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AN INVESTIGATION OF THE TRANSFER OF URANYL NITRATE ACROSS THE WATER–TRIBUTYL PHOSPHATE INTERFACE BY THE METHOD OF PHOTOGRAPHIC PHOTOMETRY

C. V. Chester

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CHEMICAL TECHNOLOGY DIVISION

Unit Operations Section

AN INVESTIGATION OF THE TRANSFER OF URANYL NITRATE ACROSS THE WATER--TRIBUTYL PHOSPHATE INTERFACE BY THE METHOD OF PHOTOGRAPHIC PHOTOMETRY

C. V. Chester

This report was prepared as a thesis and submitted to the Faculty of the Graduate School of the University of Tennessee in partial fulfillment of the degree of Master of Science in the Department of Chemical Engineering.

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SUMMARY

The resistance of the water—tributyl phosphate (TBP) interface to diffusion of uranyl nitrate was investigated by a photographic photometric technique. The resistance was below the limit of detectability in the experiments, even with a surface-active agent present in the system. The sensitivity of the experiments established an upper bound for the interfacial resistance to diffusion equivalent to that of a 25-μ film of TBP under steady-state diffusion. The results indicated that the rate-limiting step in solvent extraction of uranyl nitrate from water by TBP is transfer of the diffusing species between the interface and the bulk phase rather than across the interface.

In the experiments a steady-state concentration profile was established across an interface by providing a source of uranyl nitrate on one side and a sink on the other in a special cell. Uranyl nitrate diffused along the concentration gradient and hence across the interface. A resistance to diffusion by the interface would have been manifested as a departure from equilibrium of the uranyl concentrations immediately adjacent to and on either side of the interface. Accurate values of the interfacial concentrations at steady state were obtained by extrapolating the profile obtained from a few point measurements on either side. The profiles were computed from densitometric measurements of photographic images of the column which were compared with similar images of standard solutions.

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CHAPTER I

INTRODUCTION

The purpose of this investigation was to determine the resistance of the water—tributyl phosphate interface (TBP) to mass transfer, specifically the transfer of uranyl nitrate from the aqueous to the organic phase. The resistance, if sufficiently large, could be important in the design of solvent extraction contactors using this chemical system, which is of great importance in the atomic energy program. If the resistance could be measured, valuable engineering design information would be obtained, and the mechanism of transfer at the interface might be elucidated.

The water—uranyl nitrate—tributyl phosphate solvent extraction system was selected for study primarily because of its importance to uranium purification in power reactor fuel processing operations. The system has the added advantages of being convenient to analyze colorimetrically and of undergoing at the interface a complex reaction likely to produce an interfacial resistance. A disadvantage is the chemical complexity of the system. The uranyl ion hydrolyzes to form several species in concentrated aqueous solutions, the different species having different absorptivities of light at different wave lengths. The complex nature of the extraction reaction at the interface produces a complicated equilibrium relation, and in diffusion, which is the rate-limiting process, there are several species diffusing in both phases. However, the steady-state technique used in these experiments circumvents virtually all these difficulties.

A steady-state concentration profile was established across an interface by providing a source of uranyl nitrate on one side and a sink on the other. The uranyl nitrate diffused along the concentration gradient and hence across the interface. A resistance to diffusion by the interface would be manifested as a departure from equilibrium of the uranyl concentrations immediately adjacent to and on either side of the interface. The interfacial concentrations can be obtained accurately at steady state by extrapolating the profile obtained from a few point measurements on either side.

Another advantage of the technique used is that the transfer rate is independent of hydrodynamic effects. The area of transfer is accurately known, and the molecular flux is sufficiently low that there is no interfacial turbulence, as proved by the nearly linear concentration profiles. The physical system is far better defined than is the case in most mass-transfer experiments.

In this work only the existence and magnitude of an interfacial resistance was sought. The fact that the resistance was smaller than the method is capable of measuring precluded the study of possible mechanisms of transfer.

CHAPTER II

THEORY

MASS TRANSFER IN THE VICINITY OF AN INTERFACE

As steady state is approached, the flux of a single molecular species of concentration C and apparent diffusivity D diffusing in the x direction normal to the interface is given by

$$J = -D_a \frac{\partial C_a}{\partial x} = -D_q \frac{\partial C_q}{\partial x} \tag{1}$$

where the subscripts a and q, respectively, denote the aqueous and organic phases. Since only the stoichiometrically neutral salt was used in this investigation, the diffusion is treated as that of a neutral species.

If we naively assume that the controlling reaction at the interface is simple, first order, and reversible with respect to component C with constant K_1 in the extraction direction and K_2 in the stripping direction, then

$$J = K_1 C_{ai} - K_2 C_{qi} \tag{2}$$

where the subscript i denotes measurement at the interface. At equilibrium J = 0, and

$$K_1 C_a^* = K_2 C_q^* \tag{3}$$

$$\text{or} \quad \frac{C_q^*}{C_a^*} = \frac{K_1}{K_2} = M$$

where M = distribution coefficient. Rearranging (2) and substituting (3) gives

$$J = K_2 \left(\frac{K_1}{K_2} C_{ai} - C_{qi}\right) = K_2 \left(MC_{ai} - C_{qi}\right) = K_2 \left(C^*_{qi} - C_{qi}\right)$$

where C^*_{qi} is the organic interface concentration that would exist if equilibrium at the interface existed with an aqueous interface concentration of C_{ai}. Since we can measure J, M, C_{ai} in the diffusion cell, we have a means of determining K_2 and K_1.

The optical system will measure concentrations at positions known to about 0.02 mm. Thus if a concentration drop $(C^*_{qi} - C_{qi})$ is observed at the interface, it can be detected if it corresponds to a concentration change greater than that over 0.02 mm of the gradient in the organic phase, and can be measured with considerable accuracy if it corresponds to 0.1 mm or more of the gradient. To phrase it another way, a resistance at the interface equivalent to the resistance presented to diffusion by a 0.1-mm layer of the organic can be measured with some accuracy.

From the previous equations

$$J = -D_{qi} \frac{\partial C_{qi}}{\partial x} = K_2(C^*_{qi} - C_{qi}) = K_2(-\Delta C_{qi})$$

To find the equivalent resistance let

$$D_q \frac{\Delta D_q}{\Delta x} = K_2 \Delta C_q$$

or

$$\Delta x = \frac{D_q}{K_2} \geq 0.01 \text{ cm}$$

Typical values for diffusivities range from 10^{-5} to 10^{-6} cm^2/sec. Assuming 10^{-6} cm^2/sec, a measurable rate constant would be

$$K_2 \leq \frac{D_q}{\Delta x} = \frac{10^{-6}\ cm^2/sec}{10^{-2}\ cm} = 10^{-4}\ cm/sec$$

This K has the dimensions of velocity because throughput rather than a homogeneous reaction rate is measured.

If we assume that the reaction of a quiescent interface takes place within a molecular distance, say 10 Å, of the interface, we can convert K to a homogeneous reaction constant by dividing by the thickness of the reacting layer:

$$K_{homogeneous} = \frac{K_2}{10\ \text{Å}} = \frac{10^{-4}}{10^{-7}} = 10^3\ sec^{-1}$$

In terms of a first order half-time, this is

$$t_{1/2} = \frac{\ln 2}{K} = 0.0007\ sec$$

Thus even a fast reaction, down to a millisecond half-time, would be expected to produce an easily measurable departure from equilibrium at the interface.

CHAPTER III

LITERATURE SURVEY

EVIDENCE FOR A CHEMISORPTION- OR MEMBRANE-TYPE RESISTANCE AT A FLUID INTERFACE

Various investigators have, from time to time, reported interfacial resistance, or effects attributable to interfacial resistance, which cannot be explained by hydrodynamic effects.

Resistances will be discussed in terms of thickness of an equivalent film of water or other pertinent solvent in order to give a physical feeling for the order of magnitude of the effects considered. The qualification of steady-state transfer must be added to the analogy as the "film" has no capacity for the solute.

One of the earliest observations of such resistance was reported by Higbie[5] in 1935, who observed that K_2 for the absorption of CO_2 in water did not go to infinity as the time of contact went to zero. His observations can be accounted for by a resistance at the interface equivalent approximately to that of a 10-μ layer of water in a system at steady state.

Higbie's evidence for the resistance is indirect, requiring extrapolation of the experimental data. It has been subject to considerable question, and has been difficult to reproduce.

In 1959 Harvey and Smith[4] reported a study, by a very sensitive interferometric technique, of the same system with transfer across a quiescent interface. The penetration of CO_2 into a plane quiescent

interface in a cell was followed by observation of the displacement of interference fringes caused by change in the refractive index of the solution with CO_2 concentration. No resistance was observed when pure water was exposed to a pure CO_2 atmosphere. The sensitivity claimed for the technique is such that interfacial rate constants up to 4 cm/sec, corresponding to a steady state film resistance of less than 0.1 μ, can be measured.

When a surface-active agent (0.41% Lissapol-N) was introduced into the aqueous phase, the rate constant was 0.028 cm/sec, which corresponds to a film of about 10 μ. This is one of the very few experiments where there is clear evidence that a surface-active agent produced a "membrane-type" resistance to mass transfer. However, it should be pointed out that the bulk solubility of the agent is zero in the gas phase, and somewhat different behavior of a gas-liquid interface from that of a liquid-liquid interface might be expected.

In 1952 Tung and Drickamer[13] reported studies of the diffusion of tagged sulfur compounds through a liquid-liquid interface in which very large interfacial resistances were observed. The experiments were carried out in a diffusion cell designed for high-pressure work using an unsteady-state technique. In an experiment some of the diffusing compound tagged with sulfur-35 was introduced at one end of a wire-gauze-packed diffusion path, and the output of a beta detector at the other end of the path was observed as a function of time. The equivalent diffusion path length was determined by calibration with a solute of known diffusivity (sulfuric acid). The diffusivity of an unknown solute

could then be calculated from the path length, concentration buildup of the tagged solute, and the equations for diffusion in one dimension. In this way diffusion coefficients were measured for SO_2 in liquid SO_2 and and in n-heptane and for sulfuric acid in phenol. The experiment was repeated for SO_2 with the cell half full of liquid SO_2 and filled the rest of the way with n-heptane in such a way that the interface was normal to the direction of diffusion. The relaxation time for the concentration profile in the cell was much longer with the two phases than with either single phase. Or, to state it another way, the apparent diffusion coefficient was much less in two phases than in either single phase. This was interpreted to mean that there was a large interfacial resistance to diffusion. This resistance turns out to be equivalent to a steady-state film of the order of a few centimeters thick.

The same phenomenon was observed for the case of diffusion of sulfuric acid through phenol and water. A marked decrease in apparent diffusion coefficient was observed when the diffusing sulfuric acid had to cross the water-phenol interface. This decrease corresponded to an interfacial resistance of the order of centimeters of solvent. These experiments showed the largest resistances reported for liquid-liquid interfaces in the literature. There are no obvious weaknesses in technique or interpretation of data, but no one has produced similar results in the same or chemically similar systems. The uniqueness of the findings after some years' lapse might lead one to question them.

Explanation of the existence of an interfacial resistance, and particularly in the systems mentioned above, was attempted by Sinfelt

and Drickamer[12] in 1955. They likened the slow reaction at the interface to a chemisorption process having a high energy of activation.

Other studies of interfacial resistance have grown out of the biological work on transfer of solutes through a cell wall. In 1948 Hutchinson[6] studied the transfer of alcohols between water and benzene with and without the presence of a monomolecular detergent film. Unfortunately, his experiments were of the stirred-bulk fixed-interface type, with diffusion and Marengoni effects ignored. It was found that the detergent film retarded the transfer, but this could easily have been due to hydrodynamic effects.

In 1950 Davies[2] presented a study of the transfer of salts from water to benzene in stirred-bulk fixed-interface equipment. The experimental work was carefully carried out, but the analysis assumed that all the resistance to transfer was in the interface and that diffusion in the bulk phases could be ignored. It was observed that the rate of stirring affected the diffusion time, and so the author made the decision to correct all his data to zero stirrer speed. The correction factor was only 0.58; i.e., the relaxation time for 100 rpm was 0.58 that for no stirring, indicating the very low efficiency of stirring. With this procedure the transfer coefficients calculated on the assumption that all resistance was of the membrane type were equivalent to steady-state films of the order of 10 to 100 cm of one of the phases.

Davies's paper included a thermodynamic analysis of solute transfer across an interface. The analysis assumed a membrane-type resistance with negligible holdup, i.e., steady state, but with a finite unspecified

thickness. Unfortunately, in the actual experiment the process was unsteady-state diffusion-penetration of quite thick films adjacent to the interface, and the analysis therefore does not apply. However, the analysis would be valid for a physical situation more nearly approximating the model used, which is probably the case in solute transfer across a cell membrane.

Studies of the Transfer of Uranyl Ion across the Water-TBP Interface

The first significant attack on the problem of transfer of uranyl ion from water to TBP was reported by Hahn[3] in 1954, who determined photometrically the concentration profile across the water-organic interface during unsteady-state diffusion. He had a very large initial concentration gradient across the interface and a very large concentration difference between the aqueous (1.0 M) and organic (0.0 M) phases. The resulting initial rate of mass transfer and associated exothermic reaction at the interface produced very strong Marengoni turbulence at the interface. The concentration scanning system was a light source and a pair of 1/4-mm collimating slits, one on each side of the column of solution, and the scanning time was 10 to 15 min for one profile. The coarse resolution, long scanning time, and turbulence at the interface made it impossible to get significant information on concentration within 1 mm of the interface.

The addition of a surface-active agent caused the concentration profile to closely approach that for theoretical diffusion as a function of time. This fact suggests the presence of interfacial turbulence, but

this was not hypothesized by the experimenter. The principal conclusion drawn from the work is that interphase transfer is not the limiting process in solvent extraction, although the concentration gradients studied were many orders of magnitude greater (initially) than those occurring in production equipment. The work is significant in that attempts were made to get quantitative information on concentration profiles adjacent to an interface being studied.

In 1958 Wischow[15] published a thesis describing an attempt to measure the kinetics of the extraction reaction in a tee mixer followed by rapid separation of the organic phase through a Teflon frit. Half-times for the approach to equilibrium of the system were of the order of a millisecond. Unfortunately, the interfacial area of the system was not measured for lack of adequate photographic equipment, and the conditions of turbulence in the mixed phases prior to and during sampling were also undefined. The reaction rates reported can be accounted for by molecular diffusion if a few assumptions are made about probable drop size. However, no quantitative treatment of the data is possible because of the uncertainties in the state of the physical system.

In 1954 Lewis[9,10] published the first of a series of studies of interphase mass transfer carried out in a well-designed stirred-bulk fixed-interface apparatus. He measured individual transfer coefficients for a variety of binary systems, which in effect calibrated the system with respect to eddy diffusivity as a function of liquid properties (such as viscosity and density) and stirrer speed. From the correlations,

eddy diffusivities may be determined and other stirred-bulk fixed-interface data rationally interpreted. The transfer of organic solutes between two immiscible phases was then measured, and the observed coefficients were compared with those predicted from the eddy diffusivity correlations. Good agreement between predicted and calculated results is claimed, except when interfacial (Marengoni) turbulence was observed. Sherwood[11] pointed out that Lewis's data were not very reproducible, and, as in most stirred-interface experiments, diffusion had been disregarded in the treatment.

Lewis then applied his technique to the uranyl nitrate-water system and a variety of organic solvents.[10] In the water-TBP system he found, in some cases, resistances of the order of 10^3 cm/sec, which corresponds to a steady-state film resistance of about 10 μ. There were also some cases in which the resistance was negative, which were attributed to interfacial turbulence. However, in every case observed, the calculated resistance (negative or positive) increased positively with time. This was attributed to "surface aging." Alternative explanations suggested by the data are (1) decay of Marengoni turbulence, (2) relaxation of unsteady-state concentration profiles, or (3) uncertainty in prediction of the theoretical transfer coefficient (the reciprocal of which was subtracted from the observed to get the resistance).

A less critical approach to the kinetics of transfer was taken by Burger[1] who reported on stirred-bulk, fixed-interface experiments in 1959. His apparatus was similar to that of Lewis. However, he treated the transfer rates as chemical kinetic processes, but used bulk rather

than interfacial concentrations. Since he had no way of relating the bulk and interfacial concentrations, he assumed them proportional, and thereby obtained empirical power relations useful only for predicting transfer rates in equipment identical to his own.

Although interfacial turbulence was observed, its source and implications were not fully appreciated. The retardation of transfer by surfactants was attributed to membrane-type "blocking" of the interface rather than increasing of the interfacial viscosity and consequent reduction of turbulence. This was despite the fact that when surfactants are present the (bulk) "concentration dependence" of the extraction transfer coefficient disappears, and the coefficients are about the same for extraction and stripping and only slightly less than the normal stripping coefficient.

Although not useful for design purposes, Burger's work is valuable for the many qualitative observations made on the behavior of the uranyl-TBP system. The observations on general behavior with surface-active agents and on coalescence are important and generally can be explained in terms of interfacial tension and viscosity changes. The need for extensive work on the hydrodynamics of the water-TBP interface during uranyl transfer is best shown by this work.

The stirred-bulk fixed-interface experiments that have come closest to the ideal of eliminating diffusion resistance in the bulk were those reported by Keish[7] in 1959. His apparatus consisted of a 0.5-in.-dia cylindrical chamber about 1 in. deep containing a coaxial

1/8-in. stirring shaft. A sharp constriction in the chamber at the interface decreased the specific interfacial area of the system to permit reasonable run times and also to prevent (it was hoped) longitudinal motion or "pumping" of the interface. He studied isotope exchange, with the phases at gross chemical equilibrium, and thereby eliminated all the problems associated with Marengoni turbulence.

The data taken were analyzed in terms of the isotope exchange law as given by Wahl and Bonner.[14] In this law, the rate of exchange is equal to a product of two factors, one containing essentially the distribution coefficient, the other a rate term. The calculated exchange rate shows the same variation with various ion concentrations as the distribution coefficient, but the rate term is remarkably constant.

The fact that the system relaxes to equilibrium (of the uranium isotope distribution) with such remarkably constant half-life for all the changes in concentration strongly suggests a diffusion-controlled process rather than the kinetic one postulated by the author. However, assuming diffusion control in a film, the calculated film thickness is of the order of 0.25 μ, which is by far the thinnest film or equivalent film yet observed. It is possible that the interfacial area (0.04 cm^2) was not well-defined as assumed, as it is possible that some vertical perturbations might have occurred which would have greatly increased the interfacial area and correspondingly decreased the equivalent film thickness calculated on the basis of ideal area.

The actual case in Keish's experiments is quite likely a

combination of diffusion and chemical kinetic control. The experiments show the reaction is very fast, and not at all limiting in engineering mass transfer operations.

CHAPTER IV

APPARATUS AND PROCEDURE

APPARATUS

The analytical technique used in this investigation is not new or particularly original. However, the development of some specialized apparatus has permitted its application to a better defined physical system than has been used previously.[3] The optical system used and the photographic technique provided measurements of concentration an order of magnitude closer to the interface.

Optical System

The optical system used consisted of an illuminator, the cell, and a camera (Figure 1). The illuminator was a Bausch and Lomb "Professional" illuminator with the lenses changed to give a focal distance of 12 ft. The aperture was stopped down vertically to 2 cm to reduce the angle of convergence of the light in the vertical plane. A heat filter, stray-light shield, and a 436-mμ (nominal) interference transmission filter were added. The illuminator was focused to project the image of the ribbon filament of the tungsten lamp in the plane of the cell.

The image of the illuminated cell was photographed on 5- by 7-in. Kodak type IV-O spectroscopic plates by a 100-mm f/2.8 Xenotar lens in a Bausch and Lomb model H macrophotographic camera. Image magnification was 5X. Variation of illumination was less than 1 per cent over the field used.

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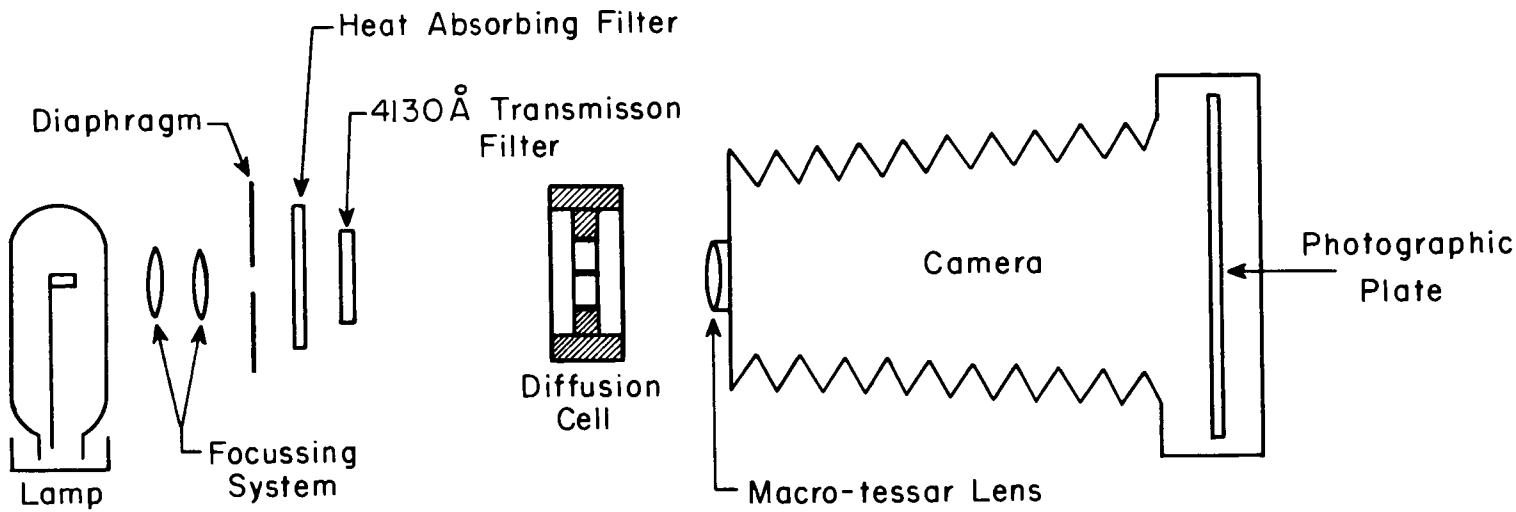

Fig. 1. Optical system for measurement of diffusion at an interface.

Diffusion Cell

The development of a diffusion cell to measure concentration profiles near an interface turned out to be the major problem in this investigation. The requirements of small size, optical accessibility, and resistance to organic solvents made it difficult to eliminate leaks in the glass-to-metal seals.

The core of the cell finally used (Figure 2) was stainless steel held between two glass plates. The required diffusion column and chambers for standards were cut in the stainless steel core. Access to the chambers and column was via channels cut in the surface of the core under the glass.

The uranyl nitrate crystal in the bottom of the diffusion column was the source, and fresh organic phase flowing across the top of the column was the sink, of uranyl nitrate. The interface under observation was about halfway up the column, its edges fixed to the lower junction between the Teflon inserts and the steel cell. This is due to the strongly oleophilic nature of the Teflon and the hydrophilic nature of a clean stainless steel surface. The average height and curvature of the meniscus were controlled by adjusting the amount of aqueous phase in the bottom half of the column.

The concentration of uranyl nitrate in the organic phase was kept near zero at the top of the column by bringing fresh organic into the top via a groove on one side of the cell core and out via a groove on the other side. A piece of 200-mesh screen at the top of the Teflon

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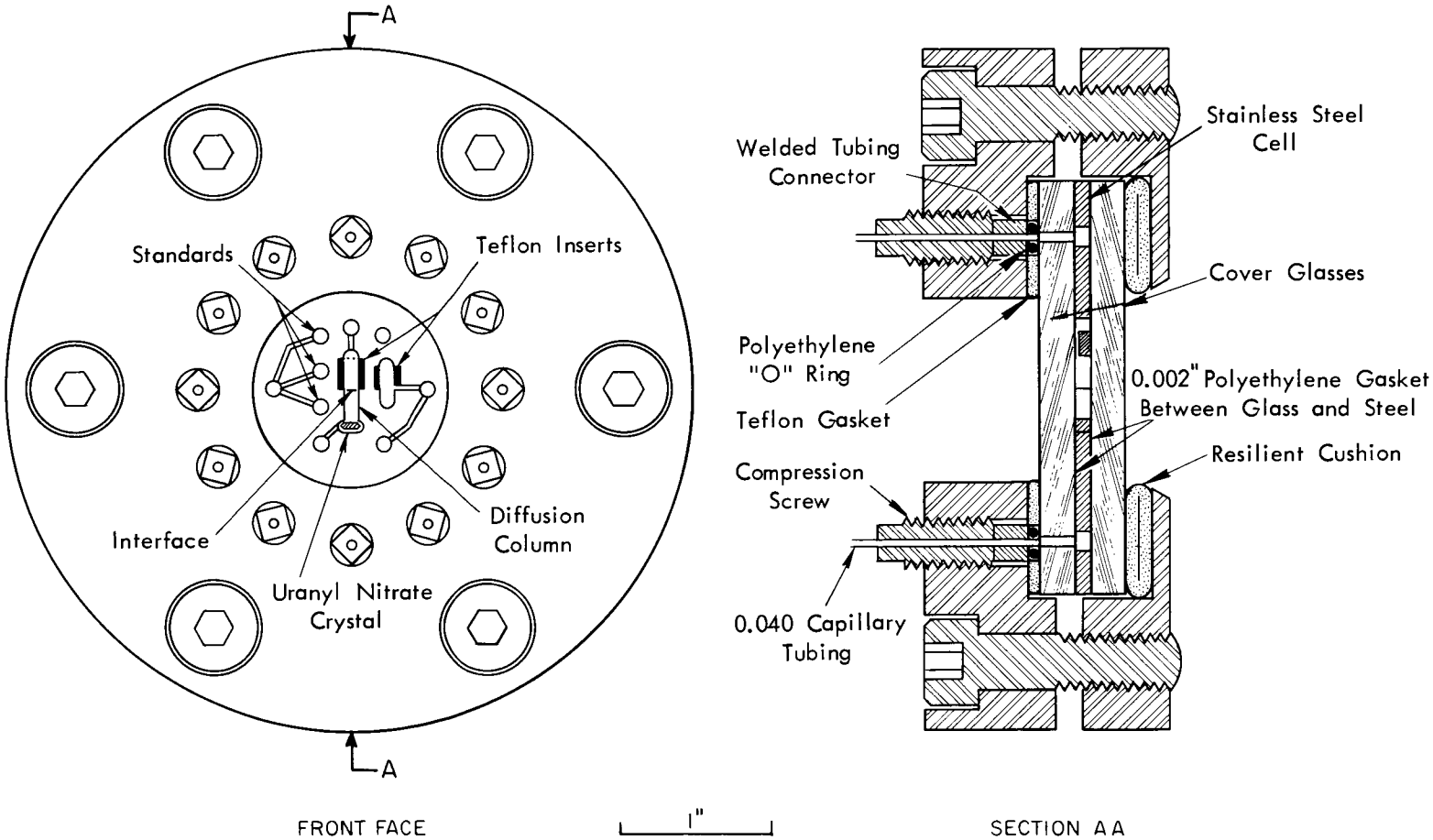

Fig. 2. Cell assembly.

inserts ensured that no eddy destroyed the steady-state profile in the column. Details of the cell core are shown in Figure 3.

The seal between the stainless steel core and the cover glasses was obtained by lapping the mating surfaces flat to 10 fringes, and then using a carefully cut gasket of 0.002-in. polyethylene film. The cover glasses, gaskets, and core were clamped between a stainless steel and a brass flange held with six 3/8-16 socket-head stainless steel cap screws. A resilient cushion of surgical rubber tubing mashed flat between the rear (brass) flange and the rear cover glass took up any creep in the polyethylene gasket while keeping constant pressure on the seal. Figure 4 is a photograph of the cell components.

Solutions were led into the cell core via 40-mil capillary tubing, a compression fitting, and holes through the front cover glass. The seal between the tubing and the cover glass was effected by the compression fitting, which was welded to the end of the tubing and supported a captive polyethylene "O"-ring against the glass (Figure 5). Compression of the "O"-ring was adjusted by 5/16-18 brass compression screws screwed into the front flange down on the compression fitting.

Micropump

A simple pump consisting of ten 10-ml syringes driven simultaneously by a geared-down, 1-rpm synchronous motor was designed and constructed (Figure 6) to provide a positive, known, steady flow of solution to the cell. The reversible synchronous motor through 3:1 spur gears drives a shaft carrying a worm for each syringe. The worm drives

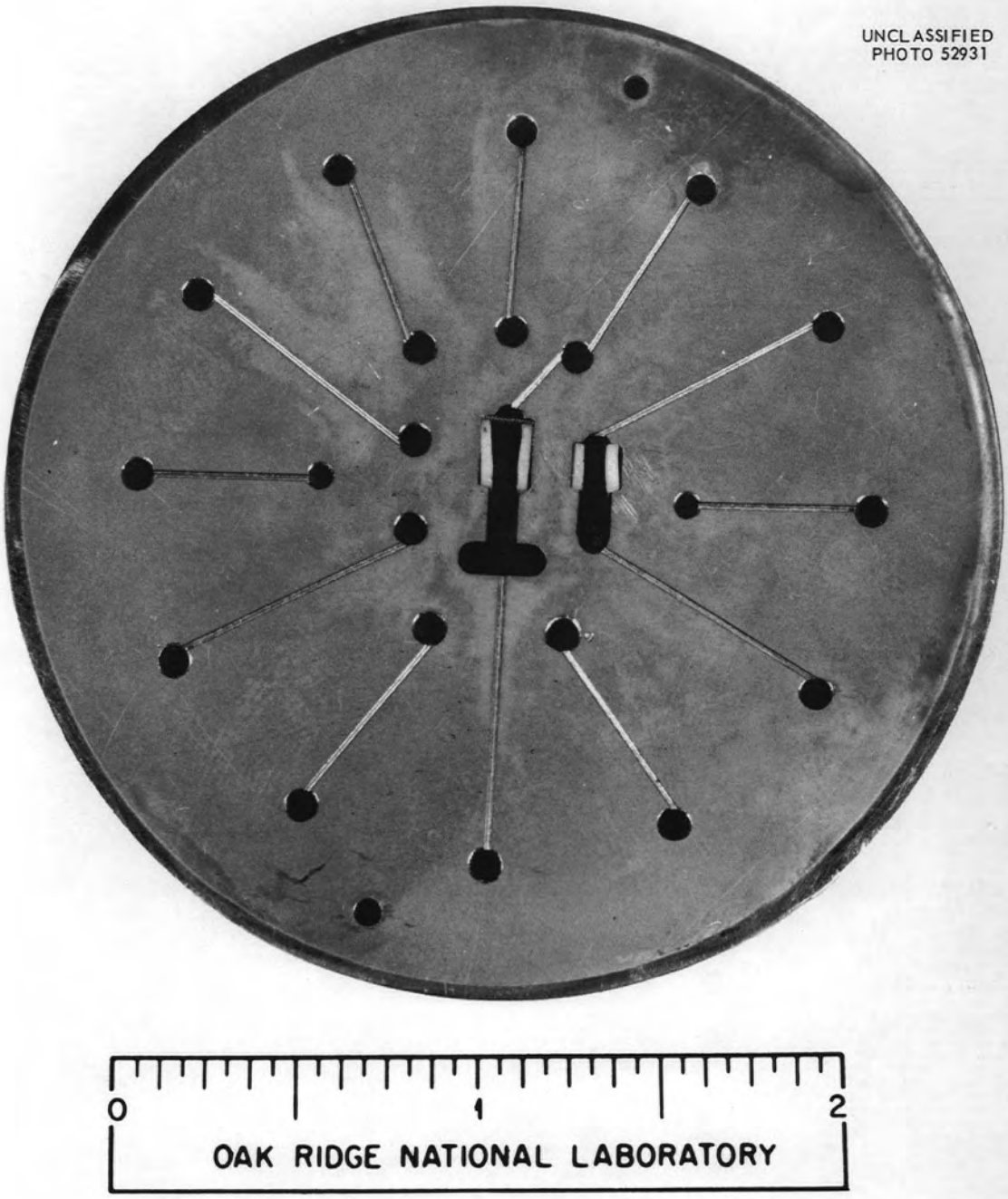

Fig. 3. Closeup of cell core.

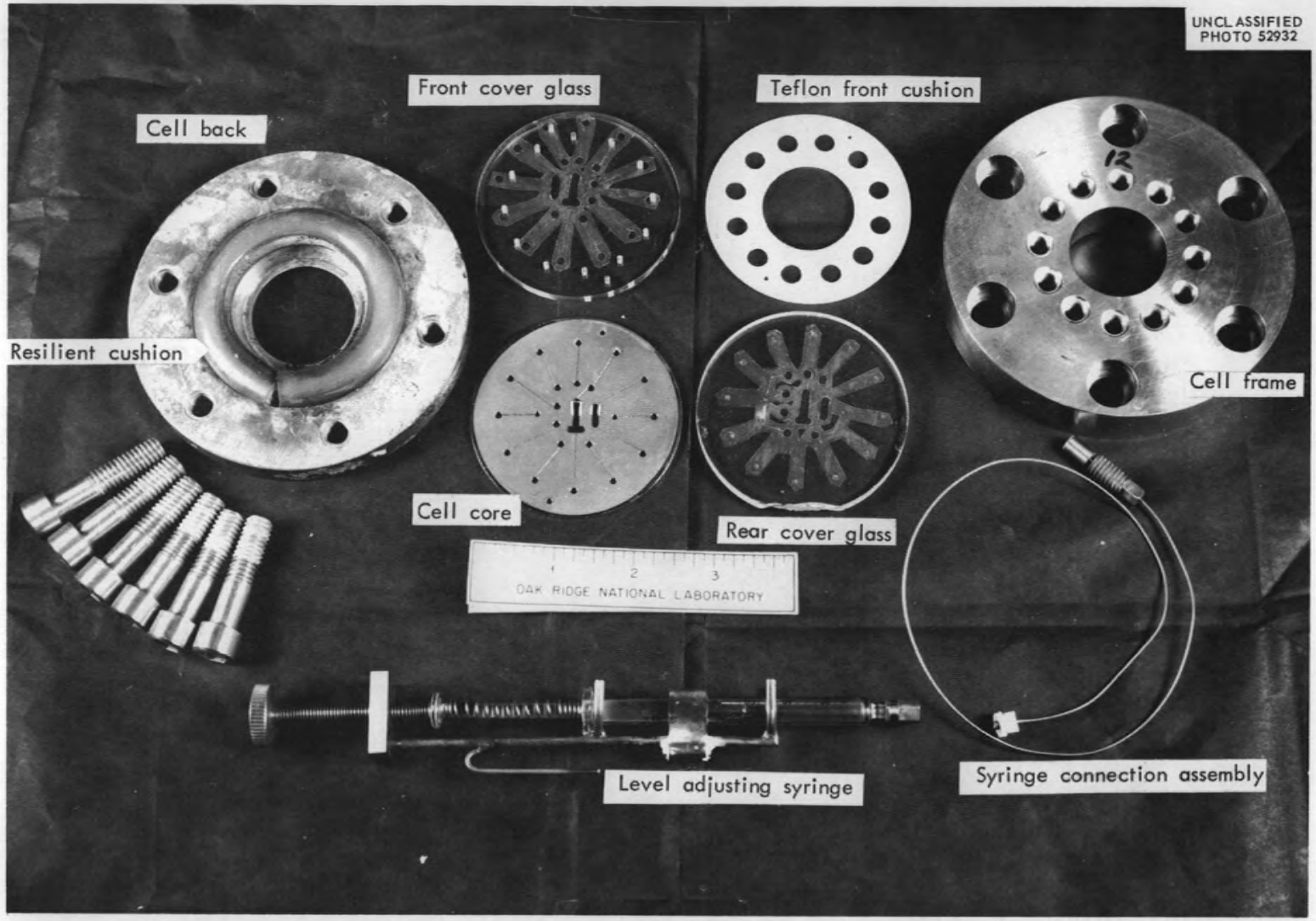

Fig. 4. Cell components.

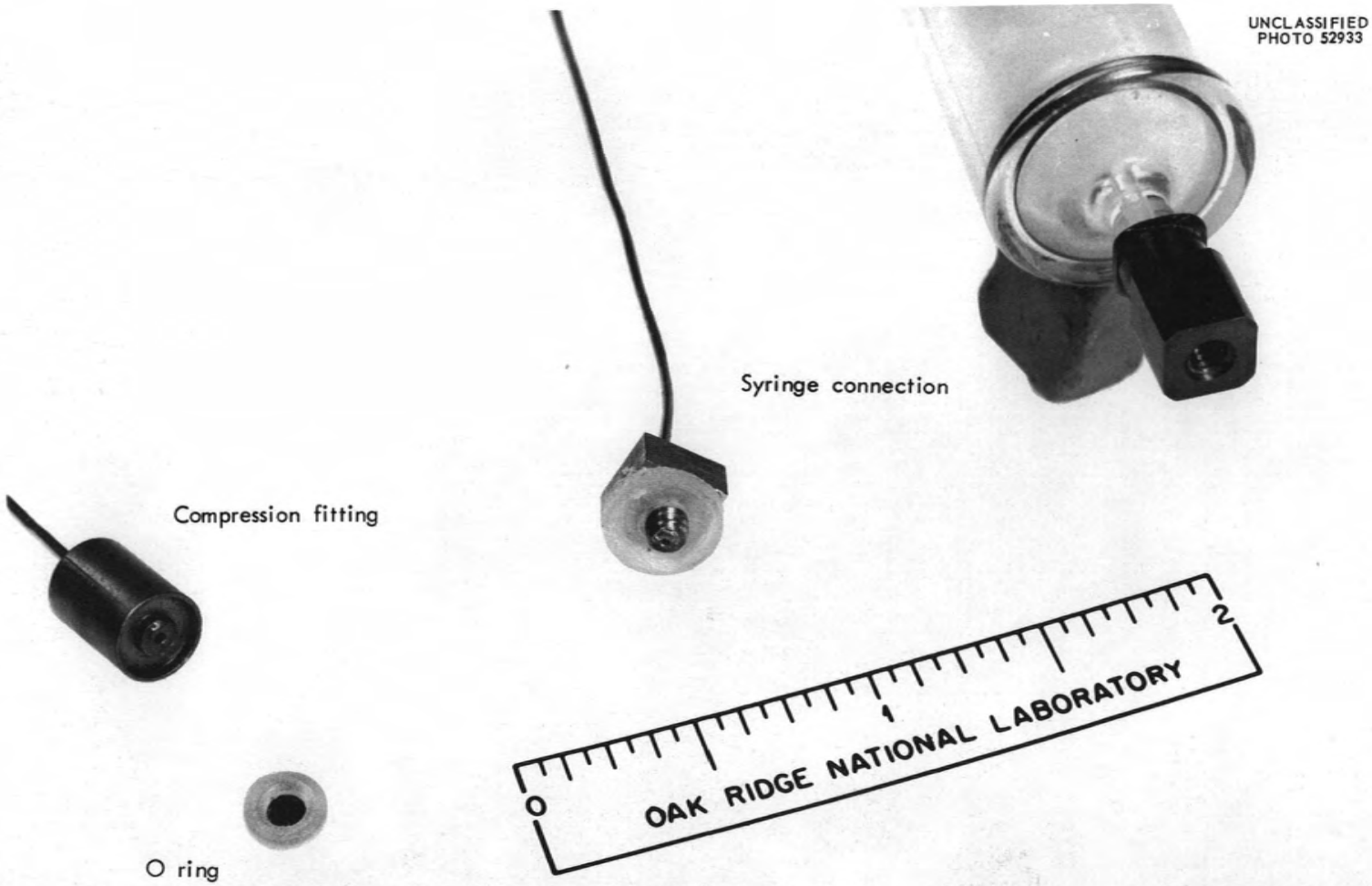

Fig. 5. Tubing fittings.

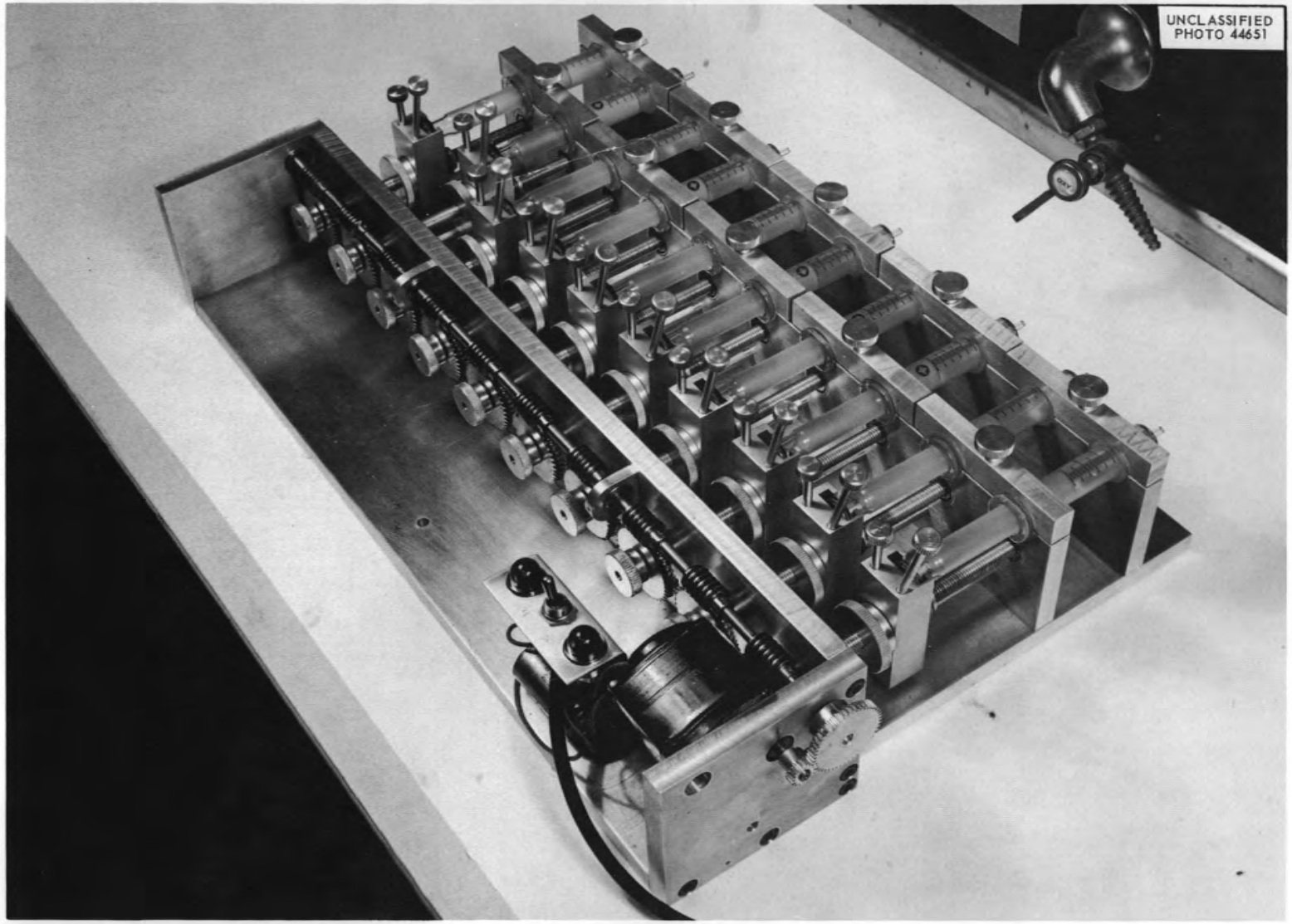

Fig. 6. Micropump.

a 40:1 wheel attached to a 1/4-20 lead screw driving the carrier for the syringe plungers. The nut on the lead screw can turn in the plunger carrier to permit adjustment of the plunger, independently of the motion of the screw. In operation the lead screws made one complete turn every 2 hr, which advanced the syringe plungers at a rate to deliver about 3.5 ml from a 10-ml syringe in 24 hr. The syringes could be loaded to hold enough solution for 4 days' continuous operation.

Leakage between the plunger and barrel of the syringe was prevented by a smear of silicone stopcock grease around the end of the plunger before it was inserted into the loaded syringe. Dissolution of the grease by the organic solvent was prevented by inclusion of about 1 ml of aqueous phase in the syringes loaded with organic. By operating the syringe vertically, the water layer was kept between the organic solution and the seal.

A special fitting was designed to effect connection between the syringe tip and the capillary tubing leading to the cell (Figure 5). The syringe tip was glued with Eastman 910 adhesive into a force fit taper.

Meniscus Adjustment

The 180° connection to the cell connected to the bottom of the column and was used to supply or remove saturated uranyl nitrate to adjust the height of the center of the meniscus. The reservoir of saturated uranyl nitrate solution was a 1-ml syringe which could be adjusted by a screw bearing against the end of the plunger (see

Figure 4). The plunger was kept against the screw by a compression spring around the plunger, and bearing on the flanges of the barrel and the plunger. The size of the syringe adjuster and length of the connecting capillary were chosen to allow immersion of the syringe and capillary in the thermostatted bath with the cell.

Thermostat

The cell was thermostatted by immersion in a water bath supplied by a Labline, Cat. No. 3052, constant-temperature recirculating bath. The temperature was observed to be constant to less than 0.2°C over the course of a run. The water bath had glass windows in two sides and provision for mounting the diffusion cell assembly between them.

The assembled experimental equipment is shown in Figure 7.

Microdensitometer

Density profiles of the plates were determined on a Leeds and Northrup model 6700 P-1 microdensitometer. The image slit was 0.020 in. wide and was located approximately 22 cm from the 16-mm objective. Thus a 35-μ section of plate was examined at a time. This corresponded to a 7-μ section of the cell with the 5X camera magnification used.

PROCEDURE

Before a run was started, the cell and syringes were taken apart and washed with acetone, benzene, acetone, water, warm concentrated nitric acid, and distilled water, in that order. The required aqueous standard solutions were prepared by dilution of a stock solution, and

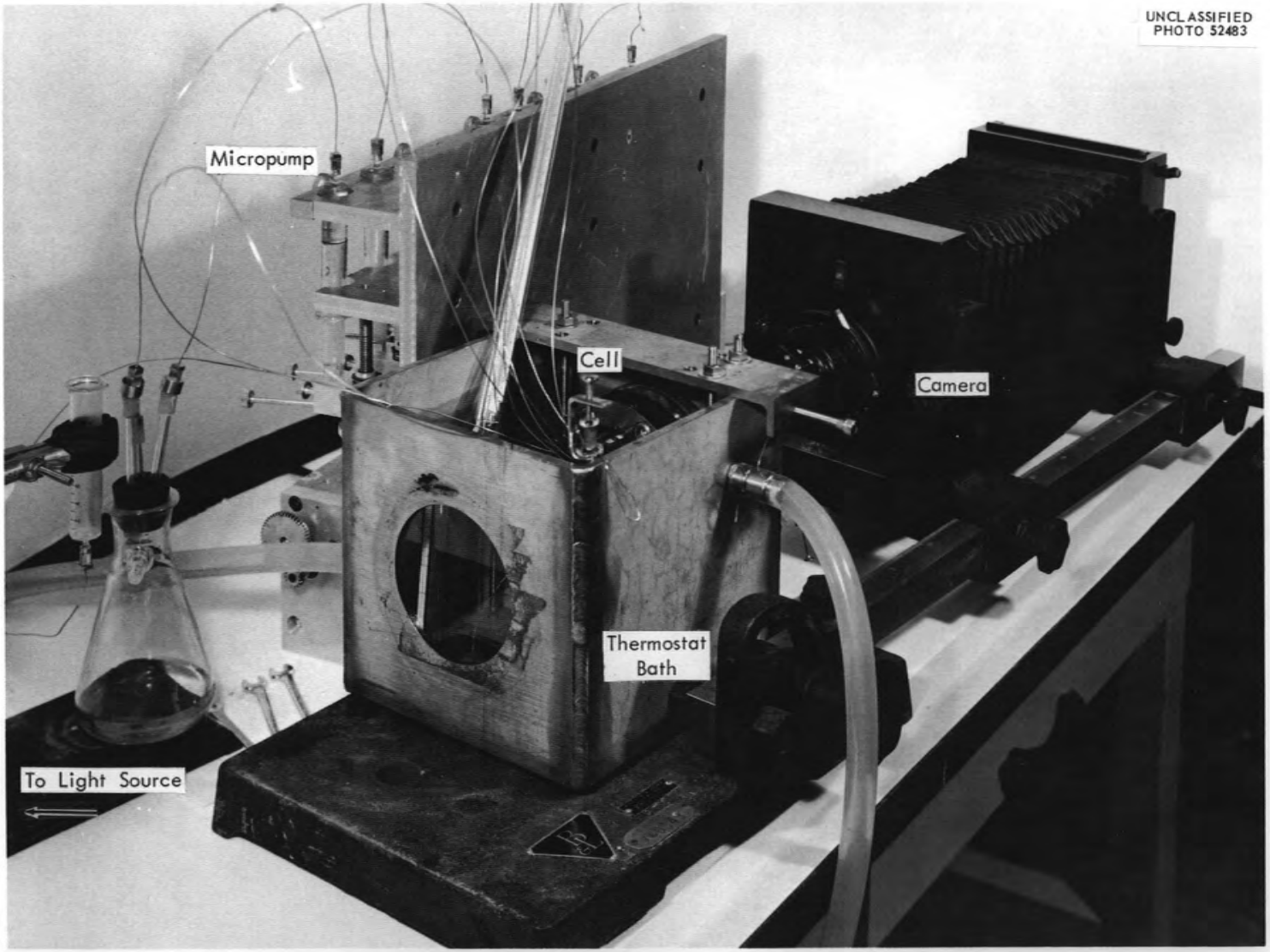

Fig. 7. Assembled experimental equipment.

the organic solutions by extraction of a known aliquot of the aqueous stock solution. The procedure for reagent purification is given in Appendix G.

The cell was reassembled with a uranium crystal in the bottom of the diffusion column. The cell was permitted to stand for a day to allow the polyethylene gaskets to creep, and the compression screws on the tubing connectors were retightened. The meniscus adjustment syringe was connected and the whole assembly immersed in the thermostatted bath.

The diffusion column was filled slowly with saturated solution to a level just below the screen and allowed to stand a few hours to permit the displacement of dissolved, adsorbed, and trapped air. Any air bubble forming in the cell would distort the diffusion path.

The aqueous solution was then brought to a level just above the screen. A 10-ml syringe filled with TBP solution was placed in the micropump and connected to the capillary tube from the one-o'clock position on the cell. This syringe was manually advanced until organic phase filled the top of the column. The pump was started. The meniscus adjustment syringe was backed off until the interface between the aqueous and organic phase was about in the middle of the column, with the ends of the meniscus at the low end of the Teflon inserts.

The syringes containing the standards were loaded, placed in the micropump, and connected to the cell.

After a couple of hours the meniscus was adjusted to have a slight curvature upward, so that it would be approximately flat by the time enough uranyl nitrate had diffused away to approach steady state.

Air bubbles in the standard cells were flushed out. The system was permitted to run for a day or more before photographs were taken.

Photographic exposures were taken using a spread of four exposure times about the time estimated. These were developed immediately, using fresh developer, and inspected visually for the proper density range. If unsatisfactory, additional exposures were taken, using appropriately corrected exposure times.

Because of the high contrast of the type IV emulsion, for any exposure only part of the concentration profile would be in the useful range of the plate. To get more information on a plate, a technique of masking the plate was developed. An opaque shield was placed between the plate and more brightly illuminated portions of the image. Then the darker portions of the image could be photographed for a long exposure, say 240 sec, the shield stripped off, and the bright portion exposed for, say, 10 sec. In this way two exposures could be obtained on one plate, with all the standards in range. And since the whole plate had the same development, the limiting slope of the sensitometric curve was the same for the whole plate. This was most useful for calibration.

Exposures were made twice a day as long as the standard solutions, uranium crystal, and cell integrity lasted. (The indication of the loss of cell integrity was a relatively sudden change in meniscus level or shape.) At the end of a run, the syringes were disconnected from the capillaries and rinsed with acetone. The cell and capillaries were cleaned and dried by pulling acetone and then air through them by means of vacuum applied to the Nos. 3, 9, and 12 capillaries, the

discharge lines. The cell was dismantled and examined for indication of leaks.

After development and fixing, plates were washed for about 1 hr in running water and then air-dried overnight. Plates to be traced on the microdensitometer had pieces of black electrical tape placed on them at appropriate intervals to check the zero setting on the densitometer, which was prone to drift. The plates were then traced on the densitometer, which had been warmed up for at least 24 hr.

Interpolation curves were prepared from the densitometer tracings of the images of the standards. These were plots of the logarithm of the plate transmittance vs concentration of the standard. From the interpolation curves and the densitometer tracing of the column, the concentration profile in the column for each run was plotted.

CHAPTER V

DATA AND DISCUSSION OF RESULTS

DATA

A sample plate is shown in Appendix A. The densitometer profiles of the six successful runs are collected in Appendix B. The interpolation graphs used to determine the interfacial concentrations are in Appendix C. The equilibrium curves for 30% and 100% TBP are in Appendix D.

The concentration profiles obtained from six successful runs are plotted in Figures 8 through 10, and the results are summarized in Table I. In the runs with 100% TBP the phases were observed to be in equilibrium within the limits of accuracy of the experiment, whether or not a surface-active agent was present. When the organic phase contained a hydrocarbon diluent (initially 70 vol % Amsco), an apparent uranium concentration greater than equilibrium was observed on the organic side. This apparent anomaly can be explained if one considers that the organic phase is a three-component solution in which counterdiffusion is taking place. The three components are TBP, uranium-TBP complex, and diluent. The TBP and uranium-TBP complex are undergoing equimolar counterdiffusion at steady state. The large concentration of the highly polar complex in the region near the interface tends to "reduce the solubility" of the diluent near the interface, or apparently increase the activity coefficient of the diluent in the solution. The result is an unknown gradient of diluent concentration up the column,

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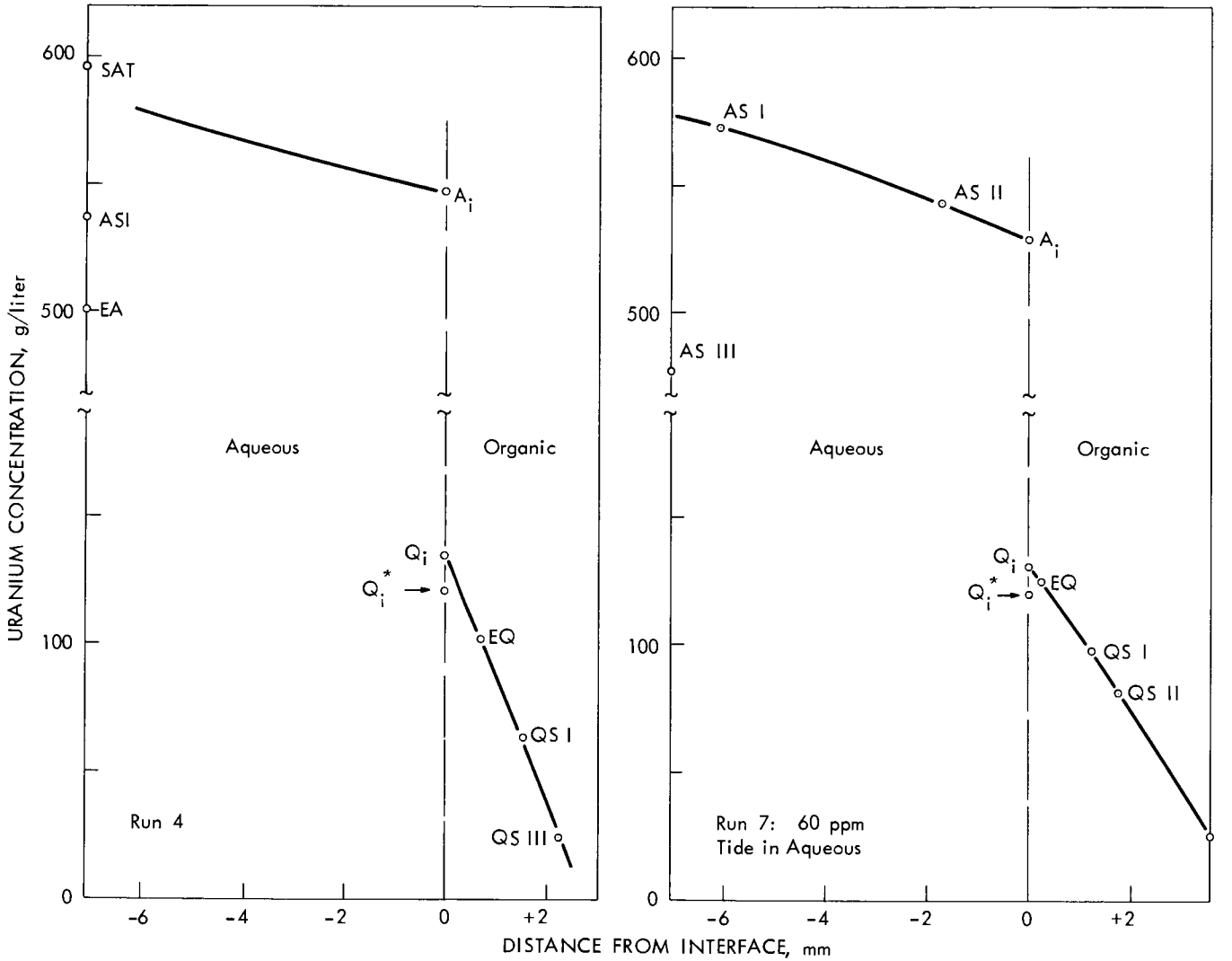

Fig. 8. Concentration profiles, 30% TBP.

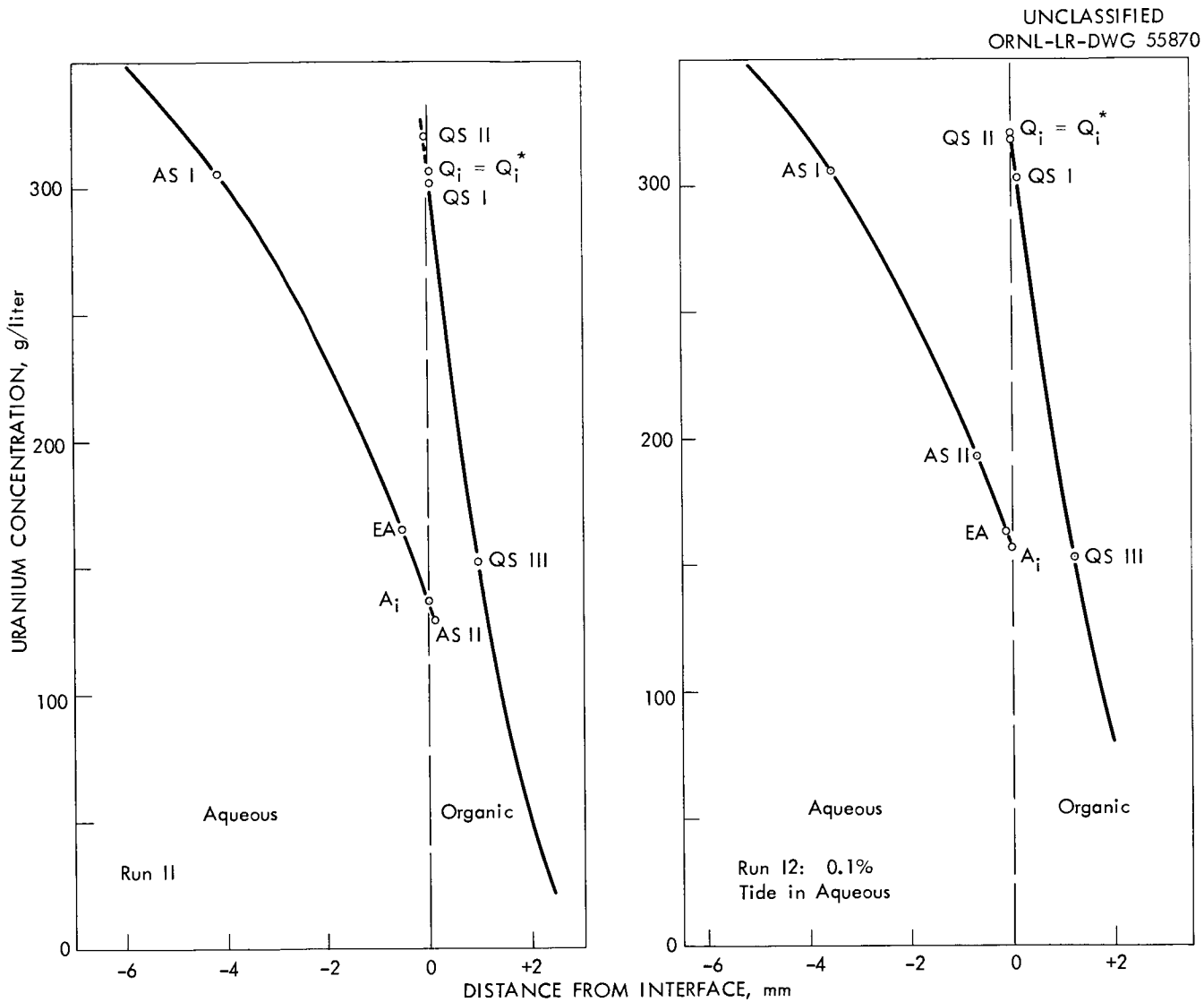

Fig. 9. Concentration profiles, high concentration series, 100% TBP.

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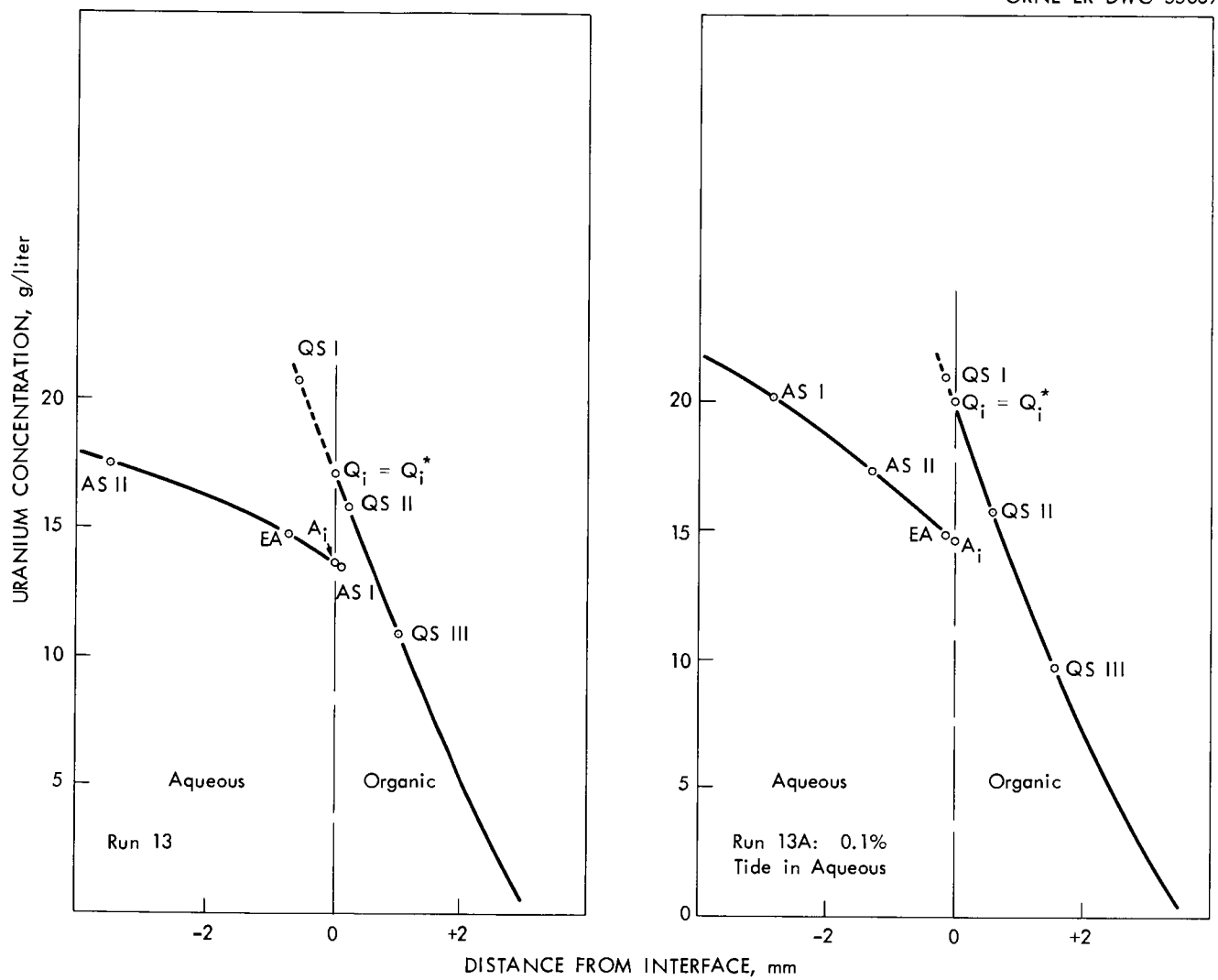

Fig. 10. Concentration profiles, low concentration series, 100% TBP.

TABLE I

RUN SUMMARY

Run No.	TBP Conc., vol %	Surface Active Agent Present	Interfacial Concentration of Uranium, g/liter		
			Aqueous C_{ai}	Organic C_{qi}	Resistance Drop $C^*_{qi} - C_{qi}$
4	30	None	547	135	-15 ± 1.44
7	30	60 ppm Tide	529	130	-10 ± 1.18
11	100	None	136	307	0 ± 4.22
12	100	100 ppm Tide	153	319	0 ± 4.85
13	100	None	13.6	16.8	0 ± 0.24
13A	100	100 ppm Tide	14.6	20.1	0 ± 0.27

and a total (complexed and uncomplexed) TBP concentration at the interface greater than the bulk concentration supplied to the top of the column. The accumulation of TBP near the interface permits the anomalously high concentration of complex at the interface. The aqueous phase is then in contact with an organic phase of perhaps 32 or 33% total TBP rather than 30%. Unfortunately, checking this hypothesis, and also determining the "true" equilibrium conditions for the dilute TBP interface, would require infrared absorptiometric techniques beyond the scope of this work.

The problem of changing dilution was eliminated by going to a 100% TBP organic phase. With only two components present (TBP and uranium-TBP complex), the analysis for one completely specifies the system. The high density of the organic phase at the interface gave some problems in maintaining geometry. By careful cleaning of the cell and glasses prior to a run and a careful filling procedure, the interface could be kept intact by surface forces even though the upper phase was denser.

Two sets of runs were made with 100% TBP. The first (runs 11 and 12), by the usual procedure, with 100% TBP as the organic phase. It was observed that the interfacial concentration in this series was very much larger than is usually encountered in solvent extraction. The concentration in the column was lowered by inserting a Teflon plug in the bottom section of the column over the uranyl nitrate crystal. Then most of the concentration drop was across the obstruction, reducing the interfacial concentrations to an interesting range. Unfortunately, this

also decreased the flux and hence the gradients, to the detriment of accuracy in the experiment. The 100% TBP runs indicated equilibrium across the interface for both the high-concentration series (C_{qi} ~300 g/liter) and the low-concentration series (C_{qi} ~20 g/liter) within the accuracy of the experiment.

SIGNIFICANCE OF THE RESULTS

It is unfortunate from the standpoint of the project that no measurable resistance could be found. By determination of the variation of resistance with chemical composition of the system, the transfer reaction might have been somewhat elucidated. However, the fact that no measurable resistance was observed is strong evidence that the rate-limiting process in solvent extraction of uranyl nitrate by TBP is that of transport to the interface, rather than transport across it.

It is also significant that the deliberate introduction of a powerful surface-active agent into the system produced no resistance at the interface; this is one more nail in the coffin of the theory that surface-active agents produce "membrane-type" blocking of the interface. It is becoming increasingly evident that surface-active agents modify only the hydrodynamics of the systems in which they are introduced. In the steady-state low-flux system used, there was no mass-transfer-induced interfacial turbulence, and consequently no fluid motion for the surface-active agent to affect. The presence of a concentration of surface-active agent at the interface very possibly modified the diffusion of uranyl nitrate across the interface. However, the effect, if

present, was so small that it was completely below detection in these experiments.

DISCUSSION OF ERROR

Sources of error. Error in the measurement of interfacial concentration arises from three basic errors: (1) in the measurement of the position of the interface (or of a concentration), (2) in the external analysis of the standard solutions used to calibrate the plates, and (3) in the densitometry of the places used to interpolate between (or sometimes extrapolate from) the standards.

The error in position of a given concentration or of the interface arises from two sources: the finite width of the light source and the finite width of the plate examined by the densitometer.

The vertical stop on the light source was 0.8 in. The distance from the source to the cell was 128 in., to give a beam with a convergence of 0.00624 radian. This was increased in the water bath and cell to approximately 0.01 radian by the higher index of refraction of water. The thickness of the cell was 0.080 in., or about 2 mm. The vertical width at the edge of the cell of a beam focused at the center was thus 0.01 radian x 1 mm = 10 μ. This was taken as the uncertainty in an illuminated position.

The width of the plate examined by the densitometer is given by dividing the width of the slit (0.020 in.) between the plate image plane by the magnification (14X) of the densitometer microscope. This latter is obtained by dividing the length of the draw tube (22 cm) by the

focal length of the objective (16 mm). The width of plate so obtained is 35 μ. If this is divided by the 5X magnification of the camera, 7 μ is obtained as the uncertainty of the position of an absorbancy in the cell. The sum of the two uncertainties, 17 μ, is taken as the net uncertainty in position.

The standard solutions used to calibrate the plate were analyzed externally by the Special Analysis Group of the Analytical Chemistry Division by coulometric and potentiometric methods. The methods are reputed to be accurate to 0.1%, and carefully made up standards and duplicate samples seem to bear out this assertion. Hence 0.1% is taken as the probable relative error in concentration of the standards.

The error of interest in plate transmittance is due largely to "noise," some from within the electronics of the instrument and some due to extraneous light-scattering centers on the inner side of the cell cover glasses. It is estimated visually that a given transmittance can be ascertained to 0.5% of full scale. The precision is this good. The absolute accuracy is not so important as the accuracy of the transmittance of a point on the profile relative to one of the standards.

Several potential sources of error have been omitted from the above discussion because they were not considered significant or are implicit in the error discussed. The location of the interface in the presence of a meniscus is a potential cause for concern. However, Teflon inserts kept the edges of the meniscus straight and parallel to the light path, possibly to better than 0.1 mil or 2.5 μ. There was no optically detectable meniscus on the glass surfaces when the cell was clean and carefully filled.

The location of the interface on the chart could be determined with any degree of accuracy desired by simply slowing down the carriage traverse on the densitometer. This had the effect of expanding the scale on the densitometer charts. The charts shown in the appendix are to a condensed distance scale for convenience in showing the density range.

The equilibrium curves for the aqueous and TBP solutions of uranium were determined by equilibration and separation at 25°C, and then by analysis as for the standards. The lack of scatter of the data and the claimed accuracy of the analysis give confidence that the accuracy is at least as good as the standards.

Uniformity of illumination was determined to be satisfactory by taking a plate of the cell filled with water.

Error Calculation

The conventional first-order error calculation, based on the sources considered above, is carried out in Appendix E. The results are summarized in Table II.

The calculation was carried out in terms of concentration, in particular, of the difference between the observed interfacial concentration in the organic phase and the interfacial organic concentration that would be in equilibrium with the observed interfacial aqueous concentration. The figure so obtained was divided by the organic-phase concentration gradient at the interface to obtain the thickness of organic phase that would produce a concentration drop equal to the

TABLE II

SUMMARY OF FIRST ORDER ERROR ANALYSIS

Run No.	Uncertainty in $(C^*_{qi} - C_{qi})$, μ			
	Due to Position	Due to Standards	Due to Transmittance	Total
4	17	15	0.07	33
7	17	25	.08	43
11	21	2.5	.05	24
12	20	2.8	.07	23
13	33.2	4.9	0.32	38
13A	34.4	5.4	1.02	41

uncertainty in concentration under the experimental conditions. The relative uncertainty in the different runs can then be compared, as well as take on some physical significance. In the runs with 100% TBP, the calculated uncertainties are a least upper bound of the resistance of the interface to mass transfer, which is less than 25 μ in runs 11 and 12.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

CONCLUSION

From this work, and the review of mass-transfer experiments on the uranium-TBP system in the literature, a few generalizations can be made:

1. Stirred-bulk fixed-interface experiments are of questionable value for obtaining quantitative data on mass transfer kinetics in any system where the transfer reactions are as fast as in the uranium-TBP system. These experiments are useful for making qualitative or comparative observations or for scouting experiments.

2. To eliminate all questions concerning interfacial area and interfacial concentration, such as arise in stirred experiments, the area and concentration profile should be under direct optical observation during some experiments at some stage of the experimental program.

3. By far the most sensitive technique for observing concentration changes during diffusion is that based on interferometry, making use of the change of index of refraction of solutions with concentration.

4. The actual transfer reaction in the uranium-TBP system is very fast, having a "homogeneous half-time" much less than 1 msec, and is not the rate-limiting step in engineering applications of solvent extraction.

5. There appears to be no blocking of the interface by surface-

active agents in this system. Any decrease in mass transfer rates observed in the presence of surface-active agents is probably due to change in the hydrodynamics of the system.

RECOMMENDATIONS

From the experience gained in this work, and from the review of the pertinent literature, the following recommendations are made:

1. Any subsequent work on the uranium-TBP interfacial chemical kinetics should use an interferometric technique similar to that of Harvey,[4] using phases with concentrations near equilibrium. Resistance to transfer as small as a few hundred angstroms of equivalent solution thickness could be detected, and separated completely and positively from diffusional effects.

2. The hydrodynamic behavior of the interface is a separate problem, and should be recognized as such and treated separately. Since transport to the interface is rate limiting in engineering operations, and this is most strongly affected by the interfacial hydrodynamics, it is to this problem that engineering research should be addressed.

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APPENDIX A

SAMPLE PLATE

Figure 11 is a photograph of a sample plate taken during run 13.

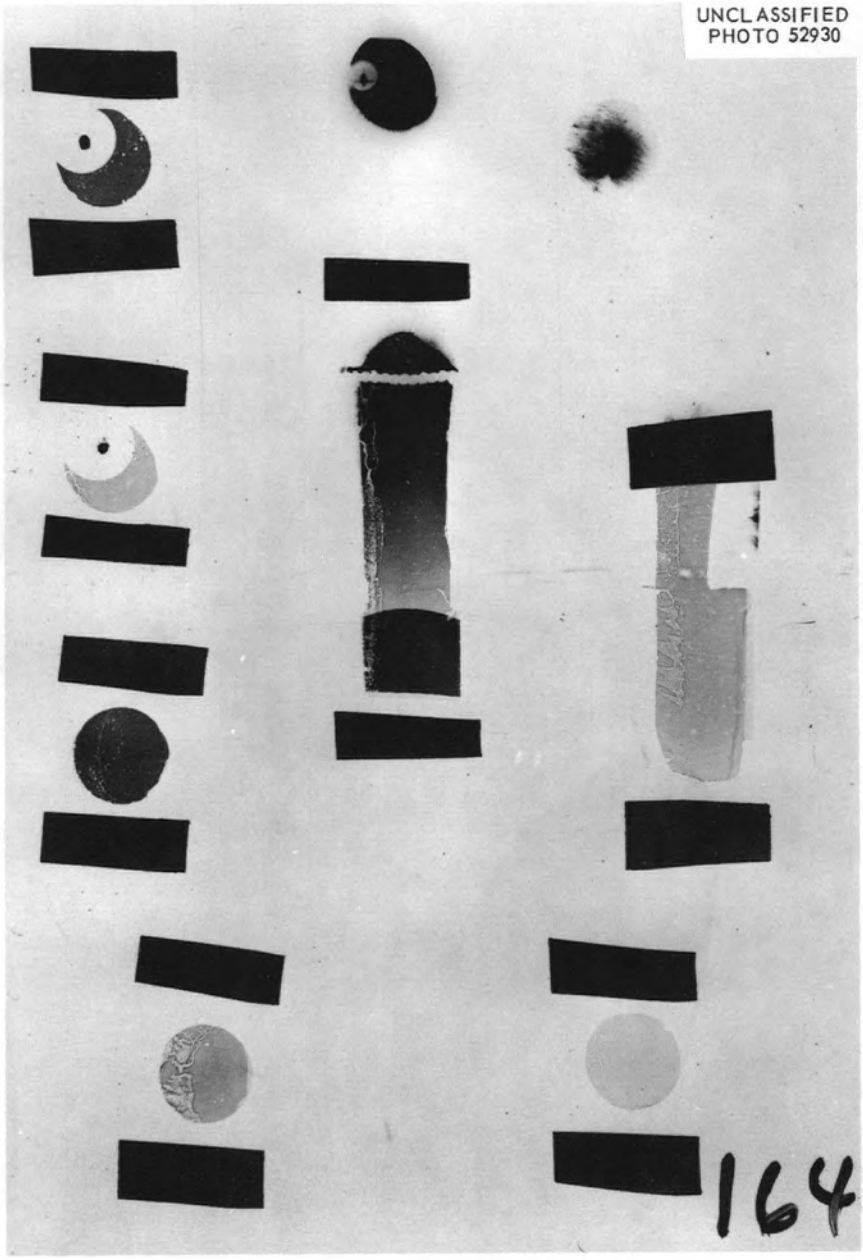

Fig. 11. Sample plate.

APPENDIX B

DENSITOMETER CHARTS

Figures 12 through 17 are tracings of the densitometer charts obtained from the analysis of plates from runs 4, 7, 11, 12, 13, and 13A.

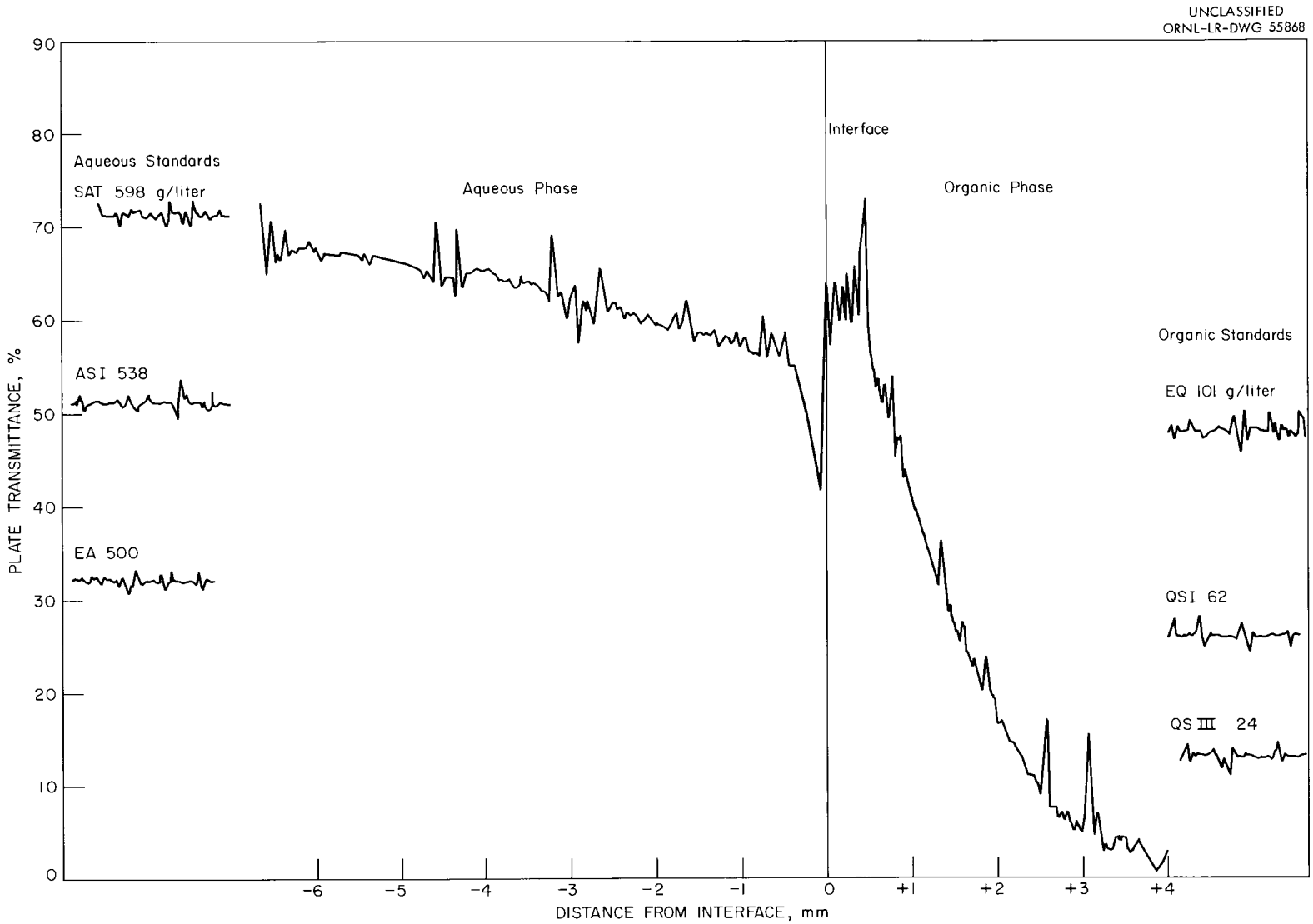

Fig. 12. Plate transmittance profile for run 4. 30% TBP, 0.1 N HNO_3 in aqueous phase.

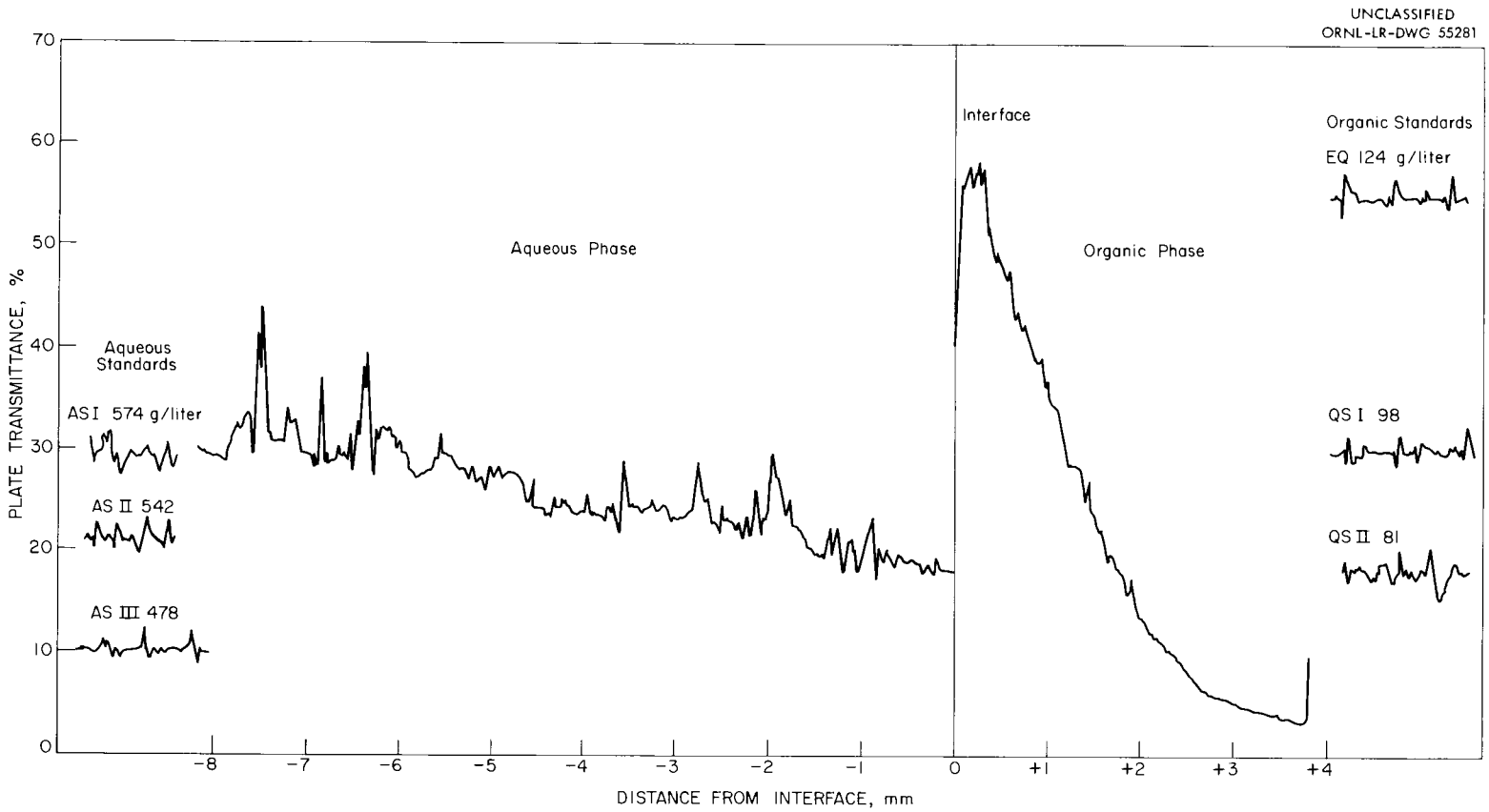

Fig. 13. Plate transmittance profile for run 7. 30% TBP, 0.1 N HNO_3 + 60 ppm tide in aqueous phase.

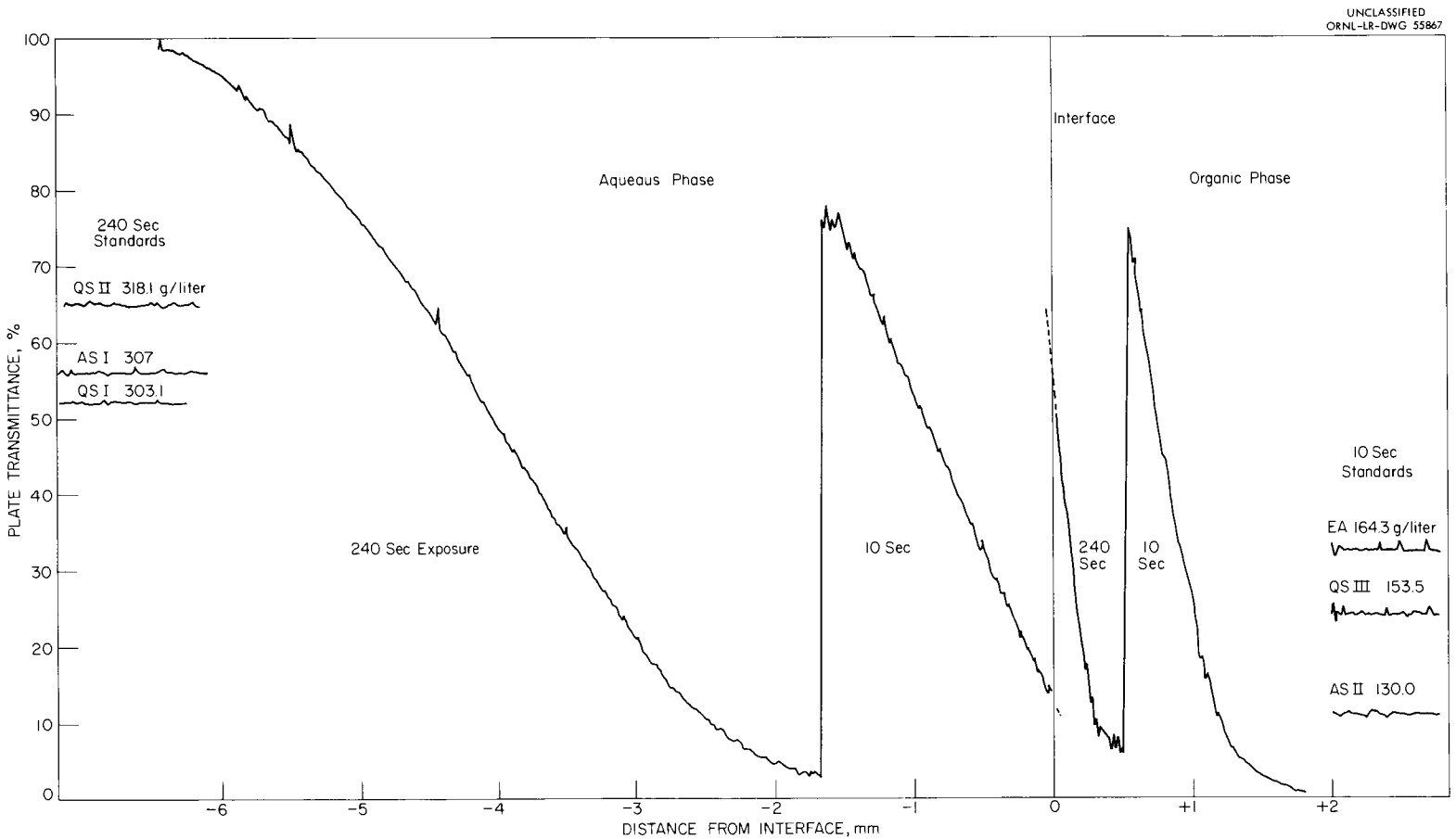

Fig. 14. Plate transmittance profile for run 11. 100% TBP, high concentration range.

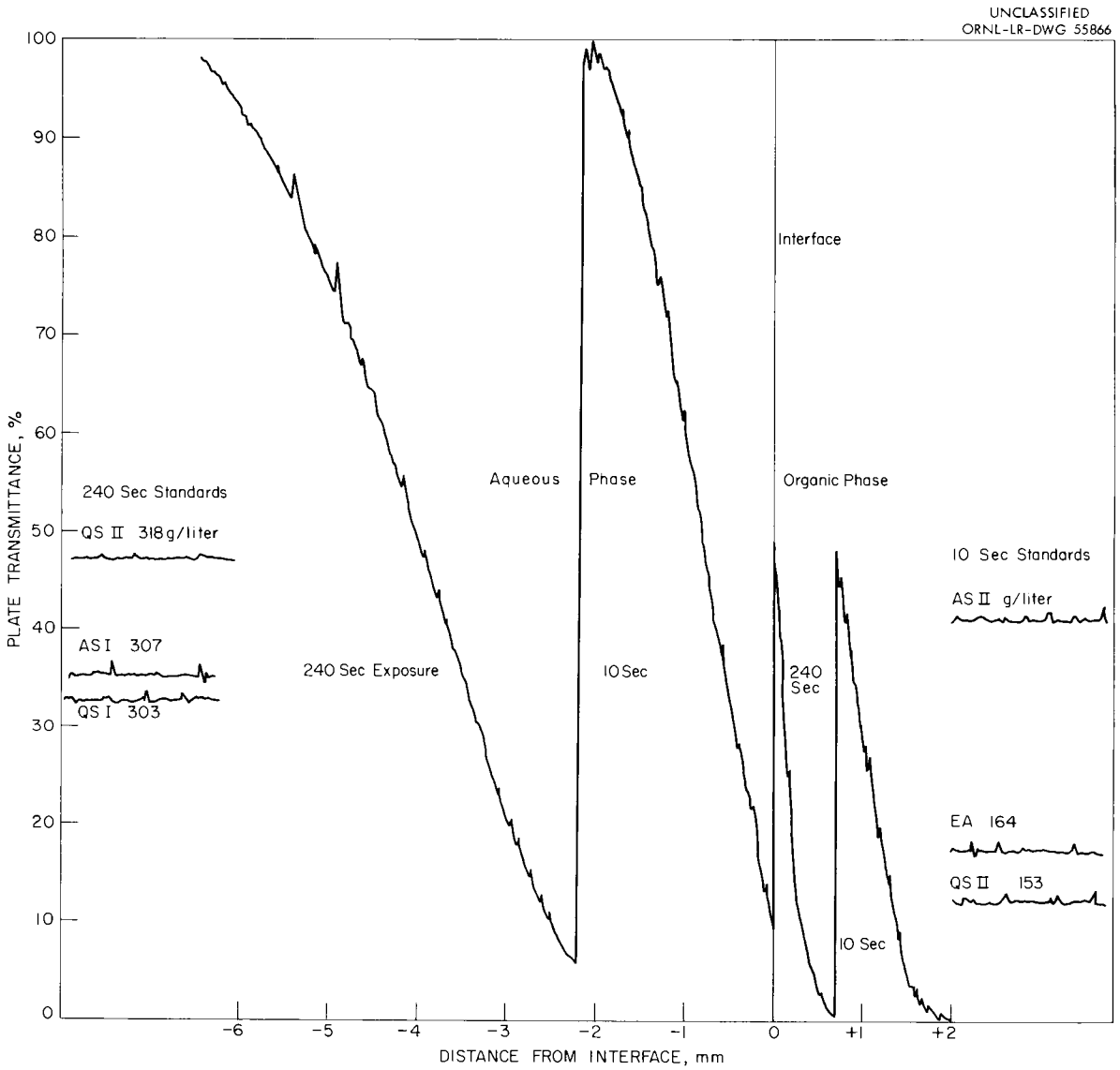

Fig. 15. Plate transmittance profile for run 12. 100% TBP, high concentration range. 0.1% tide in aqueous phase.

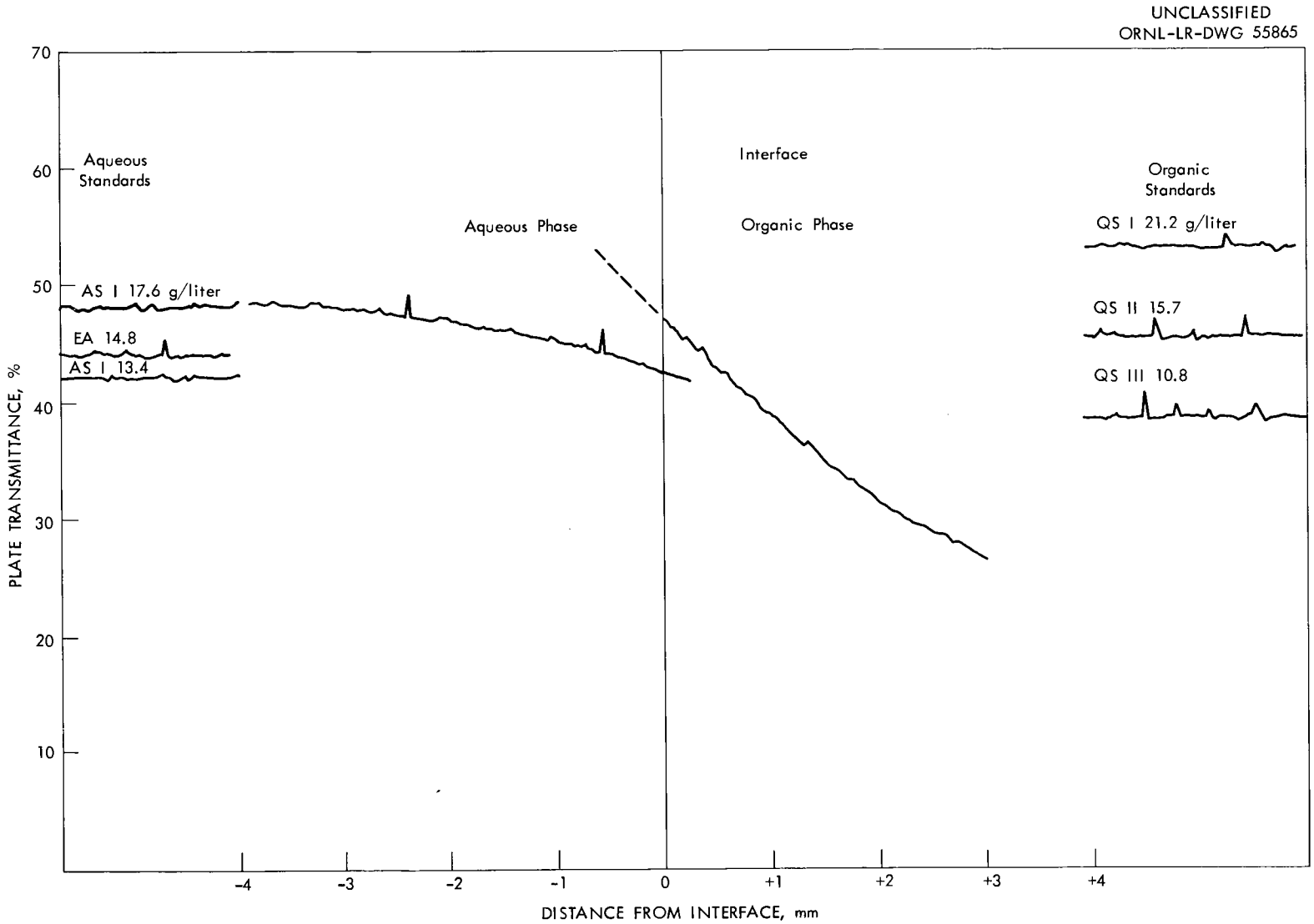

Fig. 16. Plate transmittance profile run 13 low concentration series 100% TBP.

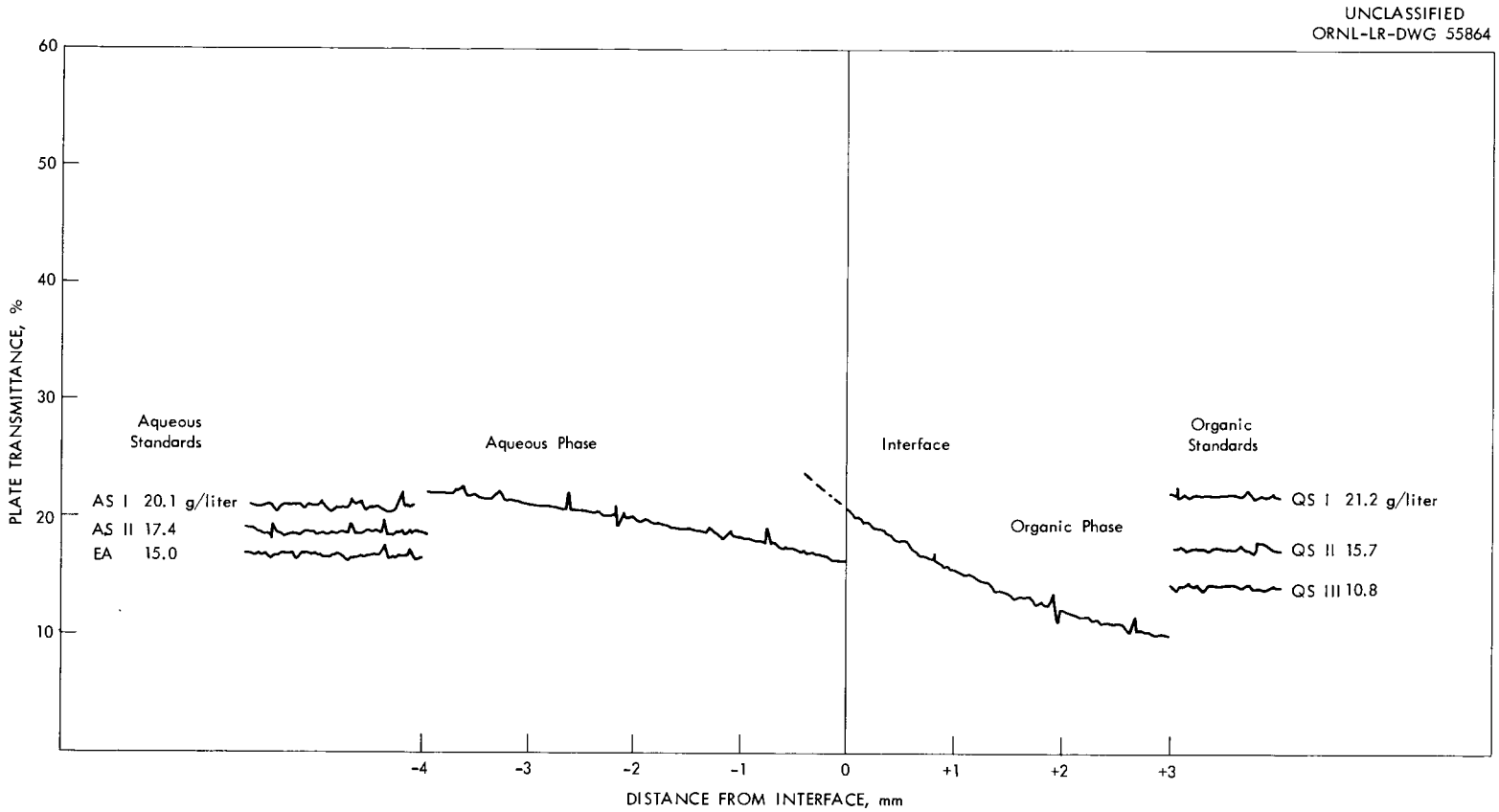

Fig. 17. Plate transmittance profile run 13A. Low concentration series 100% TBP 0.1% tide.

APPENDIX C

INTERPOLATION CURVES

Figure 18 shows interpolation curves for runs 4 and 7 obtained as outlined in Appendix F. The values of the interfacial concentrations are determined graphically from these and the densitometer charts.

Figures 19 and 20 are scaled-up concentration profiles obtained directly from the densitometer charts without the use of interpolation curves. This simpler and more accurate procedure for obtaining interfacial concentrations was possible in runs 11, 12, 13, and 13A because the standards were selected to fall around the interface concentrations.

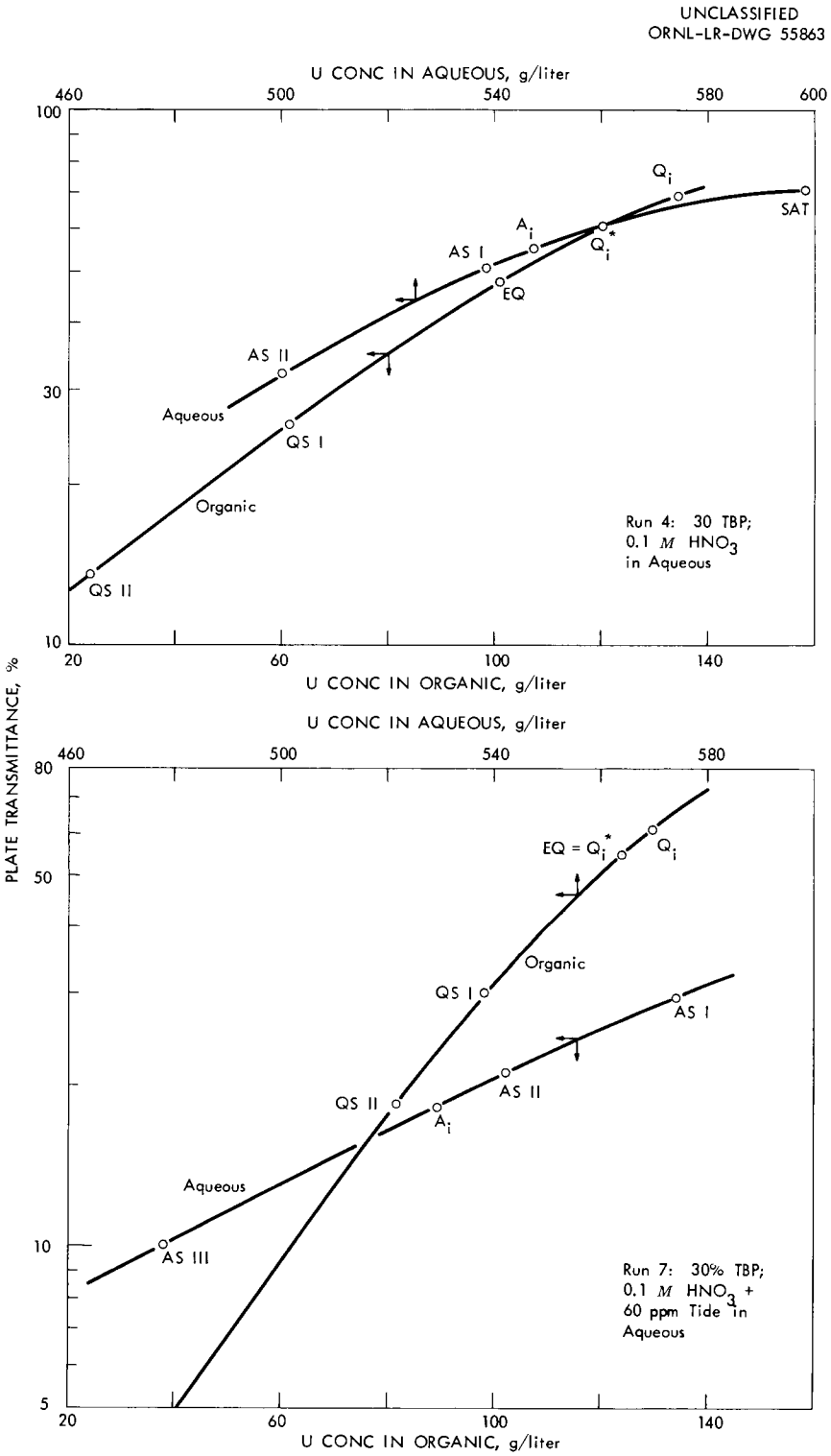

Fig. 18. Interpolation curves for densitometer charts.

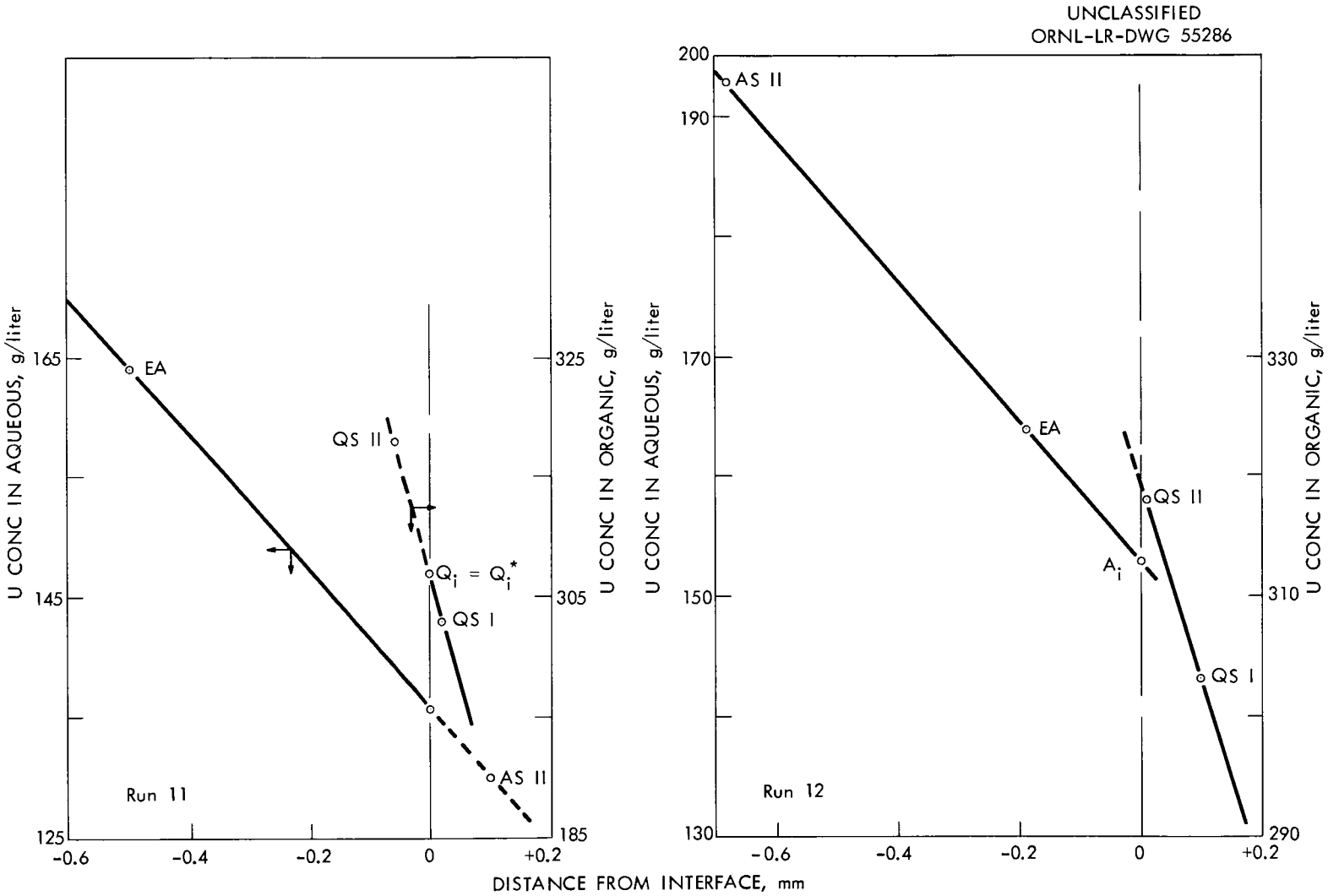

Fig. 19. Uranium concentrations in vicinity of interface.

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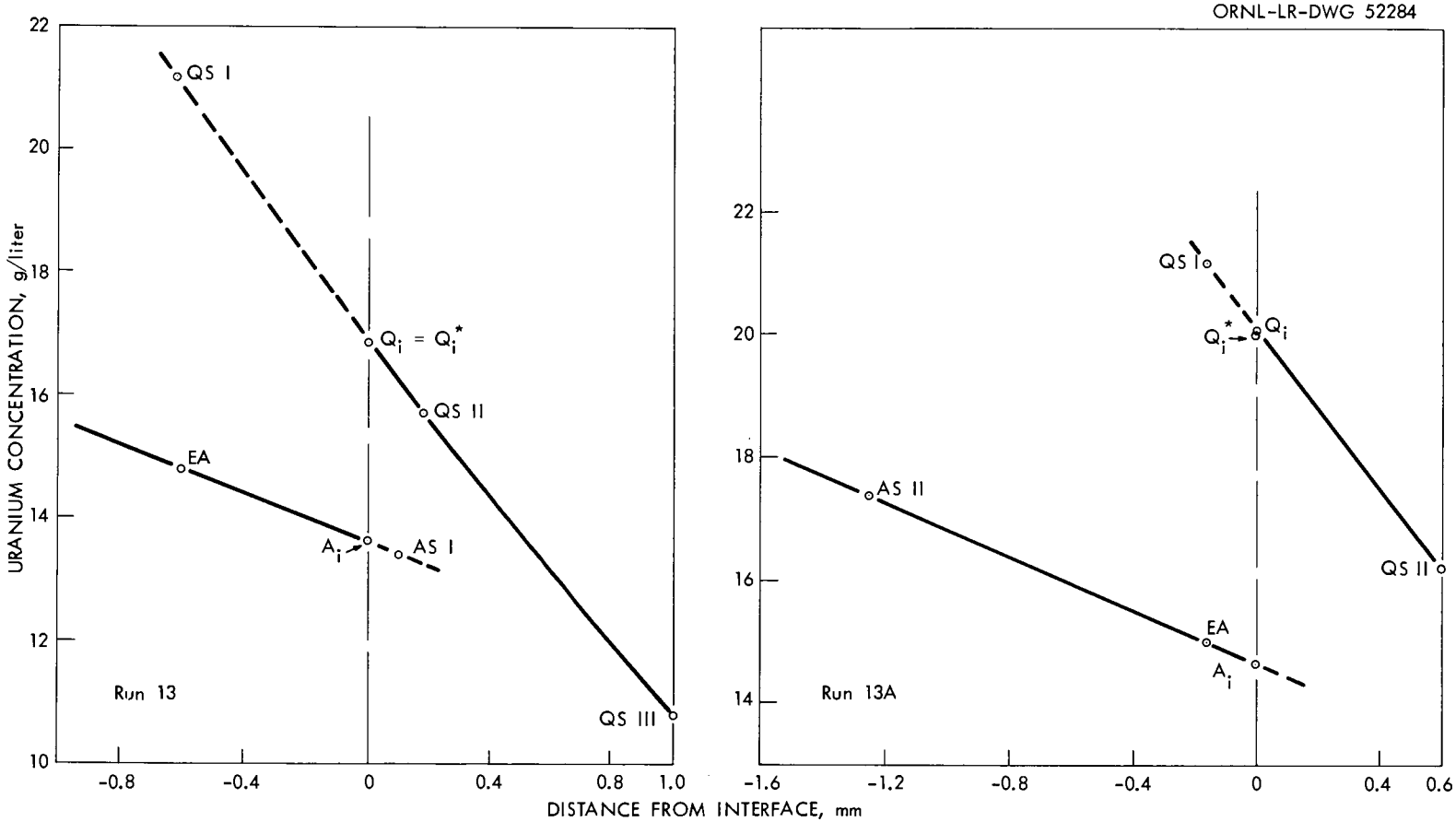

Fig. 20. Uranium concentrations in vicinity of interface.

APPENDIX D

EQUILIBRIUM CURVES

Figures 21 and 22 are the equilibrium distribution curves for uranyl nitrate in tributyl phosphate solutions of interest in the experiments.

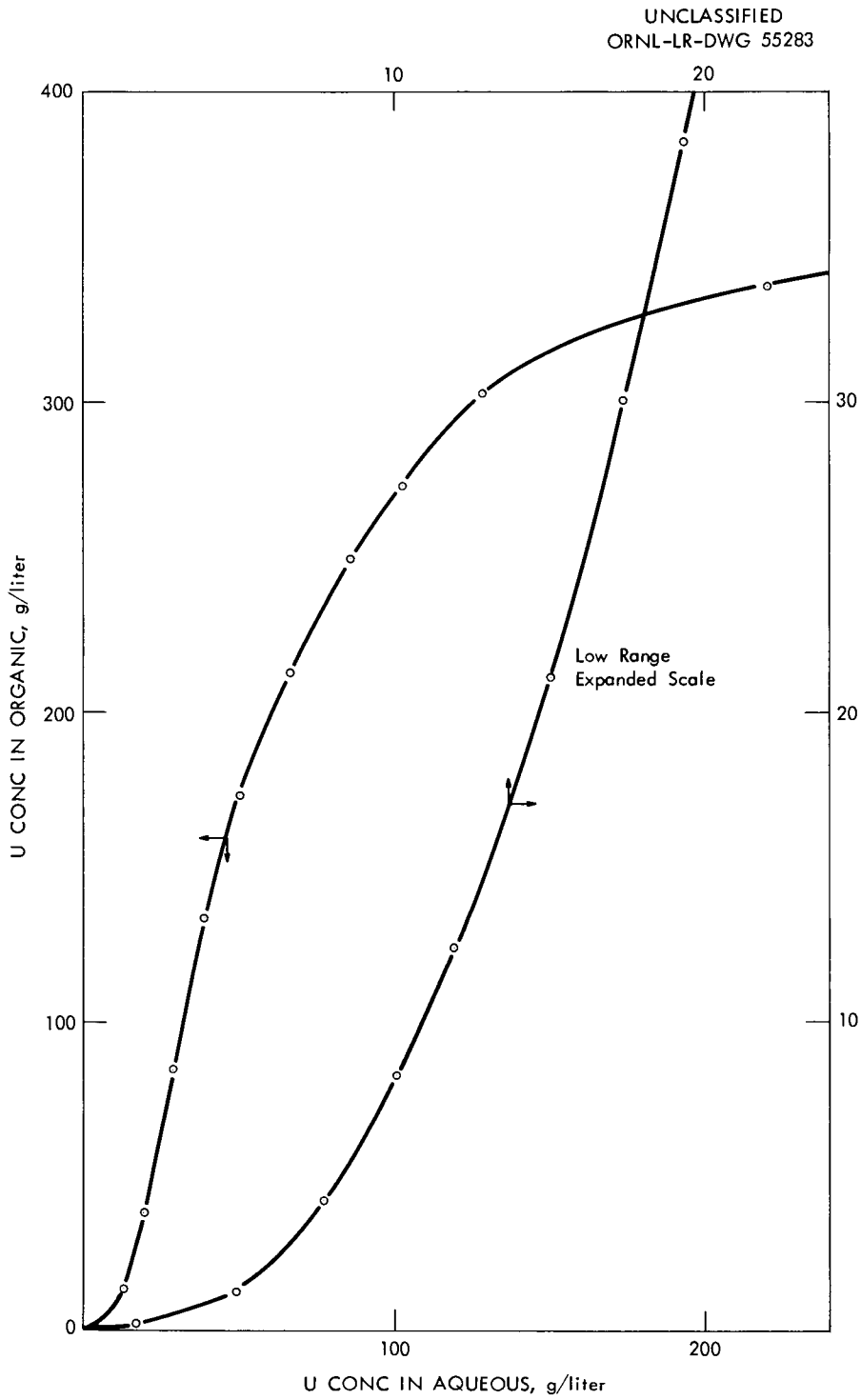

Fig. 21. Equilibrium distribution of neutral uranyl nitrate between 100% TBP and water.

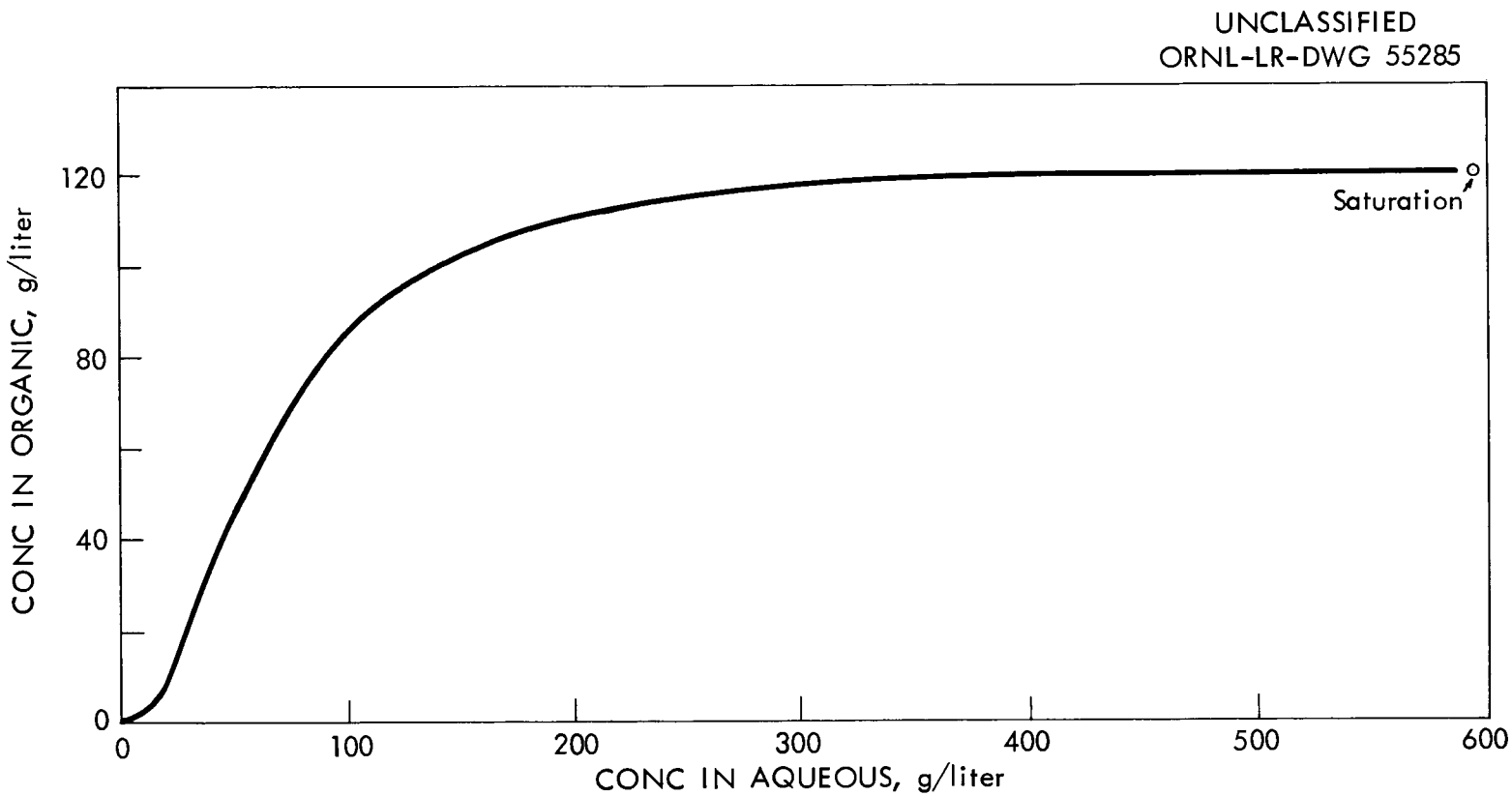

Fig. 22. Equilibrium distribution of uranyl nitrate between 30% TBP and 0.1 N HNO_3 in water.

APPENDIX E

CALCULATION OF PROBABLE ERROR

Using the conventional first-order error analysis, the error in concentration at the interface is approximated by the expression for total differential:

$$dC_i = \frac{\partial C_i}{\partial x} dx + \frac{\partial C_i}{\partial C_s} dC_s \frac{\partial C_i}{\partial T} dT$$

where dx is the uncertainty in position, dC_s is the uncertainty in concentration of a reference standard solution, and dT is the uncertainty in measured plate transmittance.

The uncertainty in the apparent resistance of the interface, $C^*_{qi} - C_{qi}$, is the sum of the uncertainties in the calculated equilibrium interfacial organic phase concentration and the observed interfacial organic phase concentration. The uncertainty in dC^*_{qi} is given by

$$dC^*_{qi} = \frac{\partial C^*_{qi}}{\partial C_{ai}} dC_{ai}$$

The partial derivative is the value of the slope of the equilibrium line at C_{ai}.

The evaluation of the uncertainty due to uncertainty in transmittance is calculated from the interpolation plots of log T vs C, which approximate the relation

$$\log T = NC + B$$

where

N = slope of the plot, nearly constant

B = a constant

$$\frac{d \log T}{dT} = \frac{1}{2.303} \frac{d \ln T}{dT} = \frac{1}{2.303} \frac{dT}{T} = N \frac{dC}{dT}$$

The uncertainty due to measurement of transmittance is then

$$\frac{\partial C}{\partial T} dT = \frac{1}{2.303N} \frac{(dT)^2}{T}$$

From the above relations, and taking all $\partial C_i / \partial C_s$ as equal to unity, the error expression becomes

$$d(C^*_{qi} - C_{qi}) = \left[\frac{\partial C^*_{qi}}{\partial C_{ai}} \frac{\partial C_{ai}}{\partial x} + \frac{\partial C_{qi}}{\partial x}\right] dx + \left[\frac{\partial C^*_{qi}}{\partial C_{ai}} dC_{as} + dC_{qs}\right] +$$

$$+ \left[\frac{\partial C^*_{qi}}{\partial C_{ai}} \frac{1}{N_{ai}} \frac{dT}{T_{ai}} + \frac{dT}{N_{qi}}\right] \frac{dT}{2.303}$$

The values of the different quantities in the expression, the contribution from each source, and the total uncertainty for each run are given in Table III. The thickness in microns of a film of the organic phase required to produce a concentration drop equal to the calculated uncertainty in concentration is also given. This is obtained by dividing the uncertainty in concentration by the observed concentration gradient in the organic phase at the interface.

TABLE III

CALCULATION OF ERROR CONTRIBUTIONS

Run No.	$\frac{\partial C^*_{qi}}{\partial C_{ai}}$	$\frac{\partial C_{ai}}{\partial x}$, g/l·mm	$\frac{\partial C_{qi}}{\partial x}$, g/l·mm	Uncertainty from Position[1] g/l	Uncertainty from Position[1] μ equiv.	dC_{as}, g/l	dC_{qs}, g/l	Uncertainty from Standards g/l	Uncertainty from Standards μ equiv.	$\frac{1}{N_{ai}}$, g/l	T_{ai}	$\frac{1}{N_{qi}}$, g/l	T_{qi}	Uncertainty from Transmittance[2] g/l	Uncertainty from Transmittance[2] μ equiv.	Total Uncertainty g/l	Total Uncertainty μ equiv.
4	0.01	5	45	0.76	17	0.55	0.13	0.68	15	300	0.55	200	0.70	0.0031	0.07	1.44	33
7	.01	9	28	0.48	17	.57	.13	.70	25	200	.18	120	.61	.0022	.08	1.18	43
11	.7	60	180	3.78	21	.136	.307	.943	2.5	65	.12	130	.55	.0085	.05	4.22	24
12	0.5	57	170	3.38	20	.153	.319	.472	2.8	57	.50	100	.10	.0122	.07	4.85	23
13	3.0	2.0	6.3	.209	33.2	.014	.017	.031	4.9	40	.42	40	.47	.0020	.32	.242	38
13A	3.0	2.2	6.5	0.223	34.4	0.015	0.020	0.035	5.4	55	0.16	55	0.21	0.0066	1.02	0.265	41

1. Using dx = 0.017 mm.
2. Using dT = 0.005.

APPENDIX F

PHOTOGRAPHIC PHOTOMETRIC ANALYSIS OF CONCENTRATION PROFILES

The photographic photometric method of analysis of a concentration profile depends on the absorption of light of some wave length by the solute of interest and monotonic response of the photographic emulsion to exposure to this light.

Absorption of Light by Uranyl Nitrate Solutions

The light transmitted by x cm of a uranyl nitrate solution of concentration C moles/liter is given by Beer's law:

$$\log I/I_o = \frac{\beta_\lambda xC}{2.303}$$

where I/I_o = fraction of light transmitted

β_λ = molar absorption coefficient, liters/mole cm

The molar absorption coefficient is a function of wave length for any molecular or ionic species. This fact makes spectrophotometry a useful tool for analysis of multicomponent solutions.

The variation with wave length of the transmittance of uranyl nitrate solutions in aqueous and tributyl phosphate solutions is shown in Figure 23. The curves shown are for 1 cm of solutions containing 10.00 ± 0.05 g of uranium per liter of solution at 25.0°C. Only a very narrow portion of the spectrum is plotted, that between 420 and 450 mμ. This is the region of interest in this experiment as it contains the bulk of the light transmitted by the (nominally) 436-mμ transmission

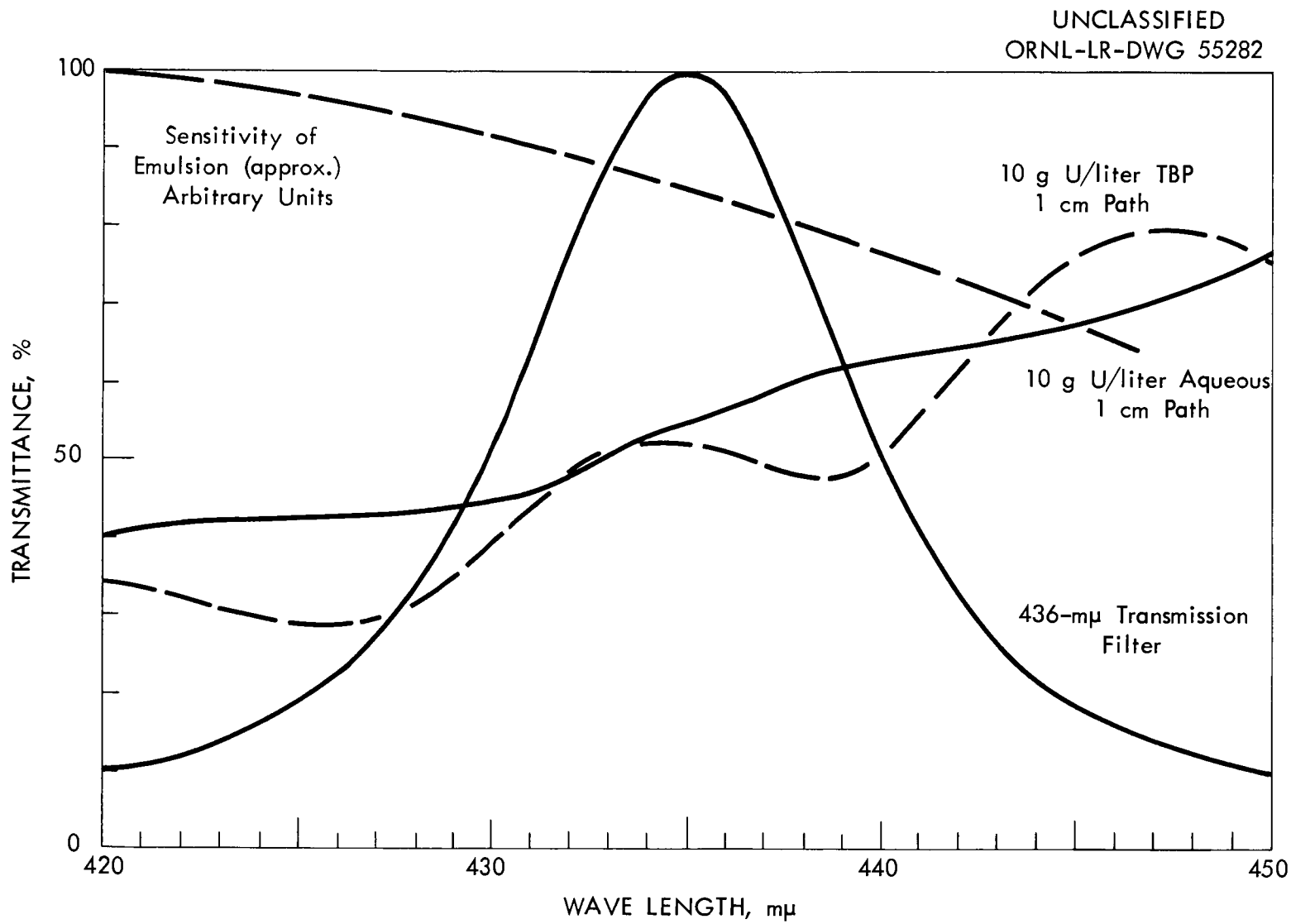

Fig. 23. Transmission spectra of uranyl nitrate in aqueous and tributyl phosphate solutions; 436-mμ filter.

filter used with the light source. The transmission curve of the filter is also plotted. All the data were taken on a Beckman DU spectrophotometer.

It is interesting to note how close the transmittance of the aqueous uranyl nitrate is to that in the organic phase. This permitted some convenience in selection of exposure times in the experiments. The effective molar absorption in the experiments was an average integrated over the transmission range of the filter and was approximately 14 liter/mole·cm. It did not appear as such in the calculations but was combined with other parameters in a calibration constant determined from standards in each run.

Behavior of Kodak Type IV-O Emulsion

If the density (defined as the negative logarithm of transmittance) of a developed photographic plate is plotted against the logarithm of the exposure (defined as the product of time and light intensity), the sensitometric curve characteristic to that emulsion and development is obtained. The curve is generally S-shaped, with a fairly linear central portion whose slope, which is qualitatively referred to as "contrast," increases with length of development.

Data for the first part of the linear region of Kodak type IV-O emulsion are plotted in Figure 24, the negative value of the density vs the logarithm of exposure. These data are qualitative checks on the system, and are not used in any run computations other than in the selection of the range of exposure times. The quantitative relation

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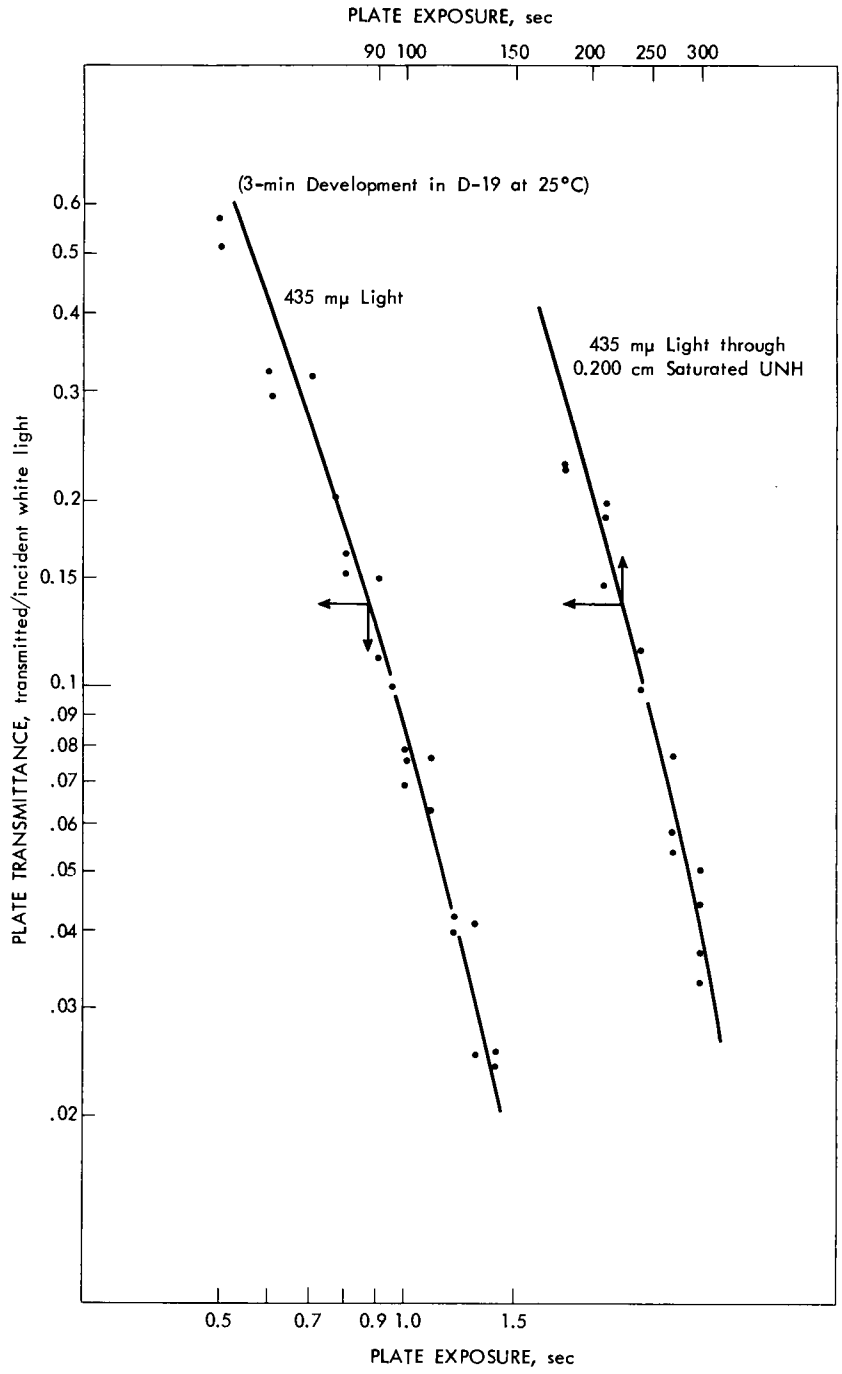

Fig. 24. Sensitometric curves for Kodak Type IV-O spectroscopic plate in 435-mμ light.

of plate density and concentration is implicit in the data and computations of each run.

However, the general form of the relation between uranyl nitrate concentration in the cell and density of its image on a plate may be derived. The equation for the linear portion of the sensitometric curve of the emulsion is

$$\rho = \gamma \log It + k$$

where $\rho = -\log T$

T = plate transmittance

γ = slope of linear portions of sensitometric curve

I = intensity of light transmitted by cell

t = exposure time

k = a constant for a given emulsion and development

Distinction should be made here between plate transmittance and cell transmittance. Plate transmittance is the fraction of incident white light transmitted by a developed dry plate, as measured on a microdensitometer, and is a function of plate exposure and development. Cell transmittance is the fraction of incident blue light transmitted by a given point in the diffusion cell, and is a function only of uranyl nitrate concentration at that point.

The relation can be rewritten as

$$-\log T = \gamma \log I + \gamma \log t$$

and the Beer's law relation previously developed is

$$\log I = -\frac{\beta_\lambda xC}{2.303} + \log I_o$$

the two may be combined to give

$$\log T = \frac{\beta_\lambda x \gamma C}{2.303} - (\gamma \log I_o t + k)$$

which is the general form of the relation between plate transmittance and concentration. The term on the right in parentheses is a constant for a given exposure on a given plate. The predicted linear relation between log T and C is found to hold very well for plate transmittances below 0.2. Above 0.2 there is curvature due to the decrease in γ at low exposures. By taking pains to standardize development procedure (3 min at 25°C in fresh Kodak D-19, 30 wipes per minute with a 6-in.-wide camel's hair brush), a very constant value of γ could be obtained. Since β and x are constant, the curves of log T vs C have a constant limiting slope at low transmittance. This provided a useful check on the interpolation between standards.

APPENDIX G

REAGENT PURIFICATION

Purification procedures for the reagents used in the experiments were designed to remove surface-active agents. The decrease of inorganic contamination was a secondary consideration as the reagents were fairly pure to start with and were used at such concentration that traces of inorganic ions would not interfere with the experiments.

Uranyl nitrate was purified by solution in 0.1 N HNO_3, filtration with decolorizing charcoal, and slow (overnight) crystallization from 40°C saturated solution. The crystals so obtained were redissolved in distilled demineralized water, filtered through a fine glass frit, recrystallized at 25°C from 40°C saturated solution, vacuum-desiccated 3 days at 10 μ Hg, and then dissolved in H_2O at 35°C. Glassware for the operation had been cleaned with hot dichromate cleaning solution followed by a hot 16 N HNO_3 wash and finally a demineralized-distilled water rinse. The water used for makeup was distilled from building demineralized water, principally to remove resin fines.

Nitric acid was commercial reagent-grade c.p. acid. It was felt that the strong oxidizing nature of the reagent would destroy traces of surface-active agents that might have been introduced in manufacture and handling, and that no further purification was needed.

The Amsco hydrocarbon diluent was commercial drum stock. It was washed with concentrated sulfuric acid to remove unsaturates, and 5 N NaOH to remove fatty acids and sulfonation products. It was washed with

demineralized water to neutrality, and run through a bed of activated alumina to remove surface-active agents. Effluent from the bed was filtered with charcoal to remove alumina fines and as added insurance against surface-active agents.

The tributyl phosphate was also commercial drum stock. It was refluxed for 24 hr with 5 N NaOH, with a slow nitrogen purge to remove hydrolysis products, mainly mono- and dibutyl phosphates. At the end of 24 hr, the cooling water was taken off the reflux condenser, and about half the caustic volume was allowed to boil away to steam distill off butyl alcohols. The TBP was then washed to neutrality, dried with charcoal, run through an activated alumina column, and again charcoal filtered. It was then stored in brown bottles in a dark cabinet at 25°C.

Acetone used to wash the cell and lines was run through an alumina column and filtered.

All reagents going into the column were stored in glass-stoppered bottles. Rubber stoppers were used for bottles containing the aqueous standards, to avoid "freezing," and it was felt that neoprene would not be attacked by aqueous solutions.

LIST OF SYMBOLS

C - concentration of uranium

D - diffusivity of uranium

I - light intensity

J - molecular flux

K - rate constant

M - distribution coefficient

N - slope of log T vs C interpolation curve

T - transmittance of a plate

t - time

x - distance

β - molar absorption coefficient, liters/mole•cm

γ - slope of sensitometric curve

Subscripts

a - aqueous phase

i - at the interface

q - organic phase

s - standard

λ - wave length of light

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The technique of permitting the establishment of a steady-state concentration profile, mapping it, and then extrapolating to the interface to get interfacial concentrations was suggested by Dr. H. F. Johnson of the Department of Chemical Engineering of the University of Tennessee. The writer wishes to acknowledge the numerous helpful suggestions of Dr. Johnson and the stimulating criticism of Dr. M. E. Whatley of the Chemical Technology Division of Oak Ridge National Laboratory.

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