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THE DENSITY OF URANYL SULFATE SOLUTIONS AND THE DETERMINATION OF URANIUM CONCENTRATION BY DENSITY MEASUREMENTS

By

J. E. Lee, Jr.
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Abstract

A study of the density of aqueous uranyl sulfate solutions is described which has had as its primary purpose the development of an analytical method for the determination of uranium in relatively dilute solutions of this salt. These solutions contain trace amounts of contaminating elements. The presence of small amounts of free sulfuric acid and moderate variations in the temperature at which density measurements are made can be compensated for by the use of equations provided for the calculation of uranium concentration.

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THE DENSITY OF URANYL SULFATE SOLUTIONS AND THE DETERMINATION OF URANIUM CONCENTRATION BY DENSITY MEASUREMENTS

INTRODUCTION

A study of the density of aqueous solutions of uranyl sulfate was undertaken for the purpose of ascertaining the feasibility of determining uranium concentration by a method based on density measurements. Such a method would be particularly applicable where large numbers of essentially pure, relatively dilute solutions must be analyzed in a minimum amount of time.

In order to prove useful as the basis for a method for the determination of uranium, the relationship between density and concentration of uranium must be such that the density change caused by somewhat less than a one percent change in uranium concentration is readily measurable and reproducible. It is desirable that the required manipulations be simple and rapid; a determination should require no more than five minutes.

There have been few earlier applications of density measurements for the estimation of uranium in uranyl sulfate solutions. Pinkston and Willson[5] used a hydrometer method for determining the uranium concentration of solutions in large storage tanks but were interested in an accuracy of only 0.001 pounds of uranium per gallon of solution.

Helmholz and Friedlander[2] determined the densities of various highly concentrated solutions of uranyl sulfate at several elevated temperatures for the purpose of determining the true uranium concentration of solutions in reactor units at high temperatures. Orban et al[4] estimated the density and viscosity of similar solutions under pressure and at high temperatures by monitoring the fall of a radioactive plummet in a special unit designed for this purpose. Equations for the use of density values for the calculation of the concentration of uranium and other constituents in solutions appears in an analytical manual by Rider and Nolin[6] and in an article by Howerton and Bruce.[3] In these cases the accuracy of the uranium determination may be impaired by the errors introduced by the additional parallel determinations that must be made for use in the solution of the mathematical expressions.

The work reported in this paper represents what is believed to be the best application of a density method for purely analytical purposes. The concentration of a single solute of such a high molecular weight can be determined with a comparatively high degree of accuracy and precision.

The scope of the present work was extended to include solutions containing free sulfuric acid and trace amounts of foreign ions.

Actual density determinations during this study were limited chiefly to solutions containing 5 to 75 mg/ml of uranium, although some information for concentrations in the range 300 to 400 mg/ml of uranium is reported. Graphic representation of practical subdivisions of these ranges yields curves which are essentially straight lines. Simple mathematical expressions have been provided

by means of which uranium concentration can be obtained from density data. Additional expressions, which include the effect of free acid and deviations in the temperature at which the density measurements are made, have also been formulated.

EXPERIMENTAL

Pycnometer Method. The first density measurements were made for the purpose of determining the slope of the concentration-density relationship for uranyl sulfate solutions. A pycnometer was used to measure the density of solutions which varied in concentration between 25 to 50 mg/ml of uranium. The coefficient of variation was determined to be approximately 0.0014 units of density per 0.1 mg/ml variation in uranium concentration. This information indicates that determinations of uranium are feasible by the density method if density measurements reliable to the fourth decimal place can be obtained.

The use of a pycnometer is not practical when determinations must be made in large numbers, however, because of the time required. A Westphal balance type of measurement is more rapid, and an instrument of this type having adequate sensitivity was sought.

Instrument Tests. A group of density determinations was made with a small Westphal balance and several modified analytical balances equipped with glass plummets. Included in this group were the Ainsworth "Chainomatic" and Mettler "Gram-atic" balances. None of these instruments appears to be entirely satisfactory for several reasons, but chiefly because of undesirable damping characteristics

which gave rise to irreproducibility of results. A recent, standard model of the Christian Becker density balance (Style SG-1) did not give values that were reproducible in the fourth decimal place.

Instrument Selection. An early model of the Christian Becker Projection Reading Balance (Model 911) was equipped with a five-gram plummet and otherwise successfully adapted for making density measurements accurately and reproducibly. This balance can be read directly from the second to the fourth decimal places by means of an optical system which projects an illuminated weight value in accordance with the deflection of the beam. There are no weights to add smaller than the 0.1-gram rider. A considerable saving of time results, since it is not necessary to wait for the beam to come to equilibrium after each trial addition of weight or change in position of the balancing chain.

The performance of this balance was completely acceptable. The inherent precision of the balance, with magnetic damping applied at both ends of the beam, is better than $\pm$ 0.0001 gram, as was shown by repeated weighings of the same sample.

Density Balance Calibration. A check was made of the accuracy of the determinations made with the density balance described in the preceding paragraph by comparison with density measurements obtained by means of a 25-ml pycnometer. A group of standard solutions was prepared in sufficient volume to provide ample fresh solutions for each type of determination.

Temperature regulation for the above determinations was achieved by means of a constant temperature bath held at 25 $\pm$ 0.1°C. The

pycnometer was filled with cooled solution and submerged in the bath in the usual manner. The side arm was capped at the proper temperature and the bottle was then weighed. The proper temperature of the solutions in the density balance was maintained by circulating water from the constant temperature bath through a jacket around the cell containing the solution being measured. This method was employed for all subsequent measurements made with this instrument.

The density values obtained by the two methods were found to be in satisfactory accord after a correction was made for air buoyancy effects on the plummet and a 5-gram weight used as a counterpoise for the plummet. These values appear in Table I. The determination of the density of water to $\pm$ 0.0001 units was achieved as a final test of the reliability of the instrument.

Table I

Comparison of Methods for the Determination

Of the Density of Uranyl Sulfate Solutions

Uranium mg/ml	Solution Density		Difference
	Pycnometer A	Density Balance B	A-B
20.0	1.0242	1.0241	0.0001
24.8	1.0309	1.0310	-0.0001
29.9	1.0376	1.0378	-0.0002
35.1	1.0445	1.0443	0.0002
40.1	1.0510	1.0511	-0.0001
44.8	1.0580	1.0580	0.0000

Exploratory Tests. The next phase of this work may be described as more or less exploratory. Actual applications of density measurements were made to determine the concentration of uranium in uranyl solutions. Standard uranyl sulfate solutions were prepared, their densities were measured, and calibration curves were prepared.

The results of these initial tests were encouraging. With proper attention to temperature and in the absence of free acid, the uranium concentrations which were determined from measured densities by means of these experimental curves were almost always within ± one percent of the value obtained by the gravimetric method.

Standard Curve. It became desirable at this point to establish as accurately as possible the true relationship between density and concentration of uranyl sulfate. The results in Table I represent one step in this direction, although further standards were needed to establish a reliable calibration curve.

Three groups of additional standards were prepared by three individuals on different dates. The densities of these solutions were determined at 25°C by means of the density balance. The solutions were then analyzed gravimetrically to verify the actual uranium concentration at the time the density was measured. The results appear in Table II.

The slope and intercept of the straight line described by the data from the first four groups of samples in Table II were obtained by the method of least squares. The equation for the straight line so derived is:

$$U = 737.4 \ D - 735.4 \qquad (1)$$

where: U = Concentration of uranium in mg/ml
D = Density

A plot of these data appears in Figure 1.

Density determinations for the fifth group of solutions (in Table II) of much higher concentration, were also made at 25°C by means of the density balance. The mathematical expression given below (equation 2) for the line derived from these data was also determined by the method of least squares.

$$U = 745.4 \ D - 743.7 \qquad (2)$$

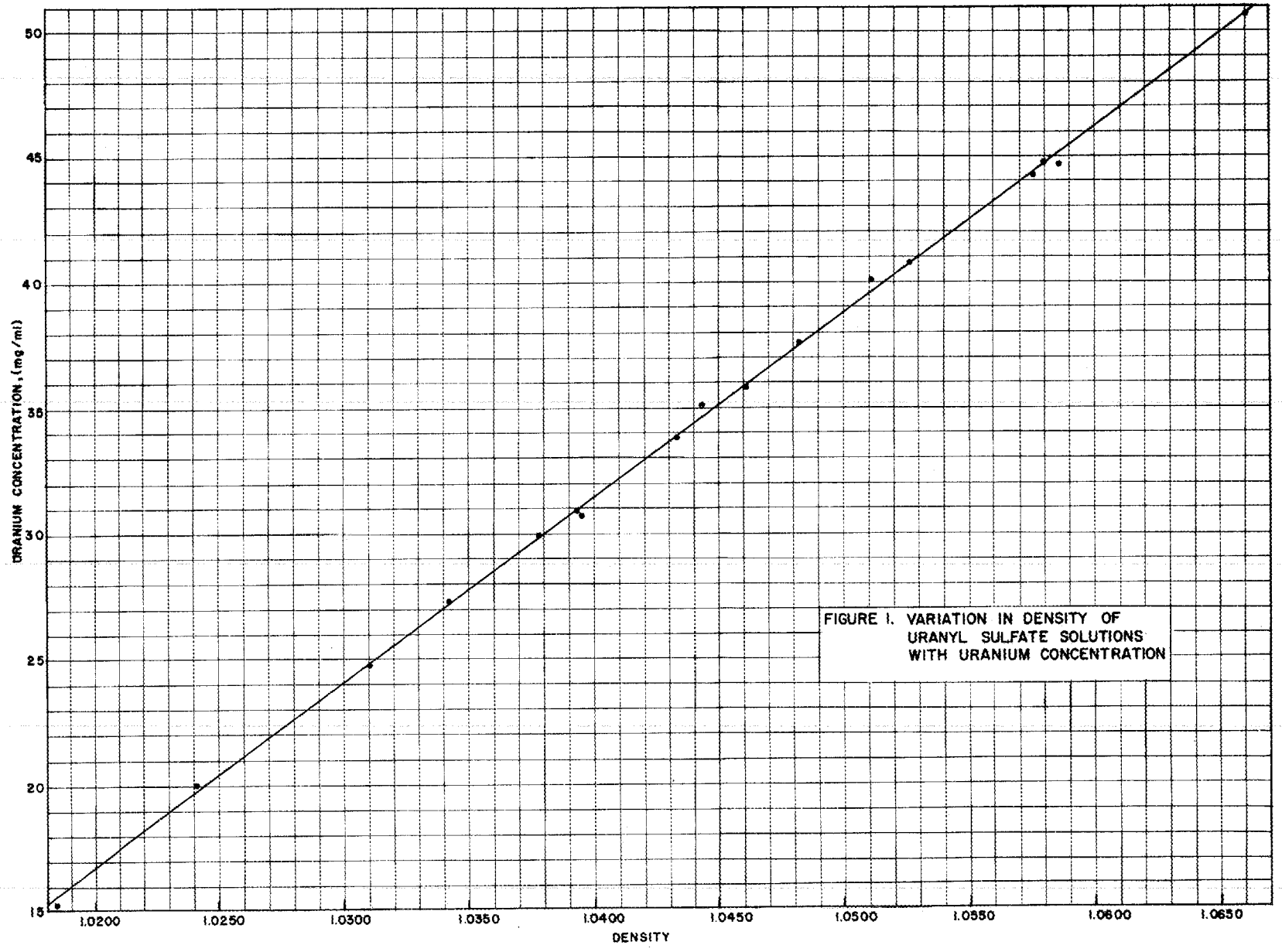

FIGURE I. VARIATION IN DENSITY OF URANYL SULFATE SOLUTIONS WITH URANIUM CONCENTRATION

Table II

Density of Standard Uranyl Sulfate Solutions

Group	Uranium, mg/ml	Density
1	33.8	1.0433
	37.6	1.0482
	27.3	1.0342
	44.3	1.0576
2	30.9	1.0393
	35.8	1.0461
	40.8	1.0526
	50.7	1.0661
3	20.0	1.0241
	24.8	1.0310
	29.9	1.0378
	35.1	1.0443
	40.1	1.0511
	44.8	1.0580
4	15.2	1.0184
	30.7	1.0395
	44.7	1.0586
5	271.0	1.3613
	355.1	1.4746
	379.3	1.5063
	404.4	1.5404

Application of the Method. The equation (1) in the preceding section was used to calculate uranium concentrations for a random group of laboratory samples for which the density measurements had been made as the samples were received over a period of two weeks time. The resulting values for the concentration of uranium were compared with those obtained by the volumetric method which consists of passing the sample through a Jones reductor, aerating, and then finally titrating with standard ceric sulfate. The results are set forth in Table III. The comparison is satisfactory.

Table III

Comparison of Volumetric and Density Methods

For the Determination of Uranium

Uranium, mg/ml		
Volumetric Method*	Density Method	Difference, Percent
A	B	A-B
24.3	24.2	0.4
24.3	24.2	0.4
24.4	24.4	0.0
28.9	28.7	0.7
30.6	30.6	0.0
30.8	30.6	0.6
31.2	31.4	-0.6
33.1	33.2	-0.3
33.3	33.3	0.0
36.2	36.5	-0.8
37.7	37.5	0.5
38.0	38.0	0.0
38.1	38.2	-0.3
39.1	39.2	-0.3
39.2	39.2	0.0
39.5	39.5	0.0
40.3	39.6	1.7
40.0	39.9	0.3
40.2	39.9	0.7
40.2	40.1	0.2
40.0	40.2	-0.5
40.2	40.4	-0.5
40.4	40.5	-0.2
40.2	40.8	-1.5
40.7	41.0	-0.7
40.7	41.0	-0.7
42.4	41.9	1.2
	Algebraic Sum	0.3

Incidence of:

A = B : 6,
A < B : 11,
A > B : 10.

* Jones reductor, ceric sulfate titration method.

Temperature Regulation. The need for close control of the temperature of aqueous solutions during density determinations is obvious from the variations in density per degree change in temperature as shown in published tables of such information, e.g., the density of water at various temperatures.[1] In the range of most interest for this work, 20 to 30°C, the average coefficient of variation with respect to temperature for the density of water is 2.6×10^{-4}. The coefficient is 2.1×10^{-4} for the range 20 to 21°C, and for the range 29 to 30°C, it is 3.0×10^{-4}. In order to measure the coefficient for solutions, it is necessary to maintain the concentration of solute constant while varying the temperature and adjusting for volume changes. A reasonable value for dilute solutions of uranyl sulfate was obtained by the following procedure:

A solution of uranyl sulfate was prepared to a given volume in a volumetric flask. The solution was prepared at the maximum temperature of the range to be observed. The flask and contents were then weighed at successively lower intervals of temperature. The volume of solution was kept constant, within the limits of the expansion of glass, by adding water up to the index line after each interval of temperature reduction. The solution was thereby held at constant uranium concentration while a change in density was effected by the addition of water. A determination in the above manner was carried out with a solution containing 25 mg/ml of uranium. The data are set forth in Table IV. The value obtained may be considered to be 3×10^{-4}, for practical application.

Table IV

Change of Density with Respect to Temperature of Uranyl Sulfate Solutions at Constant Uranium Concentration

Temperature Range, °C	Density Change, Total	Coefficient of Variation, x 10^4
20-25	0.0015	3.0
25-30	0.0013	2.6
30-35	0.0015	3.0
35-40	0.0016	3.2
20-40	0.0057	2.9
25-35	0.0028	2.8
20-35	0.0041	2.7

The coefficient, 3×10^{-4}, may be incorporated into the expression for the density-concentration relationship (equation 1) to yield the following modification, where t is the temperature (°C) at which the density measurement is made:

$$U = 737.4 \left[D - 0.0003 (25-t) \right] - 735.4$$

Equation (3) holds true for density measurements made within 10°C of the standardization temperature, 25°C, at which the slope and intercept constants were calculated.

Contamination Tests. In order to provide assurance that contaminants present in trace amounts do not adversely affect the density method for the determination of uranium, tests were conducted with controlled amounts of the typical contaminants, chromium and nickel. These ions were added to solutions of uranyl sulfate, the uranium concentration of which was approximately 25 mg per ml. The various concentrations of nickel and chromium and the resulting increases in density are given in Table V.

Table V

Effect of Trace Contaminants on the

Density Method for the Determination of Uranium

Contaminant, γ/ml		Density Increase
Ni	Cr	x 10^4
500		1.2
200		0.4
100		0.2
	500	1.2
	200	0.6
	100	0.3

These values, when compared with the coefficient of variation of density with respect to uranium concentration, 1.4×10^{-3} per 0.1 mg, indicate that the presence of 500 micrograms per ml of either of these contaminants caused only a 0.4 percent variation in the apparent concentration of uranium. Such a value is less than the accuracy normally required for this determination. On the basis of similar information, the tolerance for any given contaminant may be established. A permissible density change caused by contaminants depends, of course, upon the magnitude of the effect of a particular ion and upon the required analytical accuracy.

Effect of Free Sulfuric Acid. A brief study was made of the effect of the presence of free sulfuric acid on the density of uranyl sulfate solutions. Consideration of the problem leads to the assumption that the effect is additive, and this was demonstrated to be the case. A group of standard solutions was prepared containing free sulfuric acid in the concentrations shown in Table VI. The densities of these solutions

were measured at approximately 30°C. The temperature of the solutions was not controlled, however, and there was no gravimetric verification of the uranium concentrations.

Table VI

Effect of Acid Concentration on Density

Uranium, mg/ml	Acid Concentration N	Observed pH	Density at 30°C
25	0.0	2.52	1.0312
30		2.45	1.0379
35		2.37	1.0452
40		2.32	1.0518
45		2.27	1.0585
50		2.23	1.0653
25	0.01	2.03	1.0318
30		2.01	1.0384
35		1.99	1.0457
40		1.97	1.0515
45		1.97	1.0591
50		1.94	1.0659
25	0.05	1.42	1.0332
30		1.41	1.0399
35		1.41	1.0468
40		1.41	1.0532
45		1.41	1.0604
50		1.41	1.0672
25	0.10	1.15	1.0348
30		1.14	1.0416
35		1.14	1.0483
40		1.13	1.0551
45		1.13	1.0620
50		1.12	1.0688
25	0.20	0.87	1.0376
30		0.84	1.0448
35		0.85	1.0515
40		0.85	1.0581
45		0.85	1.0648
50		0.85	1.0713

Graphic representations of the above data yield parallel lines for each normality reported. It is significant to note that the presence of even small amounts of free acid obscures the pH effect due to variations in concentration of uranium. It thereby becomes possible to identify easily the range of free acid content in solutions having a wide range of uranium concentration.

The information dealing with the effect of free acid, shown in Table VI, was used to expand further the mathematical expression for the density-concentration relationship. Expressing the free acid (H_2SO_4) concentration in terms of normality, the modification of equation (1) becomes:

$$U = 737.4 \times D \times 10^{-0.013\,N} - 735.4 \qquad (4)$$

where U = concentration of uranium, mg/ml
N = normality of solution with respect to H_2SO_4
D = density

When equation (1) is modified to include corrections for variations in both acid content and temperature, the following expression results:

$$U_{mg/ml} = 737.4 \times 10^{-0.013\,N} \left[D - 0.0003\,(25-t)\right] - 735.4 \qquad (5)$$

In actual use equations (4) or (5) would require the use of pH vs. normality and logarithmic tables to translate the pH values for acidic solutions into a numerical value suitable for use in the above equation.

Experimental Technique. A brief outline of the general procedure used to obtain density values with the density balance is appropriate. The balance, a relatively straightforward adaptation of an analytical balance, has already been discussed. The plummet replaces the left-hand pan and is counterpoised by brass weights on the right-hand pan.

The plummet is suspended in a small cylinder having double walls for circulation of water at constant temperatures. The solution capacity of the container is 13 ml for the 5-gram plummet. The cylinder, or cell, is placed in a heavy steel base which aids in retaining the proper position under the plummet.

Proper cleaning of the plummet after each measurement is achieved by rinsing first with water, then with acetone. The cell is dried by wiping with absorbent tissue held in a large pair of forceps.

The total time required for the complete operation is no more than three minutes provided the sample material does not vary widely from the temperature of the thermostated cell. The rapidity with which the balance reading is obtained largely accounts for the short time cycle, although systemization of the loading and cleaning operations is of great importance.

The incidence of errors caused by lack of temperature equilibrium and evolution of dissolved gases are minimized as a result of the inherent characteristics of the balance. Since the second, third, and fourth decimal places of the weight value are projected by the light beam on an illuminated scale, it is possible to observe the drift caused by small temperature changes in the solution. If dissolved gases are being evolved from the solution during the measurement, the disturbance of buoyancy is such that the balance completely fails to reach equilibrium, i.e., ceases to drift.

The calculation of a density value from the buoyancy readings obtained with the aid of a modified balance, as described above, is made by means of the following expression:

$$D = \frac{Z - R - 0.0012V + \frac{0.0012\ (Z-R')}{8.4}}{V}$$

where D = density, at 25°C
Z = zero reference weight of the plummet in air
R = density balance weight reading for the plummet suspended in a test solution
R' = density balance reading to one decimal place
V = volume displaced by the plummet
0.0012 = weight of 1 cc of air at 25°C, and
8.4 = density of brass (in balance weights)

The portion of the expression,

$$0.0012V + \frac{0.0012\ (Z-R')}{8.4}$$

is the correction for the buoyancy of air on the plummet and on the brass removed during a measurement of density. A typical calculation for the balance used for this work with a 5-gram plummet would be:

$$\text{Density} = \frac{11.0000 - R - 0.0060 + \frac{0.0012(11.0-R')}{8.4}}{5}$$

Since the R value for the densities of solutions containing 5-75 mg of U is of the order of 5.+ the correction factor is 0.0053. The expression thereby reduces to:

$$D = \frac{11.000 - R - 0.0053}{5}$$

CONCLUSION

Relatively accurate measurements of the density of aqueous uranyl sulfate solutions can be obtained easily with the equipment and technique described in the foregoing paragraphs. The high atomic weight of the uranium constituent of these solutions affords a favorably large coefficient for the change in density with respect to change in concentration. A rapid, precise method for the determination of uranium is thereby made possible, since relatively small concentrations or concentration changes are readily detected.

The simplicity of the analytical procedure, the speed with which determinations can be made, and the overall precision and accuracy are satisfactory when compared with any of the more conventional gravimetric, volumetric, or potentiometric analytical methods usually employed for this determination.

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