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ATOMIC ENERGY

RESEARCH ESTABLISHMENT

THE DETERMINATION OF URANIUM BY HIGH-PRECISION SPECTROPHOTOMETRY

BY

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HARWELL, BERKS.

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ABSTRACT

A procedure is described for determining the uranium content of relatively pure samples of U_3O_8 and uranium metal with a precision (1σ) of $\pm$ 0.04 per cent. The sample is dissolved in nitric acid and this solution is then converted to standard conditions of acidity by evaporating to fumes of sulphuric acid. After dilution with water to a standard volume, the absorbancy of the sample solution is measured at 430 mμ, using a reference solution of accurately known uranium content. The uranium content of the sample is then obtained either by referring the absorbancy difference to a calibration graph or by calculation using a factor derived from the calibration graph.

The main factors which influence the accuracy of the determination are discussed in detail.

A.E.R.E. HARWELL

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ILLUSTRATIONS

1. INTRODUCTION

The accuracy required from the analytical chemist can vary very widely, but in recent years there has been an increasing demand for analytical methods which would give an accuracy of better than 99.9%. Since about 1949 spectrophotometry has been developed to such an extent that this technique is now making a valuable contribution in this type of high-accuracy work. Moreover, in specific cases spectrophotometric methods have decided advantages over conventional procedures since they are rapid and simple in operation and chemical separations can generally be avoided. These methods have resulted from the introduction of the differential system of measurement which employs reference solutions of high absorbancy. Hiskey and co-workers[1] were among the first to show that the accuracy of the spectrophotometric methods can be increased by using high-absorbancy reference solutions. It does not follow, however, that under these conditions maximum accuracy can be attained within the concentration range where solutions obey the Beer-Lambert law. For solutions failing to obey this law, it is possible to determine experimentally the concentration range for maximum accuracy.

It was thought that the differential spectrophotometric technique should be of advantage in the determinationof macro-quantities of uranium, especially in uranium base materials. The volumetric method for uranium is subjected to serious interference from other elements, as the reagents used to reduce the uranium to the tetravalent state before titration with ceric sulphate, generally reduce many other elements. Moreover, the conventional gravimetric method for uranium, involving precipitation as ammonium diuranate followed by ignition to U_3O_8, also leaves much to be desired. Many other elements are precipitated by ammonia under the same conditions and so cause contamination of the final U_3O_8. It was considered that the absorptiometric technique would be free from many of the above objections and would result in some improvement in the determination of macro-amounts of uranium.

The soluble compounds of uranium have been the subject of extensive research in recent years, the absorption spectra being used to postulate the ionic species present in solution. Kaplan, Hildebrant and Ader[2] studied the absorption spectra of uranyl nitrate in both aqueous and ketone media. Spectra for uranium in hydrochloric and perchloric acid solutions have been reported by Sutton[3].

Recently Rabinowitch[4] carried out a comprehensive survey of the absorption spectra of uranyl compounds. Spectra are shown for free uranyl ions and also for hydrolysis products, for uranyl ions complexed with acid anions and for uranyl compounds in organic solvents. Some indication is also given of the absorption spectra for solutions with pH values greater than 5.

A study of the available information revealed that the absorption spectra were least affected by changes in the acid concentration when the acidity was high. Further the most effective control of acidity can be attained by evaporating sample solutions to fumes of sulphuric acid and investigations were therefore limited to the determination of uranium in sulphuric acid solutions. Uranyl sulphate solutions absorb light at two wavebands, from 275 to 325 mμ and from 400 to 450mμ, the corresponding peak absorbancy indices (g/l/cm) being 1.1 and 0.055 respectively. Unfortunately light of the first waveband is subjected to serious interference from many elements, including iron, molybdenum, niobium, zirconium etc. Many of these difficulties do not arise with the higher waveband, and since the applicability of this technique was just as important as the best accuracy, investigations were therefore limited to the higher waveband.

Moreover, since the ultimate accuracy attainable in a determination is dependent on the largest single error from any one operation of the procedure, extensive experiments were carried out to assess the degree of control needed for the attainment of maximum accuracy under these conditions.

2. THEORETICAL

2.1 Preliminary Remarks

In spectrophotometric work the technique consists of taking absorbancy measurements on solutions containing known concentrations of the element being determined and then constructing a calibration graph. Absorbancy measurements on sample solutions are then converted to concentration by reference to this calibration graph. All measurements are therefore relative to a primary standard measurement.

Absorbancy measurements are obtained by 'setting' the instrument with one solution and then determining the absorbancy of another solution. When zero 'setting' is employed, the instrument must be balanced at zero with the solution of smallest absorbancy. In precision spectrophotometry where all absorbancies are relative to that of a solution of high absorbancy (reference solution), the absorbancy of the second solution (test solution) is positive when it is greater than that of the reference solution and negative when it is less. In the latter case the instrument must be balanced at zero with the test solution, unless the absorbancy difference is very small.

Two types of errors are frequently encountered in spectrophotometric work, designated in the text as 'intrinsic' and 'fractional' errors. The first type of error is constant at all levels of absorbancy and is generally associated with the 'matching' of the cells, reagent blanks etc. The fractional type applies to absorbancy errors which change in direct proportion to the absorbancy measurement. These errors are commonly associated with such factors as variation in cell thickness, temperature, and solution conditions.

2.2 Definitions.

Let C_1 = the concentration of the reference solution

C_2 = " " " " test solution

A_1 = the theoretical absorbancy of the reference solution under standard conditions in a 1.0 cm cell

A_2 = the theoretical absorbancy of the test solution under standard conditions in a 1.0 cm cell

b_1 = path length of reference cell (1) in cm

b_2 = path length of second cell (2) in cm

R_1 = absorbancy reading of reference solution in cell (1)

R_2 = " " test solution in cell (2)

R_3 = " " reference solution in cell (2)

R_4 = absorbancy reading of test solution in cell (1)

ε_1, ε_2 etc = intrinsic absorbancy errors (positive)

f_1, f_2, f_3 etc = fractional absorbancy errors (positive)

E_1 = intrinsic absorbancy error of cell (2) with respect to cell (1) (positive).

2.3 Solution Errors

A) Standard Conditions

Using perfectly matched cells of 1 cm. thickness and assuming that there are no errors in the reference and test solution under standard conditions.

Then $R_1 = A_1$ and $R_2 = A_2$

Setting R_1 on zero then $R_2 - R_1 = A_2 - A_1$ ...1

Similarly $R_3 = A_1$ and $R_4 = A_2$

Setting R_3 on zero then $R_4 - R_3 = A_2 - A_1$ ...2

Subtracting (2) from (1) $R_2 - R_4 = 0$ ...3

and adding (1) and (2) $R_2 + R_4 = 2(A_2 - A_1)$ ...4

B) When the solution conditions are identical for each member of a pair but different from the standard conditions. If f_1 is the fractional absorbancy error in each solution and ε_1 is the intrinsic absorbancy error in each solution it can be shown that under these conditions

$R_2 - R_4 = 0$ ...1

and $R_2 + R_4 = 2(A_2 - A_1) + 2f_1 (A_2 - A_1)$ ...2

On relating these expressions to those obtained under standard conditions A, then for solution conditions B in matched cells, the error is as follows:-

for $R_2 - R_4$ Zero ...3

for $R_2 + R_4$ $2 f_1 (A_2 - A_1)$ ...4

C) When the solution conditions vary for each member of a pair. If f_2 is the fractional absorbancy error in the reference solution, f_3 is the fractional absorbancy error in the test solution,

ε_2 is the intrinsic absorbancy error in the reference solution

and ε_3 " " " " " test solution.

It can be shown that

$$R_2 - R_4 = 0$$

and $R_2 + R_4 = 2(A_2 - A_1) + 2(A_2f_3 - A_1f_2) + 2(\varepsilon_3 - \varepsilon_2)$

Relating these expressions to those obtained under standard conditions A, then for solution conditions C in matched cells the error is as follows:-

for $R_2 - R_4$ Zero

for $R_2 + R_4$ $2[(A_2f_3 - A_1f_2) + (\varepsilon_3 - \varepsilon_2)]$

2.4 Cell Errors

When solutions are under standard conditions A and cell (1) and cell (2) are employed, the following treatment applies,

D) When $A_2 > A_1$

Then $R_1 = A_1b_1$ and $R_2 = A_2b_2 + E_1$

Setting R_1 on zero, then $R_2 - R_1 = A_2b_2 - A_1b_1 + E_1$ ...1

Similarly $R_3 = A_1b_2 + E_1$ and $R_4 = A_2b_1$

Setting R_3 on zero then $R_4 - R_3 = A_2b_1 - A_1b_2 - E_1$ ...2

Subtracting (2) from (1), $R_2 - R_4 = (b_2 - b_1)(A_1 + A_2) + 2E_1$ ...3

Adding (1) and (2), $R_2 + R_4 = (b_2 + b_1)(A_2 - A_1)$ ...4

Relating these expressions to those obtained under standard solution conditions A the use of unmatched cells results in the following errors:-

for $R_2 - R_4$, $(b_2 - b_1)(A_1 + A_2) + 2E_1$ ...5

for $R_2 + R_4$, $(b_1 + b_2 - 2)(A_2 - A_1)$ ...6

It is clear that conditions can also arise when $A_2 < A_1$

Setting now R_2 on zero, $R_2 - R_1 = A_1b_1 - A_2b_2 - E_1$ ...7

Setting R_4 on zero, $R_3 - R_4 = A_1b_2 - A_2b_1 + E_1$ ...8

Subtracting (8) from (7), $R_1 - R_3 = (b_1 - b_2)(A_1 + A_2) - 2E_1$ ...9

Adding (7) and (8), $R_1 + R_3 = (b_1 + b_2)(A_1 - A_2)$ ...10

From (3) and (9) it follows that $R_2 - R_4 = -(R_1 - R_3)$

and from (4) and (10) $R_2 + R_4 = -(R_1 + R_3)$

On relating equations (9) and (10) to those for standard conditions A, the errors resulting from the use of unmatched cells are as follows:-

for $R_1 - R_3$, $(b_2 - b_1)(A_1 + A_2) - 2E_1$ ...11

for $R_1 + R_3$, $(b_1 + b_2 - 2)(A_1 - A_2)$ ...12

2.5 Combination of Cell and Solution Errors

E) When solution conditions B and cells (1) and (2) are employed, it is found that

$$R_2 - R_4 = (1 + f_1)(b_2 - b_1)(A_1 + A_2) + 2E_1 \quad ...1$$

and $$R_2 + R_4 = (1 + f_1)(b_1 + b_2)(A_2 - A_1) \quad ...2$$

On referring to standard conditions A, then the total error from the use of unmatched cells and solution condition B is as follows:-

for $R_2 - R_4$, $(1 + f_1)(b_2 - b_1)(A_1 + A_2) + 2E_1$ ...3

for $R_2 + R_4$, $[(1 + f_1)(b_1 + b_2) - 2](A_2 - A_1)$ ...4

Moreover, by referring equations (1) and (2) to those for cell conditions D, the solution error from the use of unmatched cells and solution conditions B is as follows:-

for $R_2 - R_4$, $f_1(b_2 - b_1)(A_1 + A_2)$ ... 5

for $R_2 + R_4$, $f_1(b_1 + b_2)(A_2 - A_1)$ ...6

On comparing equation (6) with equation B (4), it will be noted that $(b_1 + b_2)$ replaces the value 2.

F) With solution conditions C and cells (1) and (2) it can be shown that

$$R_2 - R_4 = (b_2 - b_1)(A_2 + A_1) + (b_2 - b_1)(A_1 f_2 + A_2 f_3) + 2E_1 \quad .....1$$

and $$R_2 + R_4 = (b_2 + b_1)(A_2 - A_1) + (b_2 + b_1)(A_2 f_3 - A_1 f_2) + 2(\varepsilon_3 - \varepsilon_2) \quad .2$$

It follows then that the total error from the use of unmatched cells and solution conditions C is as follows:-

for $R_2 - R_4$, $(b_2 - b_1)[A_1(1 + f_2) + A_2(1 + f_3)] + 2E_1$ 3

for $R_2 + R_4$, $(b_1 + b_2)[A_2(1 + f_3) - A_1(1 + f_2) - 2] + 2(\varepsilon_3 - \varepsilon_2)$.....4

Similarly the solution error is

for $R_2 - R_4$, $(b_2 - b_1)(A_1 f_2 + A_2 f_3)$ 5

and for $R_2 + R_4$, $(b_1 + b_2)(A_2 f_3 - A_1 f_2) + 2(\varepsilon_3 - \varepsilon_2)$ 6

2.6 Systems for obtaining absorbancy values

i) One system used for determining absorbancy values is to reserve a pair of cells marked reference cell (1) and test cell (2) respectively, and always balance the instrument at zero absorbancy setting, using the reference solution in cell (1)[5].

By retaining two cells for all measurements any errors from variations in cell path lengths are avoided. Further all readings are related empirically to concentration via the second cell and the slope of the calibration graph (or calibration factor) is solely dependent on the path length of the second cell. However, allowance must be made for any difference in path length of the two cells and for any intrinsic absorbancy difference between the two cells. The correction value is determined by reading the reference solution in cell (2) against the same reference solution in cell (1) and appropriately correcting all subsequent readings. It is imperative that this value should not alter during exchange of the solutions in cell (2) and frequent checking of the correction value during a series of readings is firmly recommended. It should be noted, however, that even when the same reference solution is used in both cells the correction value is dependent on the absorbancy of the reference solution. It follows, therefore, that when a series of reference solutions is used, the cell check value for each reference solution should be accurately determined and close agreement to these values ensured before taking readings on test solutions.

The cells should be carefully cleaned before taking any readings and of the many treatments used to prepare the cells the following gave the most reproducible results:-

The cells were immersed in warm sulphuric-chromic acid for approximately 5 minutes and washed with a vigorous stream of water. They were then rinsed with distilled water, inverted on a hard filter paper and allowed to drain for a few minutes. The cells were then rinsed three times with acetone (A.R.) and again inverted and allowed to drain and dry. Using the cell covers to prevent dust particles entering the cells, the outer surfaces were polished with a dry 'Selvyt' cloth and any adherent dust particles were removed by a jet of clean compressed air. After use, the cells were always dried and contact with liquid for long periods was avoided.

Solutions were removed from the cells by suction, using a narrow bore polythene tube, care being taken to avoid contamination of the inner cell surfaces by contact with the polythene tube. The cells were rinsed twice in this manner with the solutions, on which absorbancy measurements were required.

ii) A second system[6] in use consists of reversing the solutions in the two cells reserved for absorbancy measurements, setting the instrument on zero, first by the reference solution in cell (1) and when the solutions are reversed, by the reference solution in cell (2). Using this system two readings are obtained. When the same two cells are used, the sum of the readings is directly related to the absorbancy difference (see the various equations for $R_2 + R_4$). Again it is imperative that the intrinsic absorbancy error of the two cells should not change during exchange of the

solutions. In this case, however, the difference between the two readings is a direct measure of the constancy attained during the reading of any pair of solutions. It still follows, however, that the reading difference is dependent on the absorbancy of the reference solution, even when the same solution is used in both cells. When a series of reference solutions is used, therefore, a reliable value for each should be obtained, a graph constructed and close agreement to these values ensured before taking readings on test solutions. The use of the same solution in each cell ensures that solution errors are constant. Typical values using the same solution in each cell are given in Table 3(a). From these the mean value for $(b_2 - b_1)$ and E_1 have been calculated, and applied to derive the calculated values for $R_1 - R_3$ and $R_2 - R_4$, shown in the calibration data given in Table 3. Comparison of these values against those obtained experimentally show the maximum experimental error to be of the order of $\pm$ 0.05%.

Comparison of the two systems

When a series of readings is taken, the first system described has the advantage in both speed and manipulation. Only one reading is taken and only one solution is exchanged. Any contamination of the second cell, however, can result in a series of erroneous measurements and frequent checking of the cell blank is necessary.

Using the second system described, frequent checking of the cell blank is minimised, as the reading difference on any of the solutions measured acts as a cell 'blank' check. Further a change in the cell 'blank' does not necessarily result in a series of erroneous readings and exchange of both solutions increases the probability that errors will be similar in each cell. By taking two readings and deriving the mean, increased accuracy should be attained and for these reasons, therefore, the double reading system was used for obtaining the absorbancy values in this work.

2.7 Principle of determining maximum accuracy

The concentration error at any point on a spectrophotometric calibration graph is defined exactly as

$$\varepsilon_c = \varepsilon_A \times \frac{\Delta C}{\Delta A} \qquad \text{I}$$

where ε_c is the concentration error

ε_A is the error in reading ΔA

and $\frac{\Delta C}{\Delta A}$ is the calibration factor

The fractional error at any concentration C_1 is therefore

$$\int_c = \varepsilon_A \times \frac{\Delta C}{\Delta A} \times \frac{1}{C_1} \qquad \text{II}$$

Now maximum accuracy is attained when the fractional error is minimum.

It follows, therefore, that maximum accuracy is attained when

$$\frac{\Delta A}{\varepsilon A} \times \frac{C_1}{\Delta C} \text{ is maximum.} \qquad \text{III}$$

Hiskey[1] has shown that for solutions which obey the Beer-Lambert law $\frac{\Delta A}{\varepsilon_A}$ is maximum when ΔA is 0.4343.

Since $\frac{\Delta A}{\Delta C}$ is constant, then maximum accuracy is attained when C_1 is maximum and further, the fraction $\frac{\Delta A}{\Delta C}$ is best determined using the differential system of measurement and a value for ΔC such that ΔA is 0.4343. For solutions which do not obey the Beer-Lambert law, however, $\frac{\Delta A}{\Delta C}$ decreases when the solutions fail to comply to this law. It follows, therefore, that a plot of the function $\frac{\Delta A}{\varepsilon_A} \times \frac{C_1}{\Delta C}$ against C_1 will show a maximum where the rate at which $\frac{\Delta A}{\Delta C}$ is changing, is equal to that for C_1.

Theoretically $\frac{\Delta A}{\Delta C}$ should be determined using small values for ΔC and ΔA. Hiskey[1] has shown, however, that the accuracy in determining ΔA decreases rapidly below a value of 0.20. ΔC should be chosen, therefore, such that ΔA is approximately 0.20. ε_A must be maintained constant and this is attained by using the same value for ΔC at various values for C_1, which results in the reading being obtained at the same place on the logarithmic scale of the instrument, when the differential system of measurement is used.

Although for solutions which do not obey the Beer-Lambert law ΔA changes when ΔC is constant for small changes in ΔA, ε_A can be still considered constant.

When ΔA is measured differentially then either a change in the meter sensitivity or in the slit-width is necessary to re-balance the instrument, when the concentration of the reference solution is changed. In order to maintain constant slit-width and yet attain satisfactory meter sensitivity, the sensitivity control should be adjusted using a reference solution of high concentration and a slit-width chosen to give satisfactory meter response. Moreover, conditions should be chosen such that the sensitivity control can be used to re-balance the instrument when the concentration of the reference solution is altered. The range of concentrations used for the reference solution is, therefore, limited and only values obtained on solutions of high concentration are shown in figure 1. In this figure are shown three curves:-

The values for curve A were obtained by adding the absorbancy difference obtained for each increment of 4 g/l uranium, to the absorbancy obtained for a solution containing 30 g/l uranium.

The values for any concentration on Curve B were calculated from the absorbancy difference obtained using a reference solution containing 30 g/l uranium and a second solution containing 34 g/l uranium. They are, therefore, the theoretical absorbancy which would be obtained at higher concentrations of uranium than 30 g/l if the solutions continued to obey the Beer-Lambert law.

The deviation of curve A from curve B shows the experimental deviation of the solutions from the Beer-Lambert law. The values for curve C were calculated using the experimental absorbancy difference obtained for each increment of 4 g/l uranium, using the following expression:-

$$\text{Relative Accuracy} = (A_2 - A_1) \times \frac{(C_1 + C_2)}{8}$$

This is obtained from III by substituting $\frac{C_1 + C_2}{2}$ for C_1, $A_2 - A_1$ for ΔA and 4 for ΔC. It can be seen that curve C shows the concentration at which the solutions fail to comply with the Beer-Lambert law, far more clearly than curve A and that maximum accuracy is attained when the concentration of the reference solution is about 48 g/l uranium, considerably greater than the concentration at which the Beer-Lambert law fails. The corresponding absorbancy for maximum accuracy is about 2.2. When the meter sensitivity is such, therefore, that the instrument can be read with certainty to $\pm$ 0.1% transmission then for small differences in absorbancy, the theoretical relative error is $\pm$ 0.01%. It can be seen, however, that the slope of the accuracy curve over the range 40-60 g/l uranium is relatively small. Thus the concentration employed for the reference solution is not critical. The use of a reference solution of lower concentration than the optimum favours the use of narrower slit-widths and 40 g/l uranium was chosen for experimental calibration purposes.

From the results obtained using different slit-widths, the following generalisations were deduced.

Decreasing the slit-width results in an increase in the slope of the theoretical curve A, the deviation of the experimental absorbancy from the theoretical decreases and the maximum accuracy, the optimum concentration for maximum accuracy and the concentration where solutions fail to comply with the Beer-Lambert law, all increase.

An approximate estimate of the extent of these changes is as follows:-

Slit-width	A per g/l/cm	Conc. at which Beer-Lambert law fails	Optimum conc.	Relative Accuracy
0.4 mm	.048	40 g/l	54 g/l	2.1
0.8 mm	.047	32 g/l	48 g/l	1.9

3. SOLUTION VARIABLES

3.1 Preliminary Remarks

Consideration of the mathematical expressions, previously derived, shows that when solution conditions are identical for each member of a pair of solutions, but different from standard conditions, then the individual points of the calibration graph and subsequent measurements referred to this graph, will only be affected by the fractional error in each pair of solutions. (See equation E(6)). When, however, solution conditions vary in each member of a pair the validity of the results is influenced by both the fractional and intrinsic errors of each solution. (See equation F(6)). In the case, therefore, where a reference solution is prepared in bulk and retained as a permanent reference solution, great care should be taken to ensure that any subsequent solutions are prepared using exactly the same reagent solutions. The inclusion of a "control" reference solution amongst each batch of solutions is to be recommended as a check on the validity of the permanent reference solution. Moreover, the inclusion of a second "control" solution, different in concentration, enables any errors to be classified as intrinsic or fractional and correction factors to be calculated.

The type and size of some of the errors introduced by variations in solution conditions, are discussed in detail under the appropriate headings.

3.2 Control of Uranium concentration

Volume of solution

Experiments were conducted to determine the precision which could be attained using 50ml. and 100ml. graduated flasks for volume adjustment and the results are shown in Table I.

The values show that the error in adjusting the meniscus was the same in both cases. Casual inspection of the flasks indicated that the neck bore of the 100ml. flasks was larger than that of the 50ml. flasks but internal bore measurements revealed that they were the same.

Although the fractional error is considerably smaller for the 100ml. graduated flasks, the four selected 50ml. graduated flasks were used and a coefficient of variation of $\pm$ 0.02% accepted as satisfactory. Weighings were made using a balance with a sensitivity of $\pm$ 0.1 mg. and all weights were greater than 1 g.

TABLE I.

COMPARISON OF 50 and 100ml. GRADUATED FLASKS

Test	Number of determinations	Deviation from mean (Range)	Std. Dev. ml.	Coeff. of Variation %
50ml. flasks - 20°C				
The same flask	6	+ .009,-.011	± .007	±.014
6 flasks selected at random.	6	+ .046,-.100	± .051	±.102
4 flasks selected from 12.	4	+ .012,-.010	±.010	±.020
100ml. flasks 20°C				
The same flask	6	+ .010,-.009	±.007	±.007
6 flasks selected at random.	6	+ .031,-039	±.024	±.024
4 flasks selected from 12.	4	+ .010,-012	±.008	±.008

3.3 Control of the acidity

In the study of the effect of acidity on the uranium absorption spectra, a series of solutions was prepared from uranyl sulphate $UO_2SO_4 3H_2O$ (analytical reagent). The uranium concentration was maintained constant at 0.75g in 50 ml and sulphuric acid additions were made so that the acidity varied over the range 0.5 to 18M. Typical spectra are shown in figure 2, from which it can be seen that for solutions less than 9M in sulphuric acid, large changes in the final acidity do not influence the character of the uranium spectrum appreciably. At acidities in the region of 18M, however, the character of the absorption spectrum is completely changed. On plotting the absorbancy values against acidity for different wavelengths in the waveband 400 to 450 mμ (fig.3) an optimum acidity was found for each wavelength at which the absorbancy is least affected by changes in the acidity.

The behaviour at 430 mμ was examined in greater detail by using the differential system of measurement, the result being shown graphically in figure 4. It can be seen that small changes in acidity will produce the least error when both the reference and the test solution are 4M in sulphuric acid.

Further, when the acidity of the test solution differs from that of a reference solution which is 4M in H_2SO_4, the resultant error is always negative, irrespective of whether the test solution is greater or less than 4M in H_2SO_4. Moreover the size of the error is dependent upon the extent of the difference in acidity between the test and sample solution. Approximating over the curve in figure 4 in the acidity range 3.5 to 4.5M in H_2SO_4, it is found that a positive or negative change of 12% in acidity from 4M results in a negative error of -0.10%. In consequence the acidity difference between the reference solution and the test solution should not vary by more than 2%, if a reproducibility of $\pm$ 0.02% is to be attained. With the system of preparing a bulk standard reference solution to be used as required over a long period, the acidity of the stock sulphuric acid used to prepare this standard and that used at a later date to prepare sample test solutions, should not vary by more than 2%.

Experiments were carried out to determine the variations in acidity which occur when the procedure of evaporating to fumes of sulphuric acid is used for the removal of other solvent acids. The experimental results are given in Table II and show that standard acidity can be attained to about $\pm$ 2% by using a fuming period of 10 minutes $\pm$ 5 minutes. No difficulty was experienced in removing hydrochloric or perchloric acids. In the case of nitric acid, however, diluting the solution with water after a single fuming resulted in the formation of brown fumes, which indicated the presence of some residual nitrogen compounds. This behaviour is associated with the formation of nitrosyl-sulphuric acid, and the amount formed seemed to be dependent on the strengths of the acids when mixed. Although no serious errors could be attributed to traces of residual nitric acid, double fuming was considered desirable. The results in Table IIa were obtained in the absence of uranium by titration with standard alkali. Results obtained in the presence of uranium are given in Table IIb. In the first set of experiments, several 2.3585g portions of selected U_3O_8 were taken and dissolved in minimum amounts of nitric acid (sp.gr.1.42). An accurately measured 20ml portion of 20N sulphuric acid was then added to each beaker and the solutions were evaporated to fumes, the process being allowed to proceed with the beakers uncovered. The solutions were fumed for various times, before cooling and diluting to 50ml with water. The absorbancy of each solution was measured against that which had been fumed for 1 minute only. The results show that the increase in error with time of fuming is quite significant under these conditions. On repeating these experiments and using covered beakers during the fuming stage, the loss of acid is very much smaller.

3.4 Control of the temperature

The effect of a change in temperature is two-fold[7], the solution volumes are changed, which results in a concentration error, and the solution characteristics may alter. The two effects can be experimentally determined by the following procedures:-

(1) Use the same solution in cell(1) and cell(2) at different temperatures and measure the temperature difference and the absorbancy difference.

(2) Use two solutions of differing absorbancy in cell(1) and cell(2) at the same temperature, and measure the absorbancy difference. Repeat the experiment, still maintaining the temperature of the solution in cell(1) and cell(2) the same but at a different value.

The first procedure gives the summation of both the volume and characteristic changes. The second procedure gives only the characteristic changes.

TABLE IIa

INFLUENCE OF FUMING PERIOD ON THE ACIDITY
(TITRATION WITH CAUSTIC SODA)

mls added 10N. H_2SO_4	mls added 12N. $HClO_4$	Conditions		N.NaOH mls	Acidity Change %
nil	10	Control Titration		12.15	-
nil	10	Just fumed - 2 min - cover on		12.05	-0.8
nil	10	Boiled gently - 2 min - cover on		11.50	-5.5
nil	10	Boiled vigorously - 2 min. cover on		10.85	-11.0
10	nil	Control Titration		10.05	-
10	nil	Boiled down and fumed	5 min	9.95	-1.0
10	nil	with cover on for stated	10 min	9.85	-2.0
10	nil	time.	20 min	9.70	-3.5
10	10	Boiled without cover (15 mins)	5 min	9.90	-1.5
10	10	Cover replaced immediately after	10 min	9.80	-2.5
10	10	H_2SO_4 commenced to fume, then fumed with cover on for stated time.	20 min	9.65	-4.0
10N. H_2SO_4	16.ON. HNO_3				
nil	5	Control Titration		8.20	-
nil	5	Boiled 5 mins - cover on		6.55	-20.0
10	5	Boiled down and	5 min	10.45	+ 4.0
10	5	fumed with cover on for	10 min	10.25	+ 2.0
10	5	stated time	20 min	10.05	nil
10	5	Boiled down and fumed for 5 mins	5 min	9.75	-3.0
10	5	Cooled, diluted to 20 mls	10 min	9.65	-4.0
10	5	with water, refumed with cover on for stated time.	20 min	9.45	-6.0
10N. H_2SO_4	10N. HCl				
nil	5	Control Titration		5.1	-
nil	5	Boiled 5 mins - cover on		3.85	-25.0
10	5	Boiled down and	5 min	9.95	-1.0
10	5	fumed with cover on for	10 min	9.85	-2.0
10	5	stated time.	20 min	9.70	-3.5

TABLE IIb

INFLUENCE OF FUMING PERIOD ON URANIUM DETERMINATION
(URANIUM 40 g/l)
CONDITIONS AS DESCRIBED IN THE METHOD

Fumed without a cover

	Time in mins.	Error %
1 - Reference solution	1	0
2 -	2	-0.06
3 -	3	-0.18
4 -	5	-0.30

Fumed with cover on

1 - Reference solution	2	0
2 -	5	-0.06
3 -	10	+0.06
4 -	30	+0.09

The first system is simple in experimental operation. The volume change can be assessed from specific gravity tables or specific gravity determinations, the error calculated, and the characteristic error derived.

Temperature errors are of the fractional type and measurements are best conducted therefore using a solution of high absorbancy. Cell (1) was filled with the solution at room temperature and cell (2) was filled with the same solution at an elevated temperature. Temperature and absorbancy readings were taken at intervals. Cell (2) was then emptied and refilled with the same solution at a lower temperature than that of the solution in cell (1) and the reading process was repeated. The values obtained are plotted in Fig. 4. It can be seen from this figure that an increase in temperature results in a positive fractional error in the absorbancy and that this is directly related to the deviation from the standard temperature.

From the experimental curve A, it can be calculated that when the temperature of the reference solution or the test solution differs by $\pm$ 8°C from the standard temperature, the absorbancy error is $\pm$ 1% A_2 and $\pm$ 1% A_1 respectively.

The temperature gradient along the cell carriage must therefore be sufficiently small to be ignored and time must be allowed for the two solutions to acquire the same temperature.

From the standard volume curve, it can be calculated that when the temperature of the reference and test solutions is the same, but differs from the standard temperature by $\pm$ 6°C then the absorbancy error is now only $\pm$ 1% $(A_2 - A_1)$.

Temperature measurements showed that the gradient along the cell housing of the Beckman instrument could be as high as 1.5°C and that the temperature in the cell housing was dependent on how long the lamp had been switched on. Both the lamp housing and the cell carriage were therefore fitted with water jackets, a circulating pump installed and the circulating water thermostatically controlled at a standard temperature.

A water bath was also thermostatically controlled so that solutions could be diluted to volume at the standard temperature.

4. SPECTROPHOTOMETER VARIABLES

4.1 Relationship between slit-width and meter sensitivity

It is essential in precision spectrophotometry that the meter sensitivity should be so adjusted that a 0.1% change in transmission will give a detectable movement of the galvanometer needle. Also the instrument must be sufficiently stable such that fluctuations are less than the above deflection.

To maintain this meter sensitivity as the absorbancy of the reference solution increases then the slit-width must be increased to re-balance the instrument.

A plot of the minimum slit-width which will give the above sensitivity against the absorbancy of the reference solution, for the two ranges available on the Beckman instrument is given in Fig. 6(a).

According to Hiskey[8] the ratio of the slit-widths (s.w.) for the reference solution and for the water blank is related to the intensities of the transmitted light by the expression $I_w/I_s = \left(\frac{\text{s.w. soln}}{\text{s.w. water}}\right)^r$ where r is a function of light losses due to setting the mirrors and aligning the optical system. The value for r should be 2 for correctly adjusted spectrophotometers. On plotting the absorbancy values obtained for uranium solutions against the logarithm of the ratio of the slit-width for the solution against the slit-width for water (see fig.6b) a straight line calibration graph was obtained with a slope of 2. This result verified that the Beckman spectrophotometer being used was in correct alignment.

Further experiments showed that at a constant slit-width, the meter sensitivity varied inversely as the transmission of the solutions. Thus slit-width, transmission and sensitivity can be intercorrelated[8] as follows:

$$\left(\frac{\text{slit-width for water}}{\text{slit-width for soln.}}\right)^2 = \frac{\text{transmission for soln.}}{\text{transmission for water}} = \frac{\text{meter sensitivity for soln.}}{\text{meter sensitivity for water}}$$

4.2 Wavelength and Waveband Selection

With the normal light source of the Beckman instrument wide slit-widths are necessary to obtain adequate meter sensitivity when reference solutions of high absorbancy are used. This arises because it is impracticable to increase the intensity of the light source. The effect of increasing the slit-width on the absorption wavelength plot can be seen by comparing figure 7 with figure 2. By increasing the slit-width eight fold, the irregularity in the absorbancy vs the wavelength plot at 430 mμ (shown in fig.2) has entirely disappeared whereas the one at 412 mμ has been hardly affected. Further the peak height at 420 mμ has decreased considerably.

Doubling the slit-width to 0.8mm produced little change from the absorbancy values shown in fig. 7 and it follows that the use of wide slit-widths considerably decreases the error introduced by inaccurate setting of the slit-width.

Errors can arise, however, from inaccurate setting of the wavelength scale and these are at a minimum where the smallest change in absorbancy occurs for unit error in setting the wavelength scale. From fig. 7 the corresponding wavelengths which satisfy this requirement are 412 and 422mμ. Unfortunately, interference by such elements as niobium and molybdenum (proposed alloy constituents for uranium base alloys) is significant at these wavelengths. At 430 mμ, however, the above interference is less troublesome and this wavelength was chosen for detailed investigation. It is not claimed therefore that ultimate accuracy has been attained in this work.

5. PROCEDURE FOR THE DETERMINATION OF URANIUM

5.1 Preparation of the Oxides

Uranium oxide (U_3O_8) can be readily produced by igniting uranium compounds to a temperature of 850°C. In an examination of this technique weighed quantities of different uranium salts were first carefully ignited at a low

temperature and then finally for 3 hours at a temperature of 850°C. After cooling and weighing, the high temperature ignition was continued for a further 30 minutes. In all cases, no change in weight was produced by this further ignition, but the amount of U_3O_8 obtained was sometimes less than the theoretical. The U_3O_8 samples were next allowed to stand exposed to normal atmosphere conditions for 60 hours and any change in weight was recorded. The general tendency was for the oxides to gain in weight on standing and full details of the results are as follows:-

Uranium Compound	Deviation of wt. of U_3O_8 from wt. theoretically expected %	Gain in weight of U_3O_8 on exposure to atmosphere for 60 hours. %
$UO_2(C_2H_3O_2)_2.2H_2O$(Analar)	-4.64	0.05
$UO_2SO_4.3H_2O$(Laboratory Reagent)	-3.06	0.02
$UO_2(NO_3)_2\ 6H_2O$ (Analar)	nil	0.03
UO_3(Laboratory prepared)	-3.09	0.012

Further evidence in support of the results in the last column was obtained from the examination of Specpure U_3O_8 and a specimen of high purity U_3O_8 prepared by cellulose chromatography. The full history of these samples was unknown, but the first had a loss in weight of 0.27% on ignition and the second a loss of 0.71%. All this evidence emphasizes the necessity of igniting all U_3O_8 samples to constant weight before use.

5.2 Solutions

Sulphuric Acid (20N) - Standard Stock Solution

Cautiously pour 555ml of Analar sulphuric acid (sp.gr.1.84) into 400 ml of water, whilst cooling the solution. Dilute to 1 litre at room temperature with water. When a further stock solution is prepared it should be within 2% of the standard stock solution.

Standard Uranium Solution (Primary reference solution)

2.3585 gm of the selected U_3O_8 was weighed for every 50 mls of solution required, transferred to a tall lipped conical flask and dissolved in the minimum amount of nitric acid (S.G. 1.42), 20 mls of the stock sulphuric acid solution were added (from a burette to $\pm$ 0.1 ml) for every 50 mls of solution required. The solution was boiled down and fumed 10 minutes, cooled, diluted to about four times the volume, boiled down and refumed a further 5 minutes.

The solution was cooled and diluted to the appropriate volume at a standard temperature of 23°C. The 250ml volumetric flask used was standardised

against the 50 ml flasks subsequently used for preparing other solutions and the appropriate weight of U_3O_8 required was calculated using the following equation:-

wt of U_3O_8 = 2.3585 x y/x

where x = weight of water contained in standard 50 ml flask at 23°C.

y = " " " the 250 ml flask at 23°C.

Reference Solution

2.3585 gm of U_3O_8 was processed as previously described. The solution was diluted to volume in a 50 ml graduated flask at 23°C.

Test Solution

Various weights of U_3O_8 were processed as previously described and the solutions diluted to volume in selected 50 ml graduated flasks at 23°C.

Sample Solution

2.3585 gm of the U_3O_8 samples, (2 gm of the uranium metal) were processed as previously described and the solutions diluted to volume in selected 50 ml graduated flasks at 23°C.

5.3 Calibration

The accuracy of the calibration graph at any concentration is dependent on the absorbancy difference used to determine its slope. For solutions which obey the Beer-Lambert law the slope can be determined with maximum accuracy when the absorbancy difference between any two solutions is 0.4343. The concentration range covered by one reference solution is dependent on the accuracy required over that range, and the choice of the concentration for the reference solution is governed by whether maximum accuracy is required at the upper, lower or centre part of the calibration range.

For solutions which do not obey the Beer-Lambert law, the concentration range used to determine the slope is now governed by the change in slope in addition to the accuracy of the absorbancy measurement.

At absorbancy differences less than 0.20, the accuracy of the determination decreases rapidly. A concentration difference of 4g per litre uranium was used, therefore, to determine the slope and the system of plotting averages applied to determine the slope at any specific uranium concentration.

When the absorbancy of the test solution is less than that of the reference solution, measurements are made by balancing the instrument at zero setting using the test solution and calibration graphs constructed in this manner show zero absorbancy at the concentration of the reference solution. Milner and Phennah[6] have shown in detail that positive and negative absorbancies must be taken into account when corrections are applied and also when calculating the concentration of the test solution. Seven solutions were prepared to cover the range of 28 to 52 gm/l of uranium. A slit-width was chosen (0.8mm) such that when the 52 gm/l uranium solution was used to

balance the instrument at zero, a movement of the absorbancy dial of 0.001 resulted in a meter deflection of 1 division and further, that the meter sensitivity control was capable of rebalancing the instrument when the 40 g/l uranium solution was used to rebalance the instrument. The absorbancy differences between the 40 g/l uranium solution and the other solutions were then obtained, using the solution reversal system and the readings obtained are given in Table III. The reciprocal of the slope (calibration factor) was calculated for all differences with respect to the 40 gm/l uranium solution. These values are shown plotted against the uranium concentration in Fig. 8, curve B. Any absorbancy difference can, therefore, be directly converted to uranium concentration or preferably, the calibration factor can be obtained from curve B and the concentration difference calculated, addition or subtraction of this value from 40 giving the uranium concentration in the test solution in gm/l. For the very small differences obtained for the samples given in Table IV the factor at 40 g/l uranium is not critical and was approximated to the nearest 0.01%, i.e. a calibration factor of 24.

For sample solutions with uranium concentrations differing greatly from 40 g/litre, improved accuracy is attained by preparing a further reference solution with a uranium content almost identical with that of the sample solution. The absorbancy of the sample solution is then measured against this new reference solution. With this system the calibration factor is obtained by reference to Curve C of figure 8 which is prepared from a consideration of the absorbancy differences of consecutive solutions used in the calibration experiments, (see Table III). This curve is constructed by determining the calibration factor for each concentration range and plotting this value against the corresponding mean concentration value for the range.

5.4 Calculating the concentration of the sample solution

(a) Single Reference Solution

The absorbancy of the sample solution is obtained with respect to the 40 g/l uranium reference solution, the corresponding factor is then derived from the graph (Fig. 8 curve B) and the uranium concentration of the test solution is calculated using the following expression:-

$$\text{Uranium concentration } (g/l) = 40.0 \pm F_1 [A_2 - A_1]$$

where F_1 is the corresponding factor on curve B to $[A_2 - A_1]$

(b) Subsidiary Reference Solution

The absorbancy of the test solution is obtained with respect to the subsidiary reference solution, the corresponding factor derived from the graph (Fig. 8 curve C) and the uranium concentration of the test solution calculated using the following expression:-

$$\text{Uranium concentration } (g/l) = C_1 \pm F_2 [A_2 - A_1]$$

Where F_2 is the corresponding factor on Curve C at $\frac{A_2 - A_1}{2}$ (reference

C_1 = zero absorbancy).

6. RESULTS OBTAINED BY THE METHOD

The results obtained on samples of U_3O_8 and a sample of uranium metal are given in Table IV.

The high purity sample was examined spectrographically for 37 elements and a positive value for the total impurities of <0.005% was obtained. The method can be considered accurate therefore within ± 0.04%. The values for the different series were obtained on different days over a period of a week and it can be seen that any instability in the primary reference solution was less than the detectability of the method.

7. CONCLUSIONS

The accuracy attained by the described procedure compares very favourably with that which can be attained by volumetric or gravimetric methods. Moreover this procedure is more specific. The need to use accurately calibrated volumetric equipment and to thermostat solutions is troublesome when only occasional samples are required to be analysed. The differential spectrophotometric technique is best suited to laboratories having to determine the uranium content of uranium base materials continuously, since the time taken in setting up apparatus and calibrating equipment is then time spent advantageously. Moreover the technique is rapid in operation and therefore convenient for control analysis.

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TABLE III

CALIBRATION DATA

BECKMAN - 1 cm CELLS - SLIT-WIDTH 0.8 mm. - 430 mμ

H_2SO_4 4M. TEMP. 23°C.

b1 = REFERENCE CELL = 1 cm

Uranium concn. g/l	C_2-C_1 g/l	R_1	R_2	R_3	R_4	R_1-R_3	R_2-R_4	$\frac{R_1+R_3}{b1+b2}$	$\frac{R_2+R_4}{b1+b2}$	(A_2-A_1) for single ref. soln.	Factor $\frac{C_2-C_1}{A_2-A_1}$	(A_2-A_1) for subsidiary ref. soln.	Factor $\frac{C_2-C_1}{A_2-A_1}$	Absorbancy Reference Water	Calc. R_1-R_3	Calc. R_2-R_4
28	-12	0.551	0	0.563	0	-.012		0.5561		-.5561	21.58			1.320	-0.0130	
30												-.1877	21.31			
32	-8	0.363	0	0.375	0	-.012		0.3684		-.3684	21.72			1.508	-0.0136	
34												-.1867	21.42			
36	-4	0.175	0	0.189	0	-.014		0.1817		-.1817	22.01			1.694	-.0142	
38												-.1817	22.01			
40		0	+.0075	0	-.0075		+.015		0	0	-			1.876		+.0148
42												+.1757	22.77			
44	+4	0	.183	0	.169		+.014		0.1757	+.1757	22.77			2.052		+.0154
46												+.1657	24.14			
48	+8	0	.350	0	.334		+.016		0.3414	+.3414	23.43			2.216		+.0159
50												+.1508	26.52			
52	+12	0	.501	0	.485		+.016		0.4922	+.4922	24.38			2.368		+.0164

TABLE IIIa

CALCULATION OF CELL ERRORS

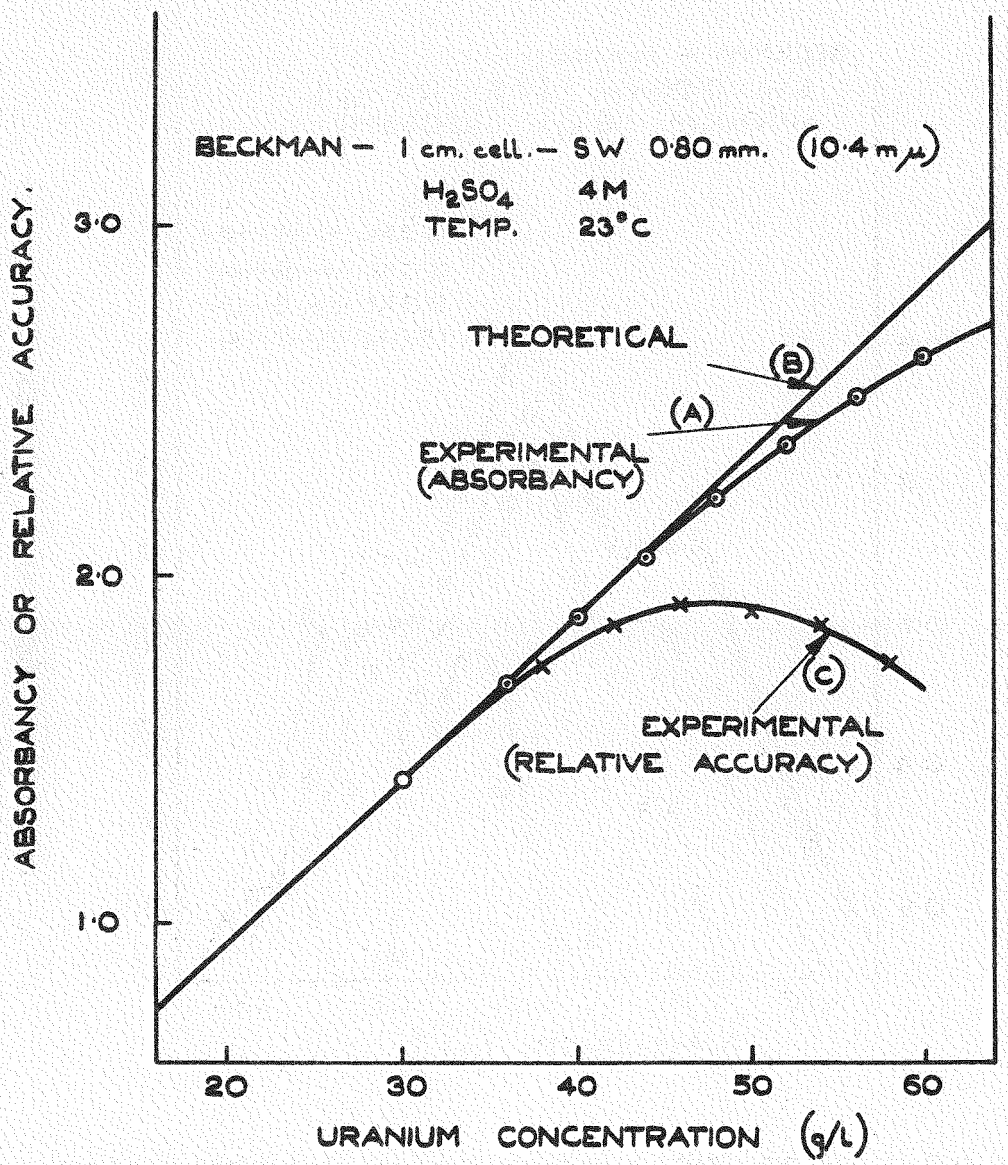
Uranium conc. g/l	A reference water	R_1	R_2	R_3	R_4	$R_2 - R_4$	b2 - b1	E_1	b2 - b1 mean	E_1 mean
28	1.320	0	+0.0055	0	-0.0055	+0.011	+0.0036	0.0011		
40	1.876	0	+0.0075	0	-0.0075	+0.015	-	0.0013	+0.0033	+0.0012
52	2.368	0	+0.0090	0	-0.0090	+0.018	+0.0030	0.0012		

TABLE IV

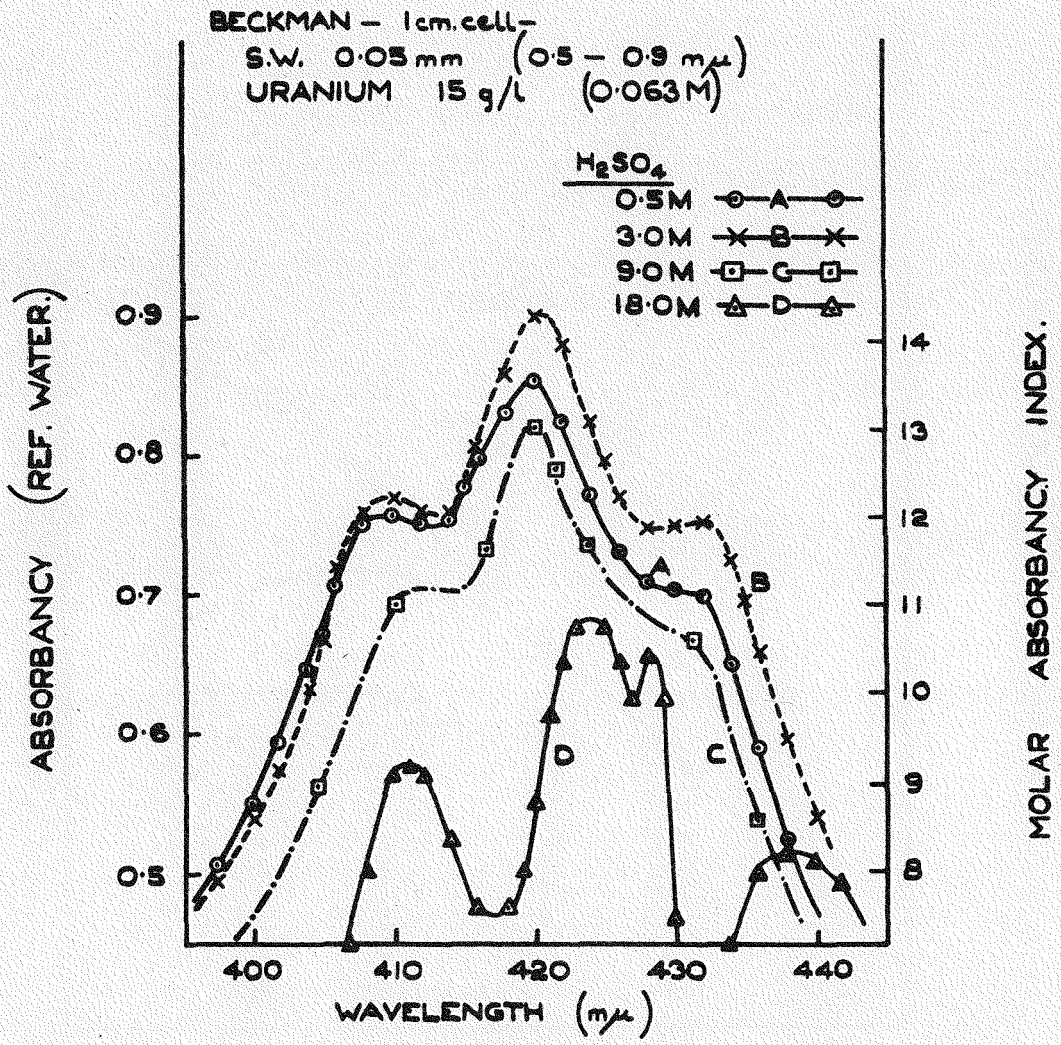
RESULTS OBTAINED ON SAMPLES OF U_3O_8 AND A SAMPLE OF URANIUM METAL
BECKMAN - 1cm CELLS. SLIT-WIDTH 0.8 mm - 430 mμ
H_2SO_4 4M TEMP. 23C

Source of Uranium	← Series → 1	2	3	Mean %	Range %	Std.Dev. from mean %	Coeff. Variation
Primary reference solution (acetate)	100.00	100.00	100.00	100.00	nil	nil	nil
U_3O_8 (High purity)	99.97	100.06	100.00	100.01	+0.05 −0.04	±0.046	±0.046%
U_3O_8 (Acetate)	100.03	100.00	99.97	100.00	+0.03 −0.03	±0.030	±0.030%
U_3O_8 (Spec.Pure)	100.00	100.00	99.97	99.99	+0.01 −0.02	±0.017	±0.017%
U_3O_8 (UO_3)	100.00	99.97	99.94	99.97	+0.03 −0.03	±0.030	±0.030%
U (metal as cast)	100.00	100.06	100.03	100.03	+0.03 −0.03	±0.030	±0.030%

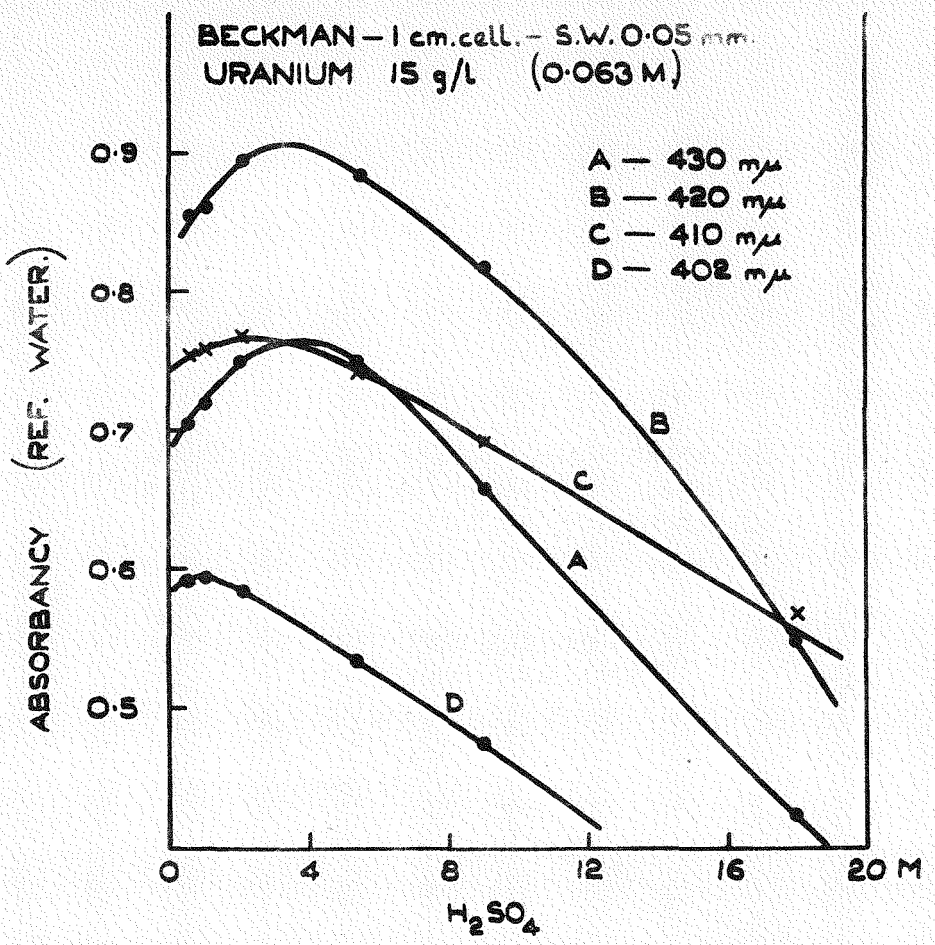
Over-all coefficient of variation ±0.031%



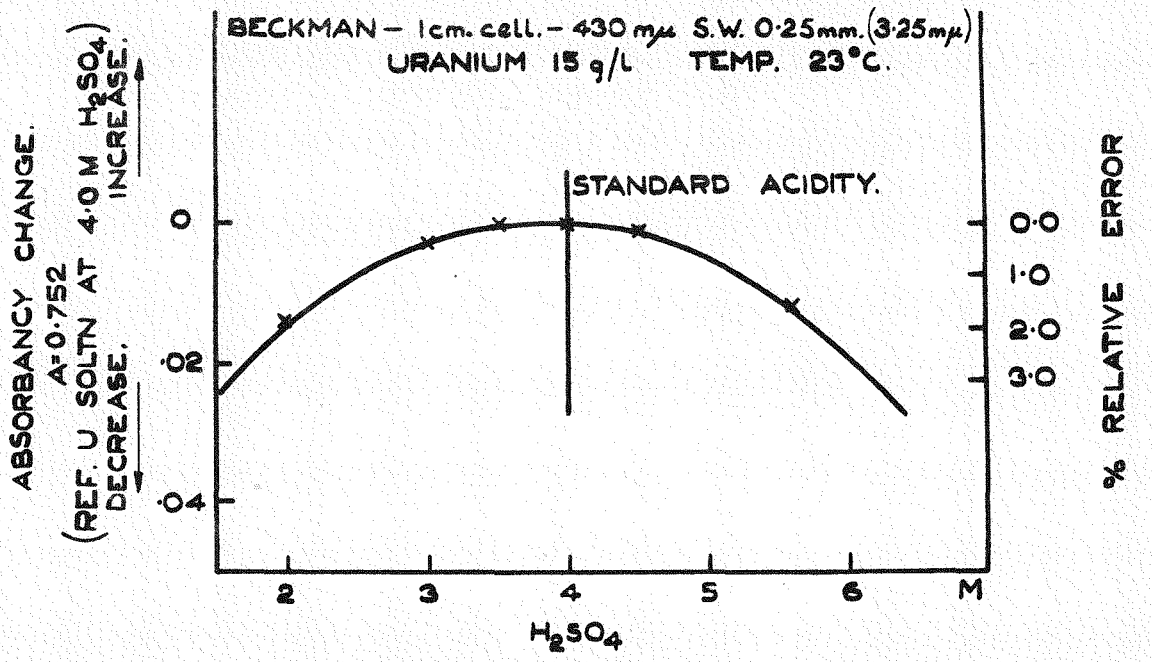
A.E.R.E. C/R 1637. FIG. 1. URANIUM CONCENTRATION RANGE FOR MAXIMUM ACCURACY.



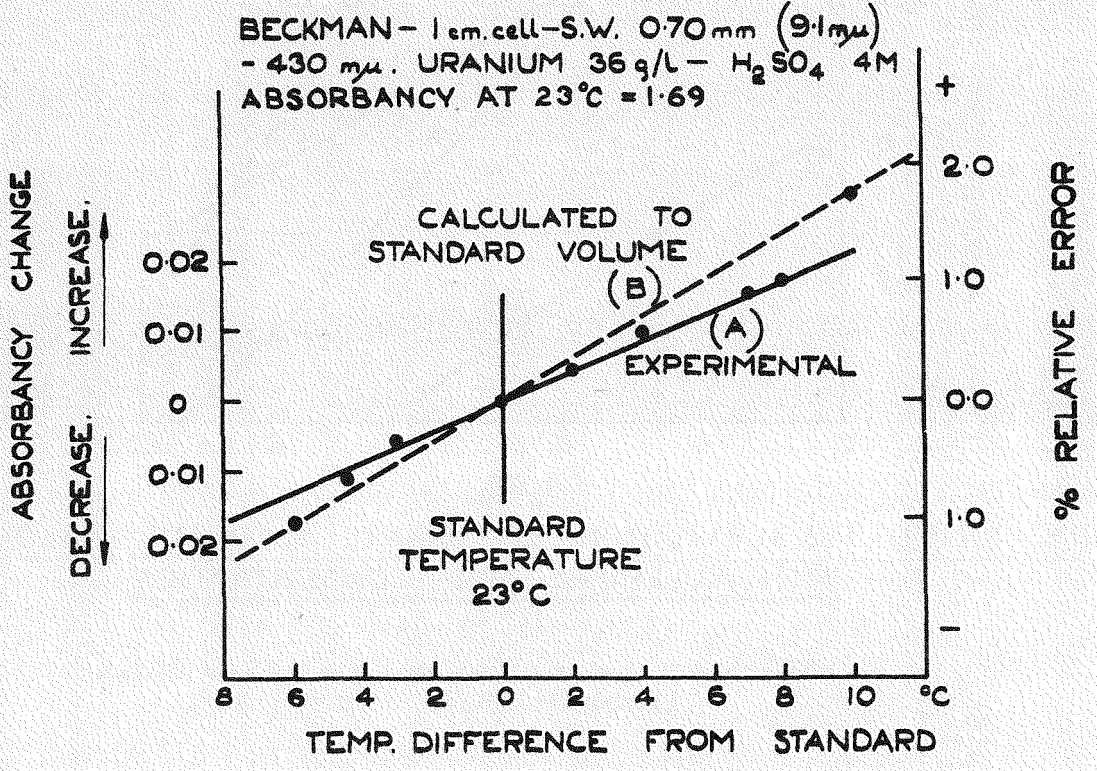
A.E.R.E. C/R1637. FIG. 2. ABSORPTION SPECTRA FOR URANYL SULPHATE.



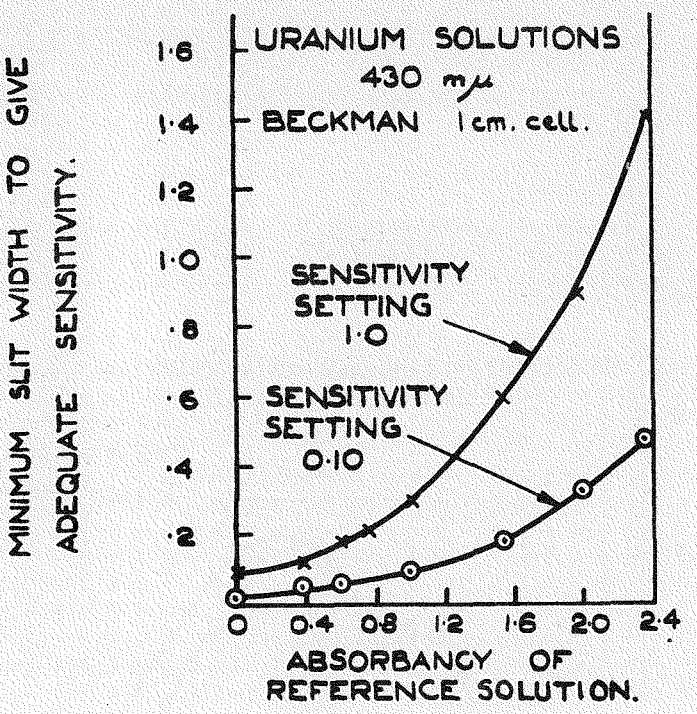
A.E.R.E. C/R 1637. FIG. 3. VARIATION OF URANYL SULPHATE ABSORBANCY WITH SULPHURIC ACID CONCENTRATION.



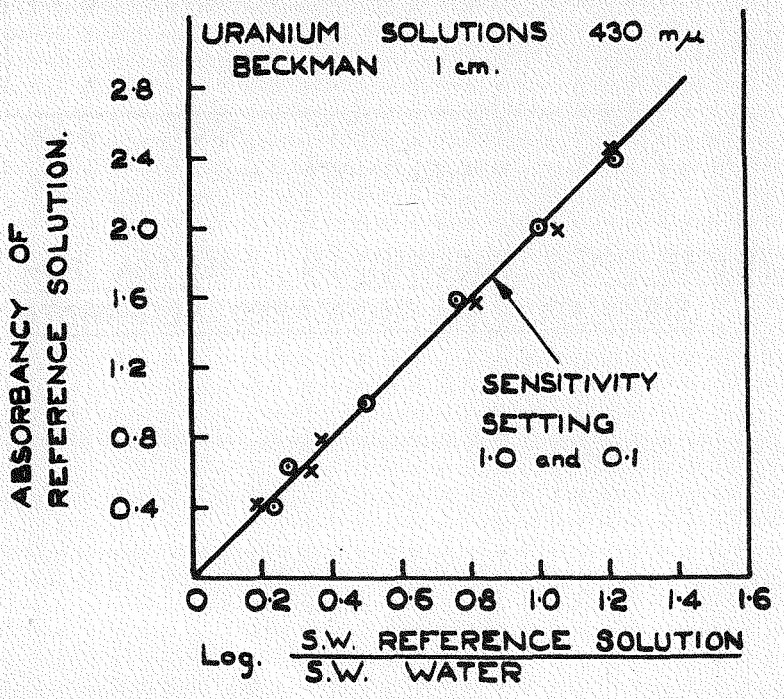
A.E.R.E. C/R 1637. FIG. 4. RELATIVE ERROR FOR DEVIATIONS FROM STANDARD ACIDITY.



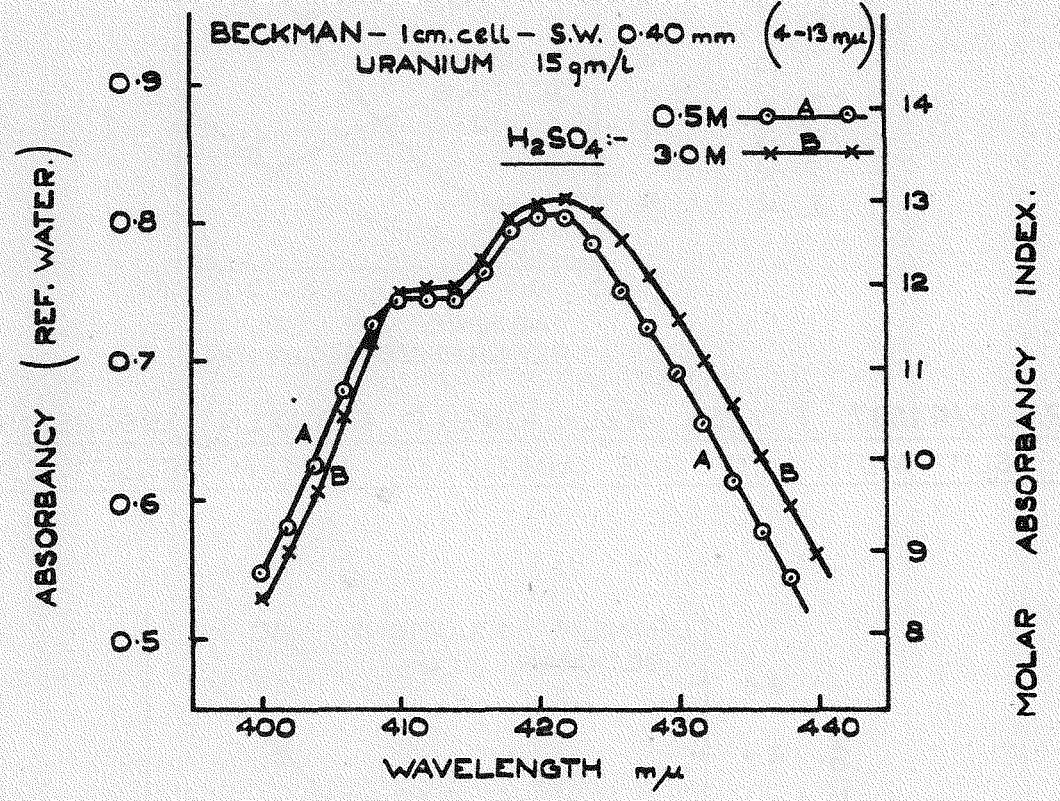
A.E.R.E. C/R 1637. FIG. 5. RELATIVE ERROR FOR DEVIATIONS FROM STANDARD TEMPERATURE.



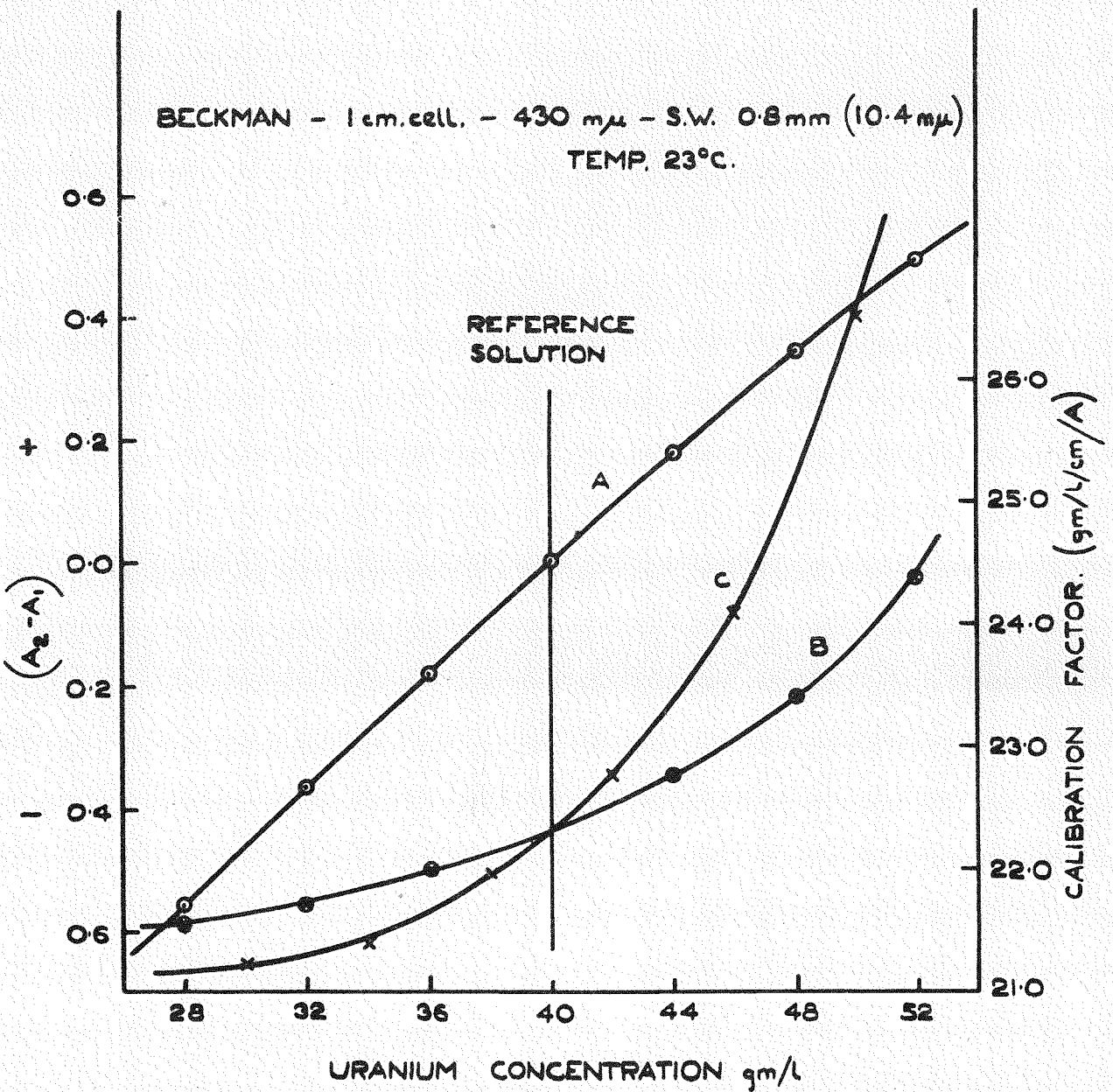
A.E.R.E. C/R1637. FIG. 6A. RELATIONSHIP BETWEEN ABSORBANCY AND SLIT-WIDTH TO GIVE ADEQUATE METER SENSITIVITY.



A.E.R.E. C/R1637. FIG. 6B. RELATIONSHIP BETWEEN ABSORBANCY AND SLIT-WIDTH TO GIVE ADEQUATE METER SENSITIVITY.



A.E.R.E. C/R 1637. FIG. 7. ABSORPTION SPECTRA FOR URANYL SULPHATE AT INCREASED SLIT–WIDTH.



A.E.R.E. C/R 1637. FIG. 8. CALIBRATION GRAPH FOR URANIUM.

(LARGE RANGE.)