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DETERMINATION OF URANIUM IN ORES
MODIFIED MERCURY CATHODE - CUPFERRON METHOD

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by
Weigh a sample of 0.5 to 5.0 grams, depending
upon the uranium content, into a 400 ml beaker. Add
10 ml 1:1 HNO₃ and heat to boiling. Add 13 ml 1:1 H₂SO₄.
If ore contains much silica add a little HF. Fuse for 5
minutes. Cool, add 5 ml 40% HBr + 5 ml concentrate HCl +

ml hydrazine sulphate, warm carefully till most of the
bromine has been removed. Cool, wash
down side

any traces of bromine. Cool by add 50 ml water and let stand
till PbSO₄ and SiO₂ settle and wash with cold
1% H₂SO₄.

DETERMINATION OF URANIUM IN ORES
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F.T. Rabbitts

Radioactivity Division

Separation of U from Certain Interfering Elements by
Mercury Cathode

to methyl orange. Add 4.0 ml 1:1 H₂SO₄ and dilute to
100 ml. Electrolyse in modified Melaven mercury cathode
cell for 30 minutes at 7 amperes and 7 volts (Note 1).
Test for complete removal of Cu, Ni, Co, Fe, & c. (Note 2).
With current still flowing, remove solution from

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DETERMINATION OF URANIUM IN ORES

MODIFIED MERCURY CATHODE - CUPFERRON METHOD

by

F.T. Rabbitts

Solution of Sample and Elimination of Arsenic,

Silica and Lead:

Weigh a sample of 0.5 to 5.0 grams, depending upon the uranium content, into a 400 ml beaker. Add 10 ml 1:1 HNO₃ and heat to boiling. Add 12 ml 1:1 H₂SO₄. If ore contains much silica add a little HF. Fume for 5 minutes. Cool, add 5 ml 48% HBr+5 ml concentrate HCl+5 ml hydriaric sulphate, warm carefully till most of the bromine has been driven off and again fume. Cool, wash down sides of the beaker and fume again to eliminate any traces of bromine. Cool, add 50 ml water and let stand till PbSO₄ and SiO₂ settle. Filter and wash with cold 1% H₂SO₄.

Separation of U from Certain Interfering Elements by

Mercury Cathode:

Add 1:1 NH₄OH to filtrate till just alkaline to methyl orange. Add 4.0 ml 1:1 H₂SO₄ and dilute to 100 ml. Electrolyse in modified Melaven mercury cathode cell for 30 minutes at 7 amperes and 7 volts (Note 1). Test for complete removal of Cu, Ni, Co, Fe, & c.(Note 2).

With current still flowing, remove solution from cell and wash mercury with 50 ml 1% H₂SO₄. Combine

solution and washings and filter if necessary using paper pulp and washing with 1% H₂SO₄. Add 16 ml 1:1 H₂SO₄ and evaporate to 100 ml.

By this procedure the following elements, if present, are quantitatively removed:

Fe, Co, Ni, Cu, Zn, Ga, Ge, Rh, Pd, Ag, Cd, In, Sn, Ir, Pt, Au, Hg, Tl, Cr, Mo, Re, Po, Bi, As, Se, Te, Pb, and Os.

Elements partially removed are: Mn, Ru and Sb.

Separation of Sexivalent U from Cb, Ta, W, Th, Ce, Ti, V and Zr by Cupferron:

Heat solution nearly to boiling and add 3% KMnO₄ dropwise till slightly pink. Cool to 5 degrees Centigrade or lower. Transfer to a 600 ml pear-shaped separatory funnel and add 15 ml cold 6% cupferron solution, till a white precipitate appears which redissolves quickly. Extract with 15-20 ml portions of chloroform till aqueous layer is water-white. Add another 5 ml 6% cupferron. Precipitate formed should be white. If not, add additional cupferron solution. Extract with chloroform again till water-white.

Transfer aqueous layer to a 600 ml beaker, add 10 ml conc. HNO₃ and warm gently till all CHCl₃ is

driven off. Then fume. Cool, wash down the sides of the beaker and again fume. Repeat. Add 2 ml 60% HClO_4 and fume strongly. Wash down the side of the beaker and fume again. Nitrates should now be absent. Adjust to 2 ml H_2SO_4 , cool and dilute to 50 ml. To ensure absence of nitrates, add a few drops of 1% KMnO_4 till solution is pink.

Reduction of Sexivalent U to Quadrivalent U by Jones

Reductor and Determination by Standard Potassium Dichromate:

Pass the 4% H_2SO_4 solution through the Jones Reductor at a moderate rate and wash reductor first with 90 ml 5% H_2SO_4 and then with 90 ml distilled water, collecting solution and washing in a 600 ml beaker. Aerate for 10 minutes using an 8" length of one-quarter inch glass tubing drawn to a fine opening (Note 3).

Wash tube, watch-glass and sides of the beaker with water. Add 25 ml 5% ferric chloride freshly made from the lump reagent (note 4), 15 ml $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$ mixture (73 ml $\text{H}_3\text{PO}_4\text{+}27\text{ml H}_2\text{SO}_4$) and 8 drops 0.01 M sodium diphenylamine sulphonate. Titrate with standard potassium dichromate using .02N for low-grade and .05N for high-grade ores till one drop changes the colour from green to deep violet. Run a blank and deduct this value from the titration found.

The dichromate solution is made by weighing the theoretical amount of the volumetric standard grade and dissolving in cold water. This has been checked against a standard sample containing 99.93% U_3O_8 (U. S. Bureau of Standards Sample MS-ST).

$$1 \text{ ml } .05N \text{ } K_2Cr_2O_7 = .007018 \text{ gram } U_3O_8$$

The reactions involved are:

1. $UO_2^{++} + H_2SO_4 + Zn = UO^{++} + ZnSO_4 + H_2O$
2. $UO^{++} + 2Fe^{+++} + H_2O \longrightarrow UO_2^{++} + 2Fe^{++} + 2H^+$
3. $Cr_2O_7^{=} + 14H^+ + 6Fe^{++} \longleftarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$
(Titration)

It has been found that the blank increases as the volume of dichromate is increased. To allow for this, a series of standard uranium sulphate solutions are titrated with potassium dichromate and the actual titration value is plotted against the number of milligrams of U_3O_8 present. A straight line is obtained and is used for determining the U_3O_8 content of unknown samples. Thus, no blank correction needs to be applied to the titration value.

Note 1 - The Modified Melaven Mercury Cathode

See appendix of this report.

Note 2 - Test for absence of Cu, Ni, Co and Fe

(1) Place 1 drop of the acid test solution, 1 drop of 1% zinc acetate and 1 drop of ammonium mercury thiocyanate (8 grams mercuric chloride + 9 grams ammonium thiocyanate + 100 ml water) in a depression on a white porcelain spot-plate. Mix with a stirring rod. If no colour results then Cu, Ni, Co and Fe have been completely removed from the solution. The precipitate of zinc mercury thiocyanate is coloured violet by copper, gray-green by nickel, blue by cobalt and reddish-brown by iron.

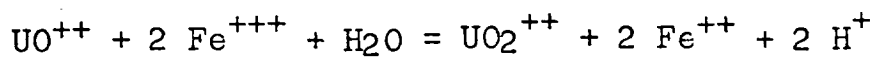
or (2) Test with potassium ferricyanide.

Note 3 - Effect of Aeration

The reductor converts the sexivalent uranium to a mixture of tri- and quadri-valent ions. This solution has a dark olive-green colour. Aeration converts the trivalent uranium to quadrivalent, which has a clear, light green colour.

Note 4 - Effect of Ferric Chloride

In the absence of iron the end point is not good because evidently the reaction between uranous ion and dichromate ion is relatively slow. Ferric ion, however, reacts very quickly with uranous ion:



and thus catalyses the reaction.

Note 5 - Cleaning the Mercury

(1) Use electrolytic method making mercury the anode. or (2) Method described in "Practical Physical Chemistry", A. Findlay, p. 197, Longman's, 7 Edit. (1941). Modify Findlay's apparatus by flanging the tube which dips into the mercurous nitrate - nitric acid cleaning solution. Tie a small piece of cloth to the flange to form a small bag to collect the dirty mercury. When full, the weight of the mercury causes it to pass through the cloth in a large number of fine droplets thus exposing the maximum surface for cleaning.

Note 6 - Application of Method

The method can be applied generally since it removes Cr, Ni, Co and other interfering elements which remain to cause difficulty after the hydrogen sulphide-cupferron method and is not interfered with by phosphate, sulphate or other anions.

REFERENCES

1. 'Electrolytic Cell for use with Mercury Cathode',
A.S. Melaven, Ind. & Eng. Chem., An. Ed., 2, 180
(1930)
2. D-H. Brophy, Ind. & Eng. Chem., An. Ed., 16, 963 (1924)
3. 'Outlines of Methods of Chemical Analysis',
Lundell & Hoffman, 94-95, 117-118, Wiley (1929).
4. 'Applied Inorganic Analysis',
Hillebrand & Lundell, 105-106, Wiley (1929).

REFERENCES (CONT'D)

5. 'Analysis of Carbon and Alloy Steels', U.S. Steel Corp., 165, 205, 208, 210, 215, 283, Reinhold (1937).
6. 'Methods of Chemical Analysis of Metals', 40-41, A.S.T.M., (1936)
7. Testbook of Quantitative Inorganic Analysis, Kolthoff & Sandell, 580, Macmillan (1936).
8. 'Mercury Cathode - Large Scale', Ind. & Eng. Chem., An. Ed., Feb. 15, 1942, p. 109.
9. 'Review of Mercury Cathode Literature', Ind. & Eng. Chem., An. Ed., April 15, 1930, p. 189.
10. C.J. Rodden, Anal. Chem. 21, 330--331 (1949)
11. 'Determination of U in Ferriferous Ores' Wallis R. Bennett, JACS 56, 277 (Feb. 1934).
12. Wells, JACS, 52, 4852 (1930).
13. Smith)
) An. Ed. Vol. 2 p. 190
14. Gibbs)
15. A Moving Mercury Cathode, Evans, Analyst, Vol. LX, p. 389.

APPENDIX

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MERCURY CATHODE CELL FOR RAPID ELECTROLYSIS

by

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By electrolysis with the mercury cathode in dilute acid solution some thirty elements may be removed quantitatively from the other elements which, because of their high decomposition potentials, are not deposited in the mercury (6). By thus removing unwanted elements, many existing procedures for determining the remaining elements may be simplified, with a consequent decrease in time and increase in accuracy of the analysis.

The procedure is well known (1, 3, 4, 5, 7, 9), but its application in the analysis of ores and metals would probably be more general if the electrolysis could be conducted more rapidly than is possible with the type of cell normally used. Some special cells have been designed for this purpose (2, 8, 10), but it is believed that the

apparatus described here is more adaptable to control and research work and requires much less time for electrolysis.

CONSTRUCTION OF CELL

The cell is made from a 700-ml. Pyrex Florence flask modified as shown in Figure 1. It contains about 4 kg. of mercury, which has a surface area of approximately 77 sq. cm. The platinum wire anode has a diameter of about 10 cm. and lies horizontally about 0.5 cm. above the mercury surface. The volume of electrolyte may be from 50 to 100 ml.

The air-inlet tube is drawn to a fine opening and dips 1 cm. below the center of the mercury surface. A slow current of air is passed through this tube, agitating the mercury and the solution above it. This method of agitation is preferable to mechanical stirring partly because it eliminates possible mechanical failures, but chiefly because it is more effective in continuously exposing a fresh mercury surface to the electrolyte. However, too violent agitation is undesirable, as fine droplets of mercury will form and remain suspended in the acid solution.

A convenient arrangement of a set of two of these cells is illustrated in Figure 2. A larger number of cells can be set up if desired.

During the electrolysis a fine mist forms in the cell and is condensed in the modified thistle tube shown. This tube is supported by a No 11 rubber stopper which fits snugly into the 5.1-cm. (2-inch) hole in the cell. The U-portion of the tube contains 5 or 6 ml. of distilled water, which readily absorbs the fine spray. A 300-ml. Erlenmeyer flask fitted with an outlet near the base is used as a leveling bottle. Electrical contact with the mercury in the leveling bottle is maintained by a 15-cm. length of platinum wire (B. and S. gage 16), which is held in place by a rubber stopper containing an air vent.

The wiring of the circuit is illustrated in Figure 3. The two cells are connected in series, but the left-hand cell can be cut out of the circuit by the snap switch on the panel above it. The switch on the right-hand side controls the main power supply. The whole assembly rests in a shallow tray, so that any mercury spilled accidentally may be recovered.

OPERATION OF CELL

Electrolysis is usually conducted in 0.3N sulfuric acid solution. The direct current supply is adjusted by a rheostat so that the amperage in each cell is not less than 6 and preferably 7 with a voltage of 5 to 6. Under these conditions most samples are electrolyzed completely in 30 to 40 minutes. After testing for the complete removal of the unwanted elements, the leveling bottle is lowered and, as soon as the mercury has drained from the cell, the electrolyzed solution is run into a 400-ml. beaker. The thistle tube and cell are rinsed with water and the rinsings are added to the beaker. If the solution contains some fine, blackish suspension (arsenic, manganese, etc.), filter pulp is added and the mixture is filtered on a No. 30 Whatman paper. Meanwhile, about 30 ml. of 2% sulfuric acid are added to the cell, the leveling bottle is raised, and electrolysis is continued for 5 minutes. This is a precautionary measure to ensure recovery of any electrolyte entrained with the mercury in the rubber tube. This wash solution is then run off, the thistle tube and cell are rinsed with distilled water as before, and the combined washings are filtered through the original paper.

In Figure 2 the right-hand cell is in the position for electrolysis, while in the left-hand cell the electrolysed solution has been separated from the mercury and is ready to be drawn off.

If the original sample is large and contains much iron, it is desirable to add a little ammonium hydroxide to neutralize the acid formed during electrolysis. Addition of ammonium hydroxide is usually indicated if the solution is not colorless after 20 minutes' passage of the current.

ACKNOWLEDGMENT

The writer wishes to express his thanks to George Ensell for help in constructing the cell.

LITERATURE CITED

- (1) Brophy, Ind. Eng. Chem., 16, 963 (1924).
- (2) Cain, Ibid., 3, 476 (1911).
- (3) Craighead, Ind. Eng. Chem. Anal. Ed., 2, 189 (1930).
- (4) Gibbs, Am. Chem. J., 13, 571 (1891); Chem. News. 42, 291 (1880).
- (5) Hillebrand and Lundell, "Applied Inorganic Analysis," pp. 105, 106, 390, New York, John Wiley & Sons, 1929.

LITERATURE CITED (CONT'D)

- (6) Lundell and Hoffman, "Outlines of Methods of Chemical Analysis," pp. 94, 95, New York, John Wiley & Sons, 1929.
- (7) Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel," p.47, New York, John Wiley & Sons, 1931.
- (8) Melaven, Ind. Eng. Chem., Anal., Ed., 2,180 (1930).
- (9) Smith, "Electroanalysis," p. 60 Philadelphia, Blakiston Co., 1911.
- (10) Steinmetz, Ind. Eng. Chem. Anal, Ed., 14, 109 (1942).

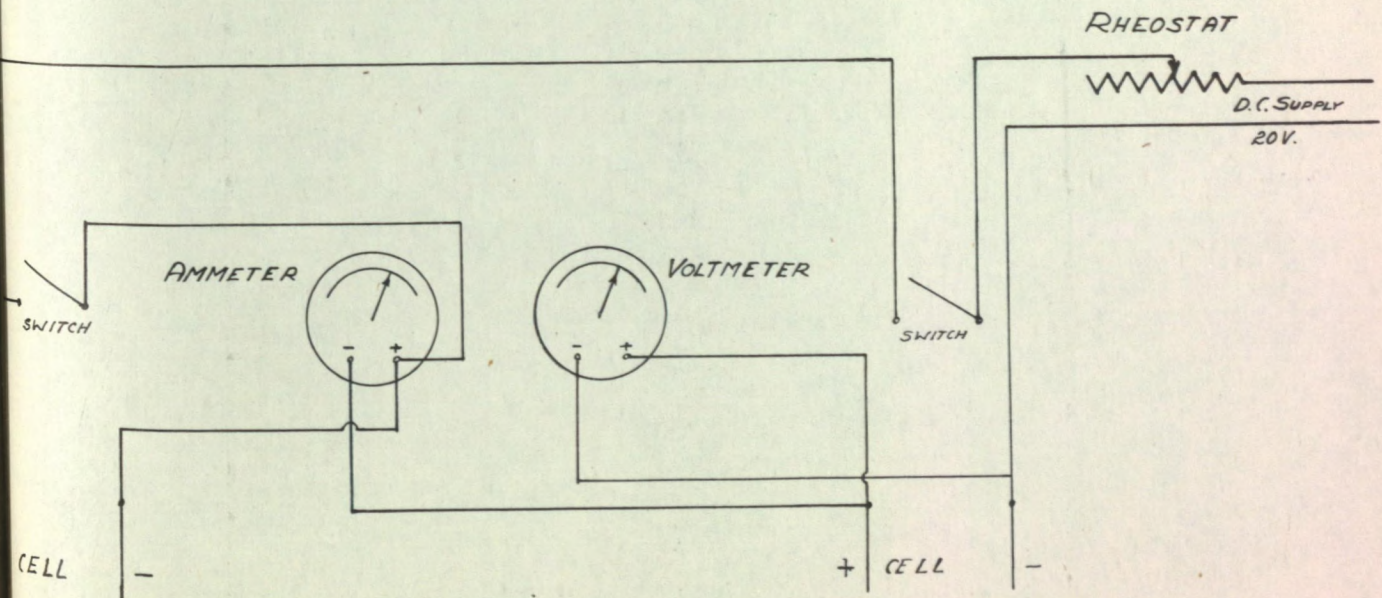
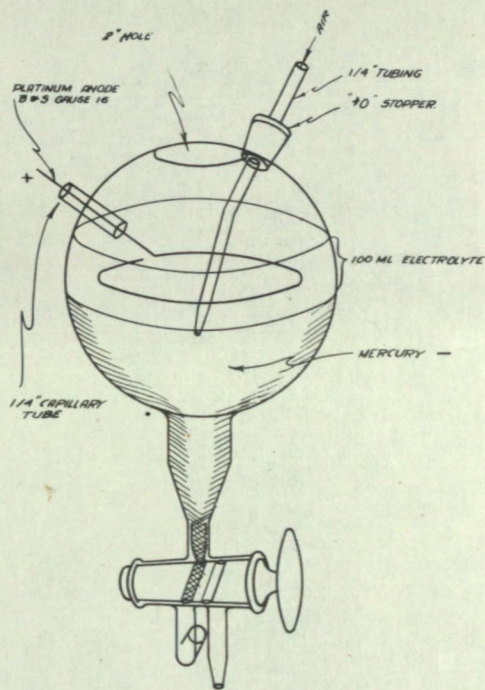
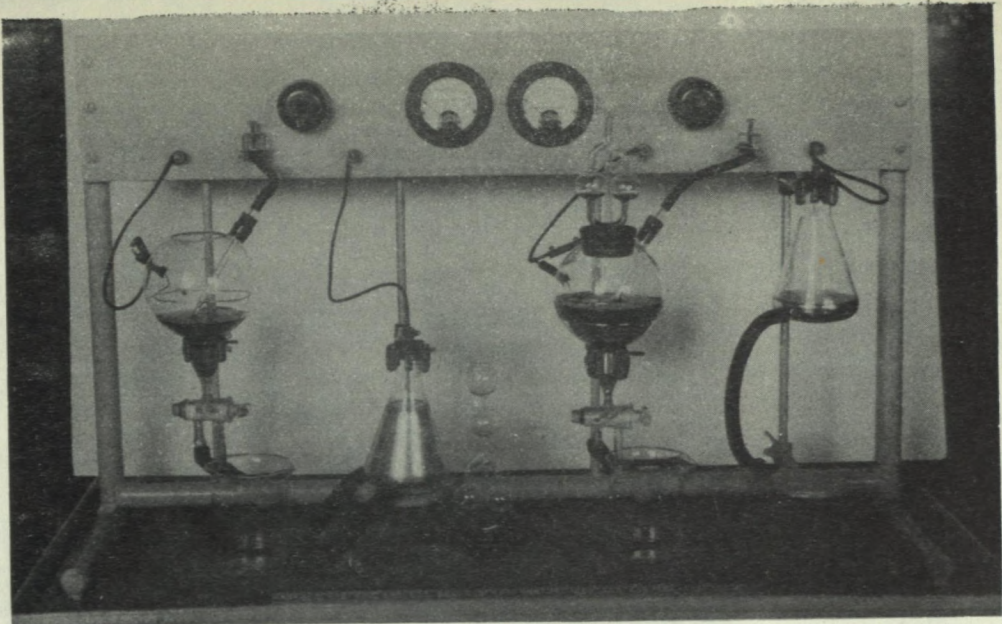


FIGURE 3. WIRING DIAGRAM