper in Iron and Steel with Diethyldithiocarbamate," *J. Research Nat. Bur. Standards* **47**, 380 (1951).

[36] V. Sedivec and V. Vasak, "The Colorimetric Determination of Copper by Sodium Diethyldithiocarbamate," *Collection Czechoslov. Chem. Communs.* **15**, 260 (1950).

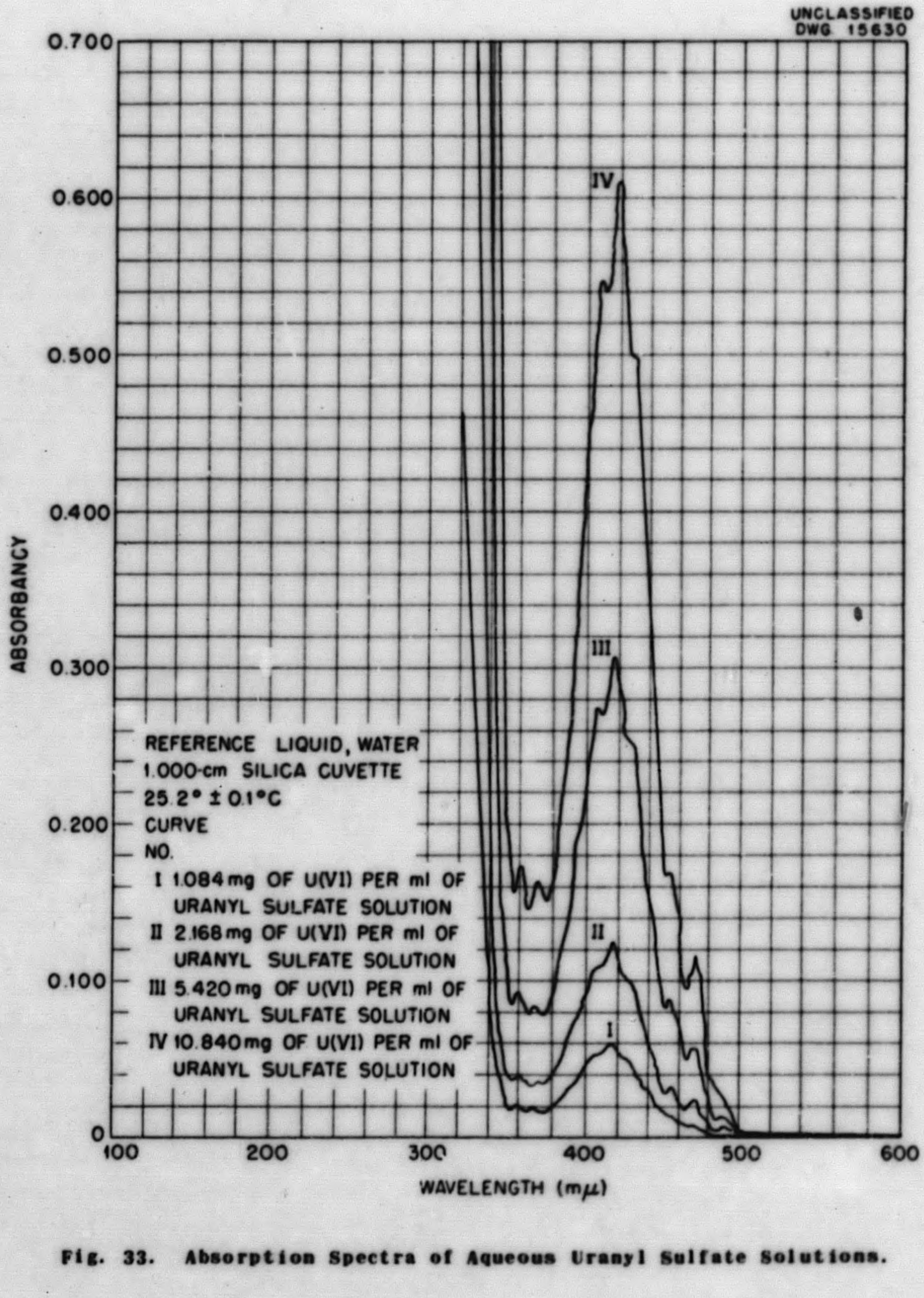

**Fig. 33. Absorption Spectra of Aqueous Uranyl Sulfate Solutions.**

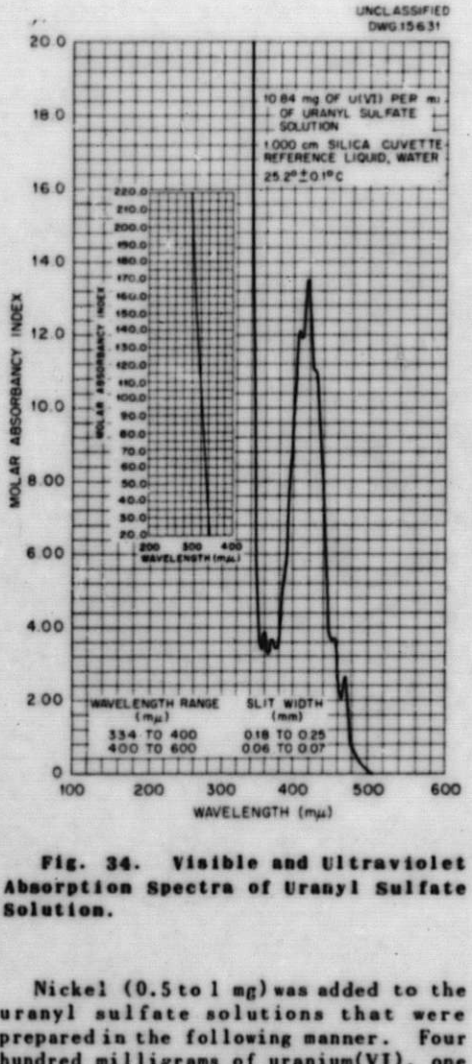

**Fig. 34. Visible and Ultraviolet Absorption Spectra of Uranyl Sulfate Solution.**

Nickel (0.5 to 1 mg) was added to the uranyl sulfate solutions that were prepared in the following manner. Four hundred milligrams of uranium(VI), one gram of ammonium citrate, and Versene in a 10- to 100-fold molar excess over total cations present were added to each of a series of standard copper(II) solutions. The pH was adjusted to 9.0 with $NH_4OH$ solution and the volume made up to 25 ml. Sodium diethyldithiocarbamate reagent was added, and the solution was extracted twice with the organic solvent. The absorbancy of the organic phase was then measured at one of the suggested wavelengths. The results obtained at various wavelengths and with each of the two solvents are shown in Table 25. These data indicate that for copper concentrations in the microgram range, absorbancy measurements with the shorter wavelength give the most precise results, with the standard deviation being approximately 1%. Copper in the milligram range can be determined at the longer wavelength with a standard deviation of 2%.

Two extractions are required for the greatest accuracy and precision, since a single extraction results in a recovery of only 90% and the standard deviation of the results in this case is 4%.

Carbon tetrachloride, being heavier than water, is a convenient solvent; however, butyl acetate has an advantage from the health hazard standpoint.

Some absorbancy measurements were also carried out with a Bausch and Lomb filter photometer equipped with 430 and 600 mμ interference filters. The precision, however, was not so good as was obtained with the Beckman DU spectrophotometer.

## DETERMINATION OF URANIUM(IV)

O. Menis

A direct spectrophotometric method for the determination of uranium(IV) in uranium oxides and uranyl salt solutions is being investigated as a replacement for the fluoride separation procedure.(37) Because of its speed,

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(37) O. Menis, C. K. Talbott, and F. E. Jenkins, "Analysis of Uranyl Sulfate Solutions," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 26, 1951*, ORNL-1113, p. 73.

## Table 25

## DETERMINATION OF COPPER IN URANYL SULFATE SOLUTIONS

Composition of test solution:
100 mg of U(VI) as $UO_2SO_4$
12 mg of Versene
500 to 1000 μg of nickel
Sodium diethyldithiocarbamate
Solution I – 1 ml of 0.1%
Solution II – 1 ml of 1.0%
$H_2O$ to make 25.0-ml final volume

Beckman DU spectrophotometer used

Length of light path of cell = 1 cm

| RANGE OF TOTAL CONCENTRATION OF COPPER (μg) | WAVELENGTH (mμ) | ORGANIC SOLVENT | FACTOR(a) | STANDARD DEVIATION(b) |
|---|---|---|---|---|
| Solution I<br>30 to 60 | 430 | Butyl acetate | 114 | 1 |
| | 440 | Butyl acetate | 115 | 1 |
| | 440 | $CCl_4$ | 117 | 1 |
| Solution II<br>120 to 1200 | 600 | Butyl acetate | $1.49 \times 10^3$ | 30 |
| | 600 | $CCl_4$ | $1.49 \times 10^3$ | 30 |

(a) Factor = μg of copper per optical density unit.

(b) Standard deviation was calculated from a series of determinations carried out under the same conditions.

simplicity, and potentially greater accuracy, the direct spectrophotometric method should be an improvement over the earlier procedure.

The spectral absorption characteristics of uranium(IV) in phosphoric acid solutions in the presence of uranium(VI) have been described by Andrews et al.(38) These authors recommended the use of 630 mμ as a suitable wavelength for the measurement of uranium(IV) concentrations. Investigations in this laboratory have indicated that the use of the absorption maximum at 660 to 664 mμ offers greater sensitivity and requires less rigid control of phosphoric acid concentration.

Plots of the molar absorbancy index vs. wavelength obtained from measurements on solutions of uranium(IV) in various concentrations of phosphoric acid are shown in Fig. 35. The molar absorbancy indexes for uranium(IV) in phosphoric acid solutions at several

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(38) L. J. Andrews, W. B. Schaap, and J. W. Gates, Jr., *A Spectrophotometric Determination of Mixtures of Hexavalent and Tetravalent Tuballoy*, CD-4003 (Feb. 17, 1945).

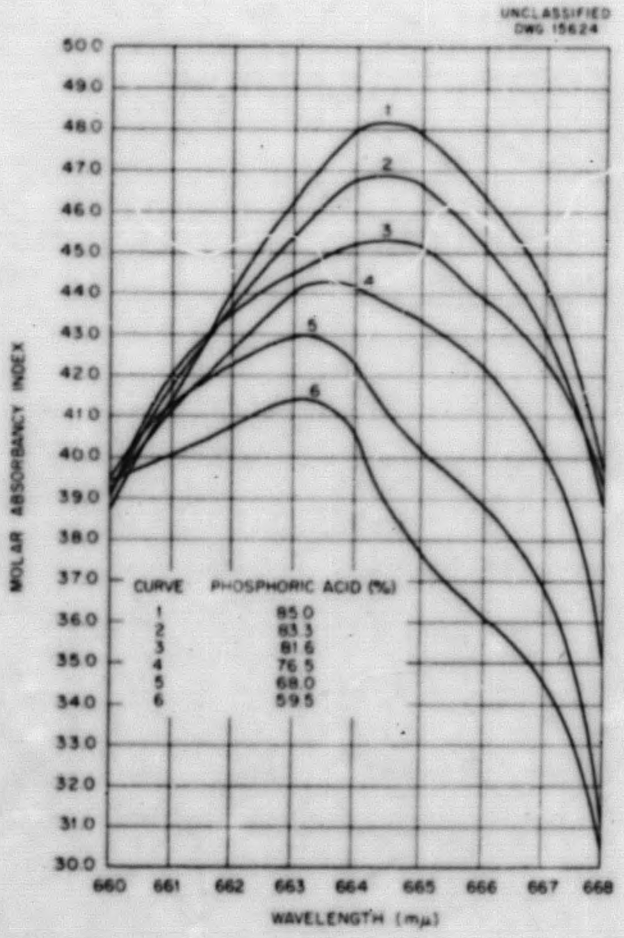

**Fig. 35. Molar Absorbancy Index of $UO_2$ in Phosphoric Acid Solutions.**

wavelengths are given in Table 26. These data indicate that at wavelengths of 660 and 661 mμ the molar absorbancy index is least dependent on the phosphoric acid concentration. At 630 mμ, the previously recommended wavelength, there is greater variation of absorbancy with acid concentration, and the sensitivity decreases. It may be observed (Fig. 35) that as the phosphoric acid concentration is decreased the absorption maximum broadens and is shifted toward shorter wavelengths.

Uranium(IV) in concentrations as low as 50 to 100 μg per milliliter can be determined with a relative error of 4% in 15 ml of aqueous sample in a total volume of 50 ml by absorbancy measurements at 661 mμ with a Beckman DU spectrophotometer employing 10-cm cells. The relative error is only ±1 to 2% on solutions of higher uranium(IV) concentration. The addition of $P_2O_5$ instead of phosphoric acid to the aqueous sample promises to increase the sensitivity of the method three- or fourfold. This variation in the method is presently being studied.

**Table 26**

**MOLAR ABSORBANCY INDEX OF $UO_2$ IN PHOSPHORIC ACID SOLUTIONS AT SEVERAL WAVELENGTHS**

See Fig. 35 for plot of data

| $H_3PO_4$ CONCENTRATION (%) | MOLAR ABSORBANCY INDEX | | | | | | |
|---|---|---|---|---|---|---|---|
| | Wavelength (mμ) | | | | | | |
| | 630 | 660 | 661 | 662 | 663 | 664 | 665 |
| 89.5 | | | 42.1 | | | 47.9 | |
| 85.0 | 32.9 | 38.8 | 41.4 | 43.9 | 44.9 | 47.9 | 47.9 |
| 83.3 | 34.5 | 39.0 | 41.5 | 43.4 | 44.8 | 46.7 | 46.6 |
| 81.6 | 34.2 | 39.0 | 41.8 | 43.6 | 44.0 | 45.1 | 45.1 |
| 76.5 | 30.4 | 38.9 | 41.0 | 42.5 | 44.0 | 44.1 | 43.3 |
| 68.0 | 29.8 | 39.3 | 41.1 | 42.2 | 42.9 | 42.3 | 40.0 |
| 59.5 | 28.4 | 39.3 | 40.0 | 40.6 | 41.4 | 40.8 | 37.6 |

## QUALITY CONTROL

R. L. McCutchen

The control programs for the general ionic analytical laboratory and the HRE control laboratory are essentially the same as those reported for the last quarter of 1951. The X-10 laboratories instituted a control program for the colorimetric determination of thorium at two concentration levels, in addition to the uranium control programs.

During this quarter the three laboratories participating in the control program reported a total of 1525 determinations. Table 27 summarizes the total number of control determinations for each laboratory.

Table 27

SUMMARY OF CONTROL DETERMINATIONS

| LABORATORY | TOTAL NUMBER OF DETERMINATIONS |
|---|---|
| General Ionic Analysis | 108 |
| HR Control | 113 |
| X-10 Laboratories | 1304 |
| Total | 1525 |

### General Ionic Analysis Laboratory

*Uranium Determination by the Fluorometric Method.* Uranyl nitrate solutions were tested by two fluorometric methods: extraction of the uranium with TBP (tributyl phosphate) and direct determination of the uranium without extraction. The results in Table 28 indicate that the best precision is obtained with the direct method.

*Uranium Determination by the Colorimetric (l-Ascorbic Acid) Method.* Last quarter it was suggested that the thiocyanate method be substituted for the *l*-ascorbic acid method for determining uranium to improve both the precision and the accuracy of the uranium test results. However, the substitution was not so feasible as it had appeared, since the addition of iron to the samples prior to the diethyl ether extraction resulted in sufficient iron being carried over into the ether phase to cause a red (iron-cyanate) color that was difficult to destroy. Therefore all colorimetric results reported were obtained by the *l*-ascorbic acid method. A summary of uranium test results obtained by the *l*-ascorbic acid method, with and without the diethyl ether extraction, is given in Table 29.

Table 28

URANIUM DETERMINATION BY THE FLUOROMETRIC METHOD

Comparison and statistical evaluation of test results for the quarter

| SAMPLE TREATMENT | NUMBER OF DETERMINATIONS | CONCENTRATION RANGE ($\mu$g/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL (%) | LIMIT OF ERROR* (%) |
|---|---|---|---|---|---|
| Extracted | 22 | 1.7 to 17.0 | 7 | 3 | 15 |
| Not extracted | 20 | 1.7 to 17.0 | 3 | 1 | 5 |

*95% probability level.

*Uranium in Bartow Clay Leach Solutions as Determined by the Fluorometric Method.* The large amounts of aluminum, phosphate, and silica that are contained in Bartow clay leach solutions caused quenching of the fluorescence of the uranium in the solution when the direct method was used and resulted in poor precision and low uranium values. However, when the uranium was extracted with TBP prior to the determination of the fluorescence of the sample, the precision improved and the test results were higher. Table 30 summarizes the results obtained by both methods.

### URE Control Laboratory

*Uranium Determination by the Jones Reductor, Ceric Sulfate Method.* Both the accuracy and precision of the uranium test results improved during this period. A comparison of the results for last quarter and for this quarter is given in Table 31.

**Table 29**

**URANIUM DETERMINATION BY THE *l*-ASCORBIC ACID METHOD**

Comparison and statistical evaluation of test results for the quarter

| SAMPLE TREATMENT | NUMBER OF DETERMINATIONS | CONCENTRATION RANGE (mg/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) |
|---|---|---|---|---|---|
| Extracted | 18 | 0.17 to 1.7 | 4 | 2 | 8 |
| Not extracted | 12 | 0.17 to 1.7 | 1 | 1 | 3 |

*95% probability level.

**Table 30**

**URANIUM IN BARTOW CLAY LEACH SOLUTIONS AS DETERMINED BY THE FLUOROMETRIC METHOD**

Comparison and statistical evaluation of test results for the quarter

| SAMPLE TREATMENT | NUMBER OF DETERMINATIONS | CONCENTRATION RANGE (μg/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) |
|---|---|---|---|---|---|
| Extracted | 10 | 20 to 30 | 3 | 2 | 8 |
| Not extracted | 10 | 45 to 55 | 4 | 3 | 10 |

*95% probability level.

*Iron Determination by the α-α'-Bipyridyl Method.* Only three iron results were reported during this period; therefore the amount of data is too small to offer any conclusion regarding either their accuracy or precision.

*Nickel Determination by the Dimethylglyoxime Method.* Both the precision and accuracy of the nickel test results were improved this quarter. The positive bias previously noted has been corrected. The results for last quarter and for this quarter are summarized in Table 32.

*Chromium Determination by the Diphenylcarbazide Method.* The precision and accuracy of the chromium test results during this period have not been so good as for the previous quarter. The results during the last month of this quarter have been low and have had a definite negative bias. Steps are being taken to correct this situation. To facilitate a comparison of the two periods, the results for both quarters are given in Table 33.

*Manganese Determination by the Periodate Method.* During this period

### Table 31

### URANIUM DETERMINATION BY THE JONES REDUCTOR, CERIC SULFATE METHOD

Comparison of accuracy and precision of test results

| YEAR | QUARTER | NUMBER OF DETERMINATIONS | CONCENTRATION RANGE (mg/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) | BIAS |
|---|---|---|---|---|---|---|---|
| 1951 | 4 | 196 | 26 to 58 | 1 | 0.4 | 2 | None |
| 1952 | 1 | 52 | 26 to 43 | 0.7 | 0.2 | 1 | None |

*95% probability level.

### Table 32

### NICKEL DETERMINATION BY THE DIMETHYLGLYOXIME METHOD

Comparison of accuracy and precision of test results

| YEAR | QUARTER | NUMBER OF DETERMINATIONS | CONCENTRATION RANGE ($\mu$g/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) |
|---|---|---|---|---|---|---|
| 1951 | 4 | 86 | 5 to 58 | 11 | 2 | 21 |
| 1952 | 1 | 21 | 12 to 60 | 7 | 3 | 15 |

*95% probability level.

only four manganese values were reported; therefore it is not possible to reach any conclusion regarding their accuracy and precision.

### X-10 Laboratories

*Uranium Determination by the Fluorometric Method.* The precision and accuracy of the uranium values reported by the laboratory in Building 3550 are slightly better than was noted for the previous quarter, whereas the reverse is true for the laboratory in Building 3019.

Table 34 gives a comparison of the data obtained during both quarters.

*Uranium Determination by the Colorimetric (Thiocyanate) Method.* The precision and accuracy of the uranium values obtained by the colorimetric method and reported by the laboratories in Buildings 3550 and 3019 are excellent. The data for the last quarter and this quarter are given in Table 35.

*Thorium Determination by the Colorimetric Method.* A control program was instituted for the colorimetric determination of thorium(39)

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(39) P. F. Thomason, M. A. Perry, and W. M. Byerly, "Determination of Microgram Amounts of Thorium: A Colorimetric Method," *Anal. Chem.* **21**, 1239 (1949).

Table 33

CHROMIUM DETERMINATION BY THE DIPHENYLCARBAZIDE METHOD

Comparison of accuracy and precision of test results

| YEAR | QUARTER | NUMBER OF DETERMINATIONS | CONCENTRATION RANGE (μg/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) |
|---|---|---|---|---|---|---|
| 1951 | 4 | 20 | 5 to 84 | 4 | 2 | 8 |
| 1952 | 1 | 21 | 7 to 36 | 10 | 5 | 20 |

*95% probability level.

Table 34

URANIUM DETERMINATION BY THE FLUOROMETRIC METHOD

Comparison of accuracy and precision of test results

| X-10 BUILDING | YEAR | QUARTER | NUMBER OF DUPLICATES | CONCENTRATION RANGE (μg/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) | ACCURACY B ± C.I. (%) | BIAS |
|---|---|---|---|---|---|---|---|---|---|
| 3550 | 1951 | 4 | 110 | 3.4 to 7.0 | 4 | 2 | 9 | −2 ± 2 | None |
| | 1952 | 1 | 62 | 2.5 to 3.0 | 3 | 1 | 7 | 0 ± 1 | None |
| 3019 | 1951 | 4 | 194 | 3.4 to 7.0 | 5 | 1 | 9 | +1 ± 1 | None |
| | 1952 | 1 | 143 | 2.5 to 7.0 | 6 | 2 | 11 | −1 ± 2 | None |

*95% probability level.

during this quarter; 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (Thoron) was used as the chromogenic reagent. In the two high concentrations of thorium (85 to 100 mg/ml), a definite positive bias was observed although the precision was of the same order of magnitude as that noted for the lower concentration of thorium (53 μg/ml). Table 36 summarizes the test results reported during this period.

### Table 35

### URANIUM DETERMINATION BY THE COLORIMETRIC (THIOCYANATE) METHOD

Comparison of accuracy and precision of test results

| X-10 BUILDING | YEAR | QUARTER | NUMBER OF DUPLICATES | CONCENTRATION RANGE (μg/ml) | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) | ACCURACY B ± C.I. (%) | BIAS |
|---|---|---|---|---|---|---|---|---|---|
| 3550 | 1951 | 4 | 110 | 341 to 682 | 0.7 | 0.3 | 1.3 | -0.5 ± 0.3 | Negative |
| | 1952 | 1 | 61 | | 1.0 | 0.5 | 2.0 | -0.5 ± 0.3 | Negative |
| 3019 | 1951 | 4 | 171 | 341 to 682 | 1.3 | 0.4 | 2.6 | +0.3 ± 0.4 | None |
| | 1952 | 1 | 155 | | 1.0 | 0.3 | 2.0 | +0.2 ± 0.3 | None |
| 3550 | 1951 | 4 | 62 | 253 to 273** | 0.1 | 0.2 | 1.2 | 0 ± 0.2 | None |
| | 1952 | 1 | 31 | | 1.0 | 0.4 | 2.0 | 0 ± 0.4 | None |
| 3019 | 1951 | 4 | 112 | 253 to 273** | 1.2 | 0.3 | 2.0 | -0.2 ± 0.3 | None |
| | 1952 | 1 | 109 | | 1.0 | 0.2 | 2.0 | -0.8 ± 0.2 | Negative |

*95% probability level.

**In gm/ml.

### Table 36

### THORIUM DETERMINATION BY THE COLORIMETRIC METHOD

Summary of accuracy and precision of test results

| SAMPLE CODE NO. | NUMBER OF DUPLICATES | CONCENTRATION | | STANDARD DEVIATION (%) | CONFIDENCE INTERVAL* (%) | LIMIT OF ERROR* (%) | ACCURACY B ± C.I. (%) | BIAS |
|---|---|---|---|---|---|---|---|---|
| | | Known | Average | | | | | |
| Th-1 | 46 | 53 μg/ml | 53 μg/ml | 2 | 0.5 | 4 | 0 ± 0.5 | None |
| Th-2 | 25 | 100.4 mg/ml | 102.1 mg/ml | 2 | 0.7 | 4 | +1.6 ± 0.7 | Positive |
| Th-3 | 20 | 84.6 mg/ml | 85.1 mg/ml | 1 | 0.5 | 2 | +0.6 ± 0.5 | Positive |

*95% probability level.

## SERVICE ANALYSES

H. P. House

Analytical service work during this quarter was principally concerned with HRP, and the project for uranium recovery from raw materials. The acceleration of work on these projects that has been effected and is anticipated has created an increase in demands for chemical analyses. In order to keep pace with these demands, the ionic analyses laboratories received a personnel increase from 35 to 43; a substantial additional increase is anticipated by the end of the fiscal year.

### ANALYTICAL SERVICES

L. J. Brady J. R. Lund
J. W. Robinson

As a result of the marked increase in the analytical work during the quarter, the number of personnel assigned to this work has been increased from 9 to 14, and a further increase to a total of 22 will be made as soon as new employees become available.

Most of the samples were derived from the following projects: reactor chemistry, experimental engineering, and radiation damage research. Over two-thirds of the samples were derived from reactor chemistry studies.

The intensive work with alkali hydroxide coolants was curtailed, and studies of fluoride salt mixtures were emphasized. Samples of fluoride salt mixtures that had been subjected either to static or dynamic corrosion tests were analyzed for corrosion products as well as for their major components, that is, fluoride, uranium, and alkali metals.

The increased interest in the minor impurities in the fluoride salts used to prepare the eutectics resulted in requests for the determination of uranium dioxide, chloride, sulfate, nitrate, and traces of free acid. Methods for the determination of nitrates and chlorides in salts of this type are now available. The Research and Development Department is attempting to develop or adapt methods for the determination of the other components listed.

The method of separating uranium tetrafluoride from uranium dioxide by dissolution of the fluoride in ammonium oxalate is being tested; and, although it will not be possible to isolate the uranium dioxide from all other components by this method, it is believed that a subsequent analysis of the oxalate-insoluble residue for uranium will make possible a rather close approximation of the uranium dioxide content of the uranium tetrafluoride.

Methods for determining the water content of samples of fluorides of alkali metals and chromium salts that have been subjected to drying and dehydration are now being studied. Sodium carbonate is being mixed with the sample to react with and retain any hydrogen fluoride produced as a result of hydrolysis when the sample is heated to expel water.

Carbonate, both in macro and micro amounts, was determined on an appreciable number of alkali hydroxide solutions.

Helium and argon gases were analyzed routinely for oxygen by analytical service personnel until the latter part of the quarter. At that time, personnel of the Experimental Engineering group who had been instructed in this work started making the determinations.

Samples of consecutive thin layers of metal from the inside surface of a section of Inconel pipe taken from a test loop used in dynamic corrosion tests are being analyzed in an attempt to determine whether any of the components of the pipe are being removed preferentially. Results to date give some indication that selective dissolution is occurring.

A limited amount of work was performed for the General Electric Company during the quarter. The sodium monoxide content of 17 sodium samples was determined, and five miscellaneous samples consisting of silicon carbide, Boral, and uranium silicide were analyzed.

It is anticipated that the increase in analytical work will continue and that the major emphasis will be on the analysis of fluoride salt mixtures and on the determination of the purity of the salts used to prepare low-melting-point salt mixtures for use as reactor fuels and coolants.

The distribution of work, as reflected by the number of determinations performed, is given in Table 37.

## ANALYSIS OF ORES AND RELATED MATERIALS

J. W. Robinson

A significant increase was noted in the number of samples that were analyzed for the raw materials program (1290 for this quarter as compared with 1054 for the preceding one). The majority of the samples resulted from pilot plant operations on Florida leach-zone materials. In the latter part of the period, however, samples derived from the newly inaugurated projects that involve the use of lignite and monazite sand contributed substantially to the work. As a result of the continued investigation of organic extractants for use in the ore processes the number of analyses of organic compounds and complexes has increased somewhat. Difficulty has been encountered in achieving precision in the determination of hydrogen in phosphonic and phosphinic acids. It is anticipated that this difficulty can be overcome by exercising closer control in ignition of these materials.

Standardization analyses have recently been carried out on leach solutions and miscellaneous materials resulting from exploratory work of the International Minerals and Chemical Company. The principal determination of interest is that of uranium by the fluorometric method.

## ANALYSIS OF METALS AND ALLOYS

J. W. Robinson

The analysis of stainless steels constituted the greater portion of work on metals. Lead-bismuth and indium-aluminum alloys were also analyzed. A number of methods were tested for the indium determination. A potentiometric titration of indium(1) with potassium ferrocyanide as the titrant was difficult because equilibrium was reached slowly and prior separation of aluminum was required. Separation of the indium as sulfide from an acetic acid solution(2) proved to be laborious and to require very careful control of conditions. The

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(1) H. B. Hope, M. Ross, and J. F. Skelly, "A Rapid Method for the Volumetric Determination of Indium," *Ind. Eng. Chem., Anal. Ed.* 8, 51 (1936).

(2) C. W. Hopkins, "Analysis of Indium Alloys," *Ind. Eng. Chem., Anal. Ed.* **14**, 638 (1942).

Table 37

SUMMARY OF ANALYTICAL SERVICE WORK AT Y-12 SITE FOR PERIOD DECEMBER 3, 1951, THROUGH MARCH 7, 1952

| LABORATORY MAKING ANALYSES | NO. OF PERSONNEL | | ORNL DIVISIONS REQUESTING ANALYSES | | | | | | | OTHERS REQUESTING ANALYSES | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TECHNICAL | NONTECHNICAL | MISC. | ELECTROMAGNETIC | STABLE ISOTOPE RESEARCH AND PRODUCTION | MATERIALS CHEMISTRY | HEED | OPERATIONS | OTHER DIVISIONS | Y-12 | AMERICAN CYANAMID CO. | GENERAL ELECTRIC CO. | TOTAL DETERMINATIONS |
| | | | Number of Determinations | | | | | | | | | | |
| HRP Analytical | 8 | 2 | | | | | 11,250 | | | | | | 11,250 |
| Analytical | 5 | 9 | 1,498 | 183 | | 3,958 | | | | | | 25 | 5,664 |
| Raw Materials | 1 | 4 | 12 | 80 | 84 | 3,200 | 8 | | 20 | | | | 3,404 |
| Metals and Alloys | 1 | 1 | 29 | | | 1,330 | 274 | 14 | 80 | 33 | | | 1,760 |
| Miscellaneous | 3 | 3 | 70 | 6 | | 1,950 | 439 | 12 | 100 | 20 | 12 | | 2,609 |
| TOTALS | 18 | 19 | 1,609 | 269 | 84 | 10,438 | 11,971 | 26 | 200 | 53 | 12 | 25 | 24,687 |

most expedient method appears to be one in which the indium is reduced to the metal with zinc,[3] dissolved in hydrochloric acid, precipitated with ammonium hydroxide, and weighed as the oxide, $In_2O_3$. However, coprecipitation of zinc is encountered; therefore two or three precipitations are required to rid the indium of significant amounts of zinc.

## ANALYTICAL SERVICES FOR THE HRP

A. F. Roemer, Jr.

Analyses of uranyl sulfate solutions that have been used in static

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[3] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 380, Wiley, New York, 1929.

and dynamic corrosion tests continue to comprise most of the work of the HRP Analytical Laboratory. In addition to uranium, the corrosion products, Ni, Fe, Cr, Mn, and, less commonly, such additives as Cu, Mo, and a few other components, are determined in these analyses. A considerable number of gas samples were analyzed for oxygen, carbon dioxide, and hydrogen. The uranium in solutions containing molybdenum is determined by a potentiometric titration with chromous chloride. A correction is made for iron if it is present in significant amounts.

There has been a considerable increase in the demand for analyses of uranium oxide slurries for corrosion products, uranium, and nitrite. The processing of these materials prior to analysis is more time-consuming than the processing of uranyl sulfate solutions. It is anticipated that expansion of the slurry testing program will add substantially to the work in the near future.