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DIRECT DETERMINATION OF URANIUM IN CONCENTRATES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

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First Issued Sydney, December, 1959

Re–issued Sydney, September, 1960

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DIRECT DETERMINATION OF URANIUM IN CONCENTRATES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

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Abstract

A direct method is presented for the determination of uranium in uranium concentrates by spectrophotometric titration with ferric sulphate, after a bismuth amalgam reduction. The oxidation of U (IV) by Fe (III) was found to be rapid and complete at room temperature, under suitable conditions. Copper, molybdenum and vanadium interfere to some extent, and their maximum permissible concentrations are discussed. A complete determination may be carried out in little over an hour with a precision of two to three parts per thousand. A "Uvispek" spectrophotometer was adapted for spectrophotometric titrations without modification of the instrument.

CONTENTS

FIGURES

1. INTRODUCTION

Methods most widely used at present for the determination of large amounts of uranium involve reduction of uranium to the +4 state with metallic reductors such as lead, zinc or cadmium, followed by titration with ceric sulphate, potassium dichromate or sodium vanadate, (Steele and Taverner, 1958). However, these methods may not be directly applied to uranium concentrates since several elements, particularly iron, interfere seriously. For this reason a preliminary separation of uranium is usually carried out. The determination may be made much more selective by the use of a milder agent, such as bismuth metal or amalgam for reduction of uranium, and a milder oxidant, such as ferric sulphate, for titration of the reduced solution. Under these conditions the only common interfering elements are those which induce the atmospheric oxidation of uranium (IV), (Hallem and Smith, 1956). This may be controlled to some extent by carrying out the reduction and titration under nitrogen.

The titration of uranium (IV) with iron (III) is usually carried out at 90°C, and the end point detected potentiometrically (Shipley, 1949; Sewalk and Goward, 1958). Titration at this high temperature is inconvenient, and the danger of atmospheric oxidation is greatly increased. It is shown in this paper that high temperatures are necessary only for the rapid establishment of equilibrium potentials at the indicator electrode, since in dilute sulphuric acid solution at room temperature the oxidation of uranous ions by ferric ions is very rapid. This reaction has previously been investigated spectrophotometrically, (Rodden, 1950; Bricker and Sweetster, 1953) and amperometrically at the dropping mercury electrode (Rodden, 1950).

A procedure for the determination of uranium in concentrates is described in this paper. Reduction is carried out under nitrogen with bismuth amalgam, and the reduced solution is titrated spectrophotometrically with ferric sulphate in a nitrogen atmosphere. Copper, molybdenum and vanadium interfere to some extent, but are not usually present in Australian uranium concentrates in sufficient amounts to cause serious error. A complete determination may be made in about 70 minutes, with a precision of 2 to 3 parts per thousand.

2. APPARATUS

2.1 Spectrophotometer

A Hilger 'Uvispek' was used without modification. A carriage for the titration cell was constructed from perspex, and shaped to fit in the position of the normal cell carriage, (Fig. 4). A raised cover for the cell compartment was also made of perspex. Three holes were drilled in the cover; two for nitrogen tubes, and one for the burette tip. Both the cover and the cell carriage were painted matt black.

2.2 Titration Cell

This is shown in Fig. 1. The T–shaped titration cell had two flat, circular windows cemented to the body of the vessel, and a light path of about 3 cm. The nitrogen inlet and outlet connecting tubes were of Nylex, painted matt black, and closed at the ends by stopcocks. Nitrogen was used both to stir the solution and to exclude oxygen. The burette port of the titration cell was closed by a small serum cap.

2.3 Reduction Vessel

This vessel, shown in Fig. 2, is a modification of that described by Scribner and Reilley (1958). By diluting the sample solution to volume before reduction, and taking an aliquot of the reduced solution, the greatest difficulty in the use of liquid amalgams, viz., quantitative separation of the two phases, is obviated.

2.4 Burette

An A–grade 5 ml. burette, graduated in 0.01 ml. divisions was used. A short piece of heavy-walled rubber tubing was fitted to the tip to act as a light seal. The burette is positioned so that its tip is just immersed in the solution in the titration cell.

2.5 Cathode Ray Polarograph

A linear–sweep cathode ray polarograph from Southern Instruments Computer Division, England, was used for the oxidation–rate studies.

2.6 Nitrogen

Commercial nitrogen containing less than 5 v.p.m. of oxygen was used without further purification.

3. THE URANOUS–FERRIC REACTION

There is some confusion in the literature regarding the rate of oxidation of uranous ion by ferric ion. Shipley (1949), Lingane (1953) and Carson (1953) have reported the reaction,

$$U(IV) + 2\,Fe(III) \rightarrow U(VI) + 2\,Fe(II)$$

to be very slow at room temperature. Others, Rodden (1950), have suggested that the reaction is rapid if carried out in a suitable medium.

In order to determine the optimum conditions for the titration of uranium (IV) with iron (III) at room temperature, the reaction was studied in sulphuric, hydrochloric and perchloric acid solutions, using spectrophotometry and cathode ray polarography. The uranium (IV) concentration may be followed on a spectrophotometer by utilizing the sharp absorption peak of U(IV) at 650.0 mμ, and both the uranium (VI), and iron (III) concentrations at any instant may be determined by cathode ray polarography. These two separate techniques showed that

(a) In sulphuric acid solutions less than 1N acid, the reaction at 20°C is rapid, equilibrium being established in less than 10 secs. even when the titration is 80% complete. The rate decreases with increasing acid concentration, but the titration is still practicable up to 5N H_2SO_4.

(b) In perchloric acid solutions the reaction is slower than in sulphuric acid, and the rate decreases with increasing acid concentration.

(c) In hydrochloric acid solutions at room temperature the oxidation of uranous ion by ferric ion is extremely slow, even at low acid concentrations. This is probably due to the formation of an iron (III) chloro complex, which lowers the standard potential of the Fe^{+2}/Fe^{+3} system.

These results show that dilute sulphuric acid is the most suitable medium for the proposed titration. The end point may be detected spectrophotometrically or amperometrically at the dropping mercury electrode.

The titration may also be carried out at room temperature in 0.5N H_2SO_4 using amperometry with two polarized platinum electrodes ('dead–stop' end point), and an applied potential of 10mV. The titration is rather slow before the end point, but the first trace of excess ferric ion causes an immediate steady galvanometer reading. Oxygen should be excluded during the titration by bubbling nitrogen. Detection of the end point is not as precise as by spectrophotometric titration.

The following potentiometric indicator systems did not give a satisfactory end point at room temperature in 0.5N H_2SO_4 : S.C.E. – Pt, S.C.E. – Hg, W – Pt and Pt – Pt (polarised 1.5 μ a). The failure of these potentiometric systems to detect the end point is apparently due to sluggishness in the setting up of an equilibrium potential at the indicator electrode.

4. SPECTROPHOTOMETRIC DETECTION OF END POINT

The spectrophotometric titration of uranium (IV) with ferric ammonium sulphate may be followed either by utilizing the sharp absorption peak of U(IV) at 650m μ (Rodden, 1950,) or the Fe(III) wave at 350m μ (Bricker and Sweetser, 1953.) Uranium (IV) in sulphuric acid solution obeys Beers' Law over the concentration range studied, and has a molar absorptivity of 42 at 650 m μ . This is a convenient sensitivity for the conditions of the determination, and, moreover, the molar absorptivity remains constant over a sulphuric acid concentration range of at least 1–7 N. It is also advantageous to work in the visible region if the spectrophotometer is to be used for other routine estimations. Uranyl, ferrous and ferric ions in sulphuric acid solution have molar absorptivities of less than one at 650 m μ .

In order to minimise oxidation of uranium during the titration, a relatively high acidity, 3.5N, was used. At this concentration of sulphuric acid the reaction is rather slow in the vicinity of the end point, and readings are not taken in this region. A typical titration plot is shown in Fig. 3. A titration may be carried out in 15 minutes.

5. REDUCTION OF URANIUM WITH BISMUTH AMALGAM

The reduction of uranyl ion by bismuth amalgam may be represented by:

$$3\,UO_2{}^{+2} + 2\,Bi + 8H^+ = 3\,U^{+4} + 2\,BiO^+ + 4H_2O$$

Conditions for the reduction are therefore favoured by high acid concentrations (Paley, 1956; Issa and El Sherif, 1956). A shaking time of over an hour is required for complete reduction in 3N H_2SO_4, 20 minutes in 5N H_2SO_4 and 5 minutes in 7N H_2SO_4. Reduction proceeds only to the +4 state in 7N sulphuric acid. Very little reaction occurs in perchloric acid solutions of any concentration.

If large amounts of oxidizing agents are present in the sample solution, they should be removed by a preliminary reduction with hydroxylamine sulphate.

6. EXPERIMENTAL

6.1 Preparation of Reagents.

Bismuth amalgam. Add 20g. of reagent grade granular bismuth metal to 900g. of pure mercury. Cover the mixture with 1N sulphuric acid and warm and stir until dissolved.. Cool to room temperature, then wash the amalgam well with water. Transfer to a separatory funnel, and allow the liquid portion of the amalgam to drain into a second funnel containing 1N sulphuric acid. Store the amalgam in this funnel and run off as needed.

0.1N Ferric Ammonium Sulphate. Dissolve 12g. of reagent–grade material in 3.5N sulphuric acid. Dilute to 250 ml. with 3.5N H_2SO_4. Standardize against pure dry U_3O_8 , using the procedure outlined.

6.2 Recommended Procedure for the Determination of Uranium in Uranium Concentrates

Weigh a dried sample of the concentrate containing 50–100 mg. U_3O_8 into a small flask. Dissolve by heating with 10 ml. of 2.5N $HClO_4$. Evaporate to fumes of $HClO_4$ to dehydrate silica and continue heating until the silica is colourless. Dilute with water, filter, and wash with hot 0.1N H_2SO_4. Add 5 ml. of conc. H_2SO_4 to the filtrate, cool, and dilute to 25 ml. in a volumetric flask.

Transfer about 15 ml. of the solution to the dry reductor tube. Insert head of vessel and connect nitrogen source. Open cock A and pass nitrogen at a moderate rate for 1 minute. Close cock A and simultaneously remove stopper from amalgam port. Add 2 ml. bismuth amalgam with nitrogen still flowing. Replace stopper and open cock A. Close cocks A and B simultaneously. Remove the nitrogen tube, and clamp the reductor in the arm of a wrist–action shaker. Shake vigorously for 5–10 minutes. Pipette 5 ml. of water into the titration cell and fit the serum cap. Place the cell in position in the spectrophotometer and pass nitrogen at a convenient rate. Set the wave length drum at 650 $m\mu$.

Remove the head of the reduction vessel and, with a dry pipette, immediately transfer a 5 ml. aliquot of the reduced uranium solution into the titration cell, through the serum cap. Insert the 5 ml. burette containing 0.1N ferric ammonium sulphate. Zero the instrument and set the absorbance scale reading at a convenient value, say 1.000. Close the nitrogen inlet and outlet taps, and with the selector switch on "measure", open the slit and adjust the "check" position to balance. Close the slit and pass nitrogen. Add the first increment of the titrant. Interrupt nitrogen flow, open slit and measure absorbance. Close slit, start nitrogen and add second increment of titrant. Repeat this procedure until a full titration curve is obtained. Correct each absorbance reading for the dilution effect and plot corrected absorbance versus titre.

7. STUDY OF INTERFERENCES

Using the procedure described above, the following elements, when present in equal concentration to uranium (wt.%), did not interfere in the spectrophotometric titration:

Ce, Co, Cr, Fe, Ni, P, Sb, Sn, Ti and W.

Copper, molybdenum and vanadium interfered to varying degrees, and were studied in more detail.

Copper. Copper is notorious for its ability to induce the air–oxidation of uranium (IV) (Halpern and Smith, 1956). Slightly low results were obtained in the spectrophotometric titration even when extreme measures were taken to exclude oxygen from the titration cell. The error is approximately proportional to the copper concentration. The maximum permissible copper content, for an error of less than 2 parts per thousand, is 3% of the uranium concentration. Since uranium concentrates processed in this country usually contain less than 0.2% copper, this limit is not likely to be exceeded.

Molybdenum. In the presence of oxygen, molybdenum causes low results in the titration of uranium with ferric sulphate. If oxygen is excluded, however, slightly high results are obtained. This is possibly due to the formation of traces of molybdenum (III) in the bismuth reductor. Molybdenum may be tolerated up to 2% of the uranium concentration.

Vanadium. Vanadium, like copper and molybdenum, induces the air–oxidation of uranium (IV). Vanadium is reduced only to the +4 state by bismuth amalgam in 7N sulphuric acid. The maximum permissible vanadium content is 5% of the uranium concentration.

The presence of large amounts of ferrous iron, while not affecting the final result, causes the spectrophotometric titration in 3.5N H_2SO_4 to be inconveniently slow. When analysing ores, where the iron content usually exceeds the uranium content, the sulphuric acid should not be more than 0.5N during the titration.

8. ANALYSIS OF CONCENTRATES AND HIGH–GRADE ORES

Table 1 shows the results obtained by the direct spectrophotometric titration on five standard uranium concentrates, and two standard high–grade ores. The concentrates were analysed by an independent laboratory using the classical method consisting of a cellulose column separation of uranium from nitric acid–ether solution, followed by precipitation with ammonia and ignition to U_3O_8. The uranium content of the ores was determined by cathode ray polarography after a mercury cathode separation (Florence, 1959).

TABLE 1

DETERMINATION OF URANIUM IN CONCENTRATES AND ORES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

Sample No.	Direct Spectrophotometric Titration % U_3O_8	Number of Determinations	Relative Standard Deviation (n–1) %	Reference Method % U_3O_8
C1	64.8	6	0.35	64.55
C2	63.1	6	0.19	63.35
C3	71.9	6	0.20	72.00
C4	23.90	4	0.33	23.90
C5	24.48	4	0.28	24.55
ore 1	8.33	3	0.54	8.3
ore 2	7.52	3	0.67	7.6

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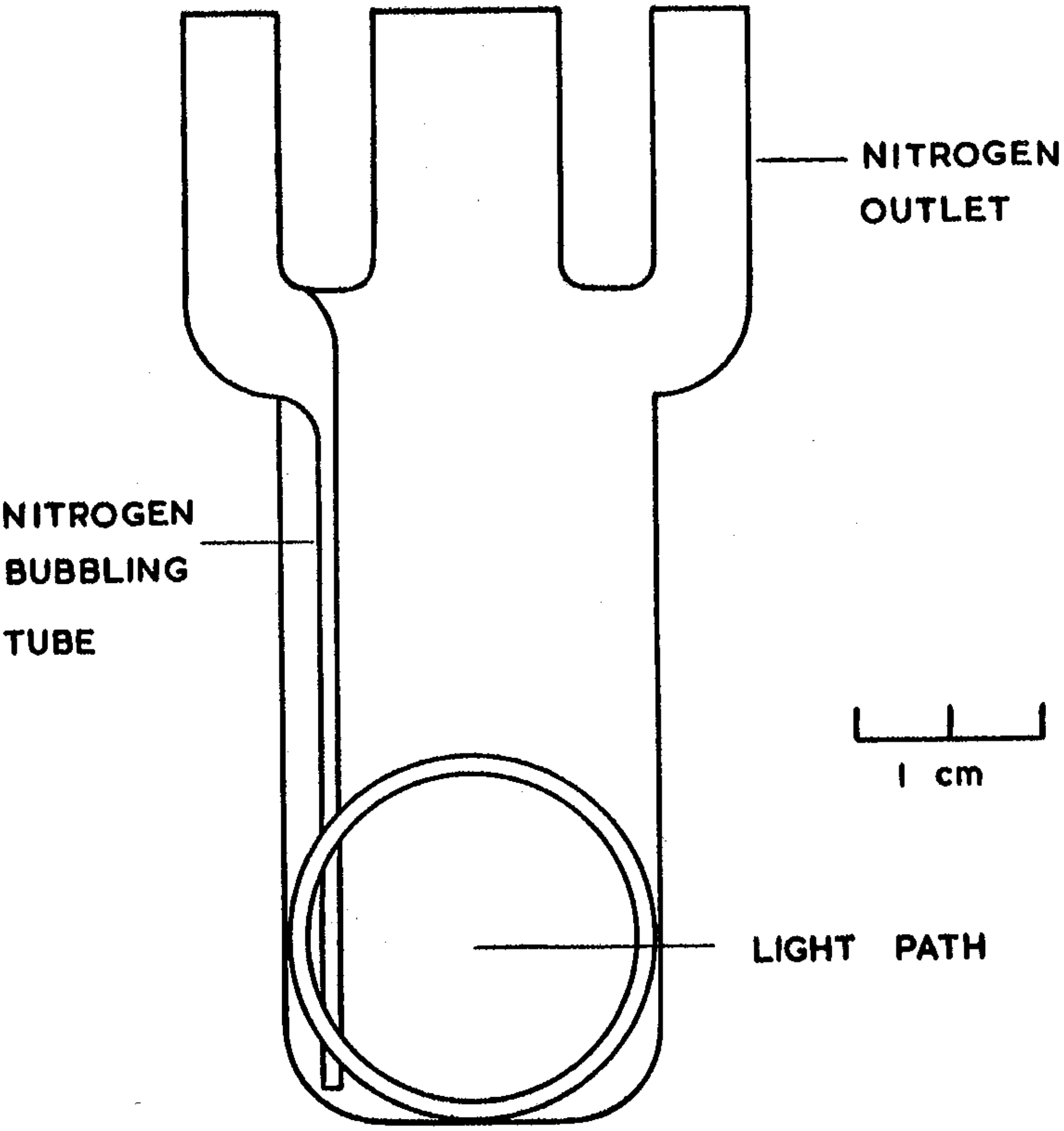

FIG.1 TITRATION CELL

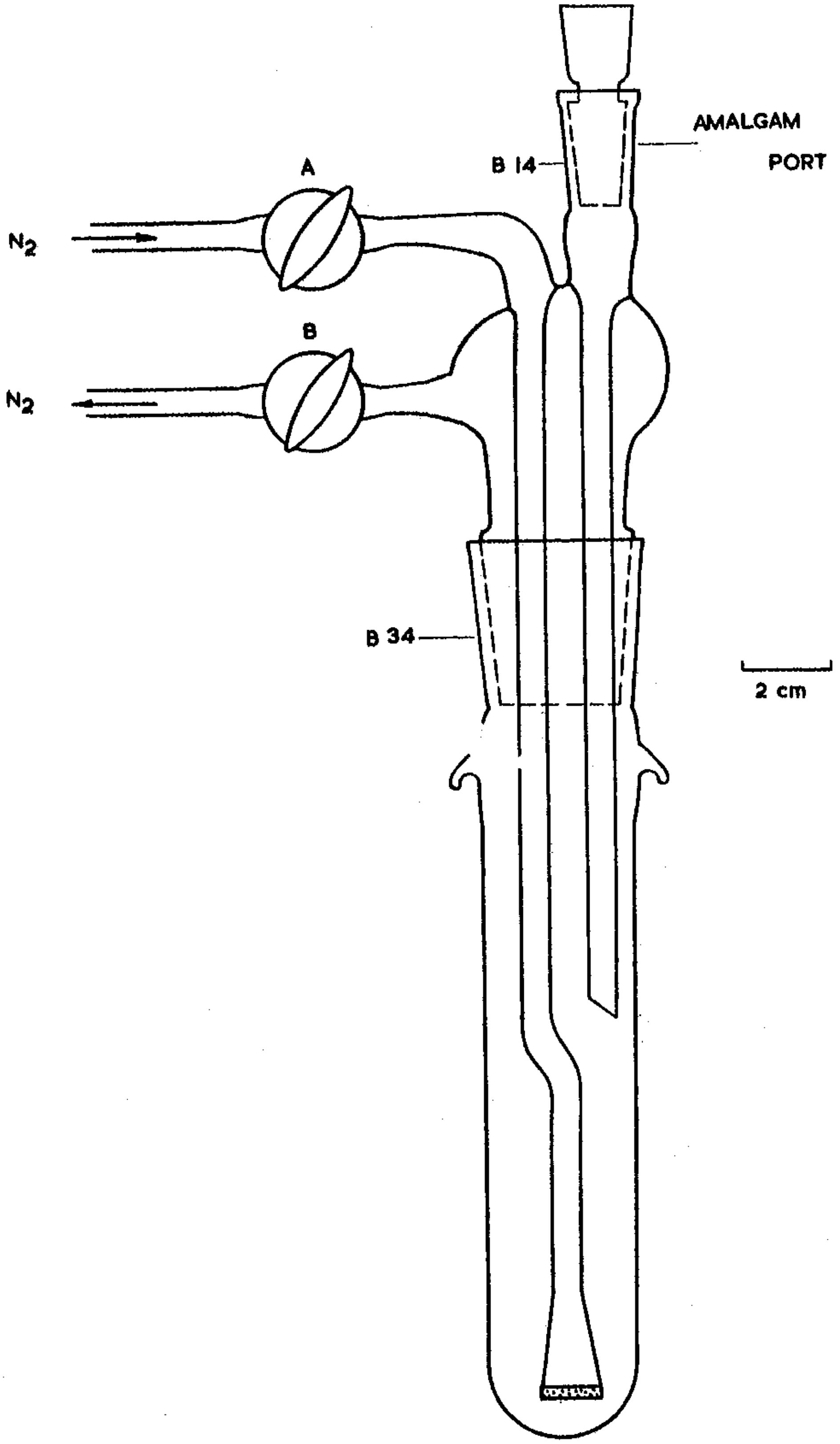

FIG 2 REDUCTION VESSEL

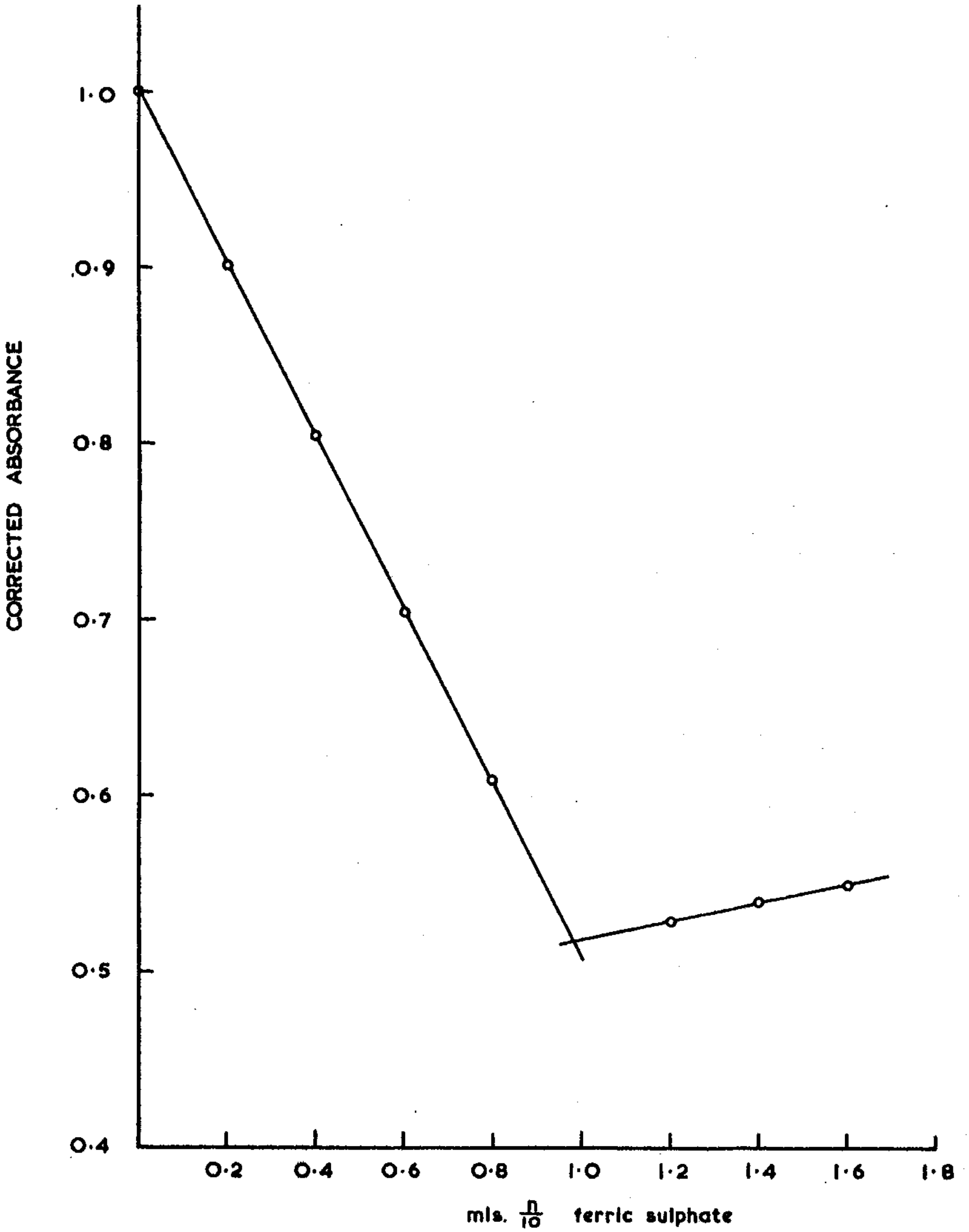

FIG 3 SPECTROPHOTOMETRIC TITRATION OF URANIUM (IV) WITH FERRIC SULPHATE

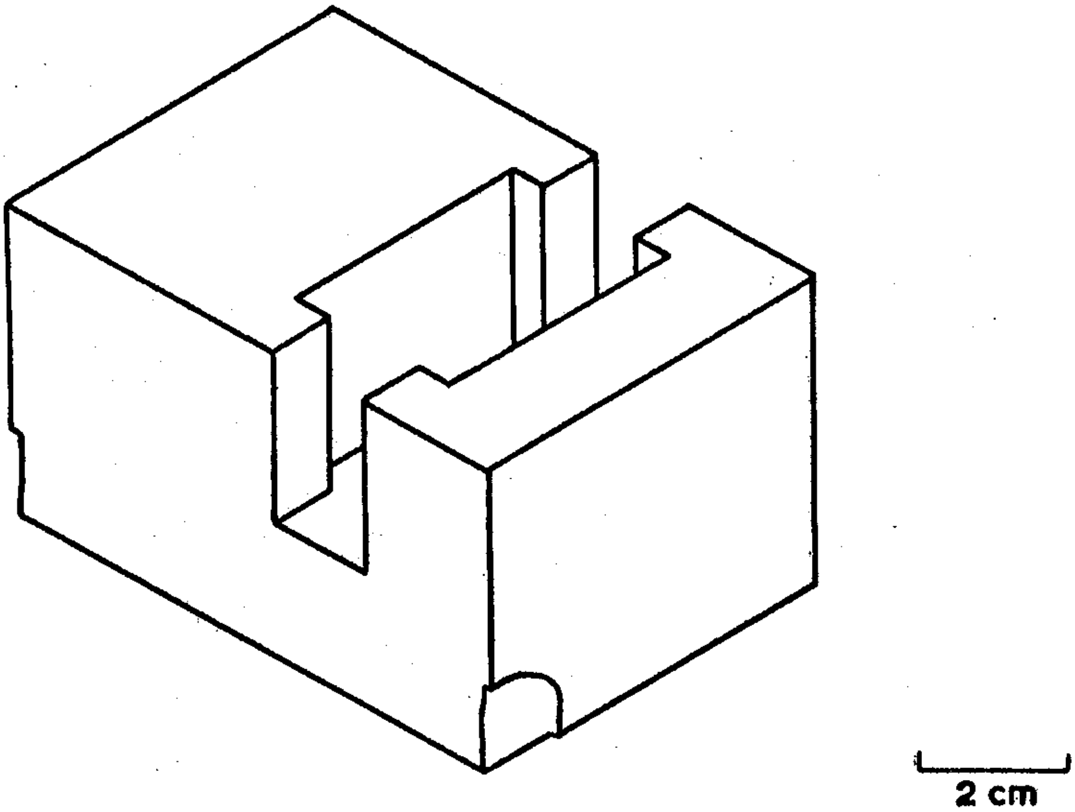

FIG 4 CELL CARRIAGE