

SER
622(21)
C212ms
109

DETERMINATION OF URANIUM IN ORES

REVIEW OF CHEMICAL METHODS

Dept. Mines & Resources
BUREAU OF MINES
OCT 31 1950
LIBRARY
OTTAWA, CANADA.

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH

OTTAWA

DETERMINATION OF URANIUM IN ORES

REVIEW OF CHEMICAL METHODS

by

F.T. Rabbitts

Radioactivity Division

Memorandum Series No. 109
September, 1950.

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

DETERMINATION OF URANIUM IN ORES

REVIEW OF CHEMICAL METHODS

by

F.T. Rabbitts

INTRODUCTION

When the investigation of radioactive ores began at the Mines Branch about five years ago it was at once evident that improved chemical methods for the determination of uranium were essential. The published methods available were time-consuming and insensitive and were lacking in accuracy and precision. It was desirable to obtain methods which would be rapid, sensitive, and accurate. These should also allow for the possible presence of any interfering elements and should be adaptable to routine analysis by technicians.

Chemical methods are necessary to provide standard analysed samples for counting and to check analyses by counter methods. Moreover, counter methods cannot be used and only chemical methods are suitable when the sample is not in equilibrium as with weathered minerals and leach residues. As leaching processes are improved, more sensitive chemical methods are required for the increasingly lower content of uranium in the leached residues. When the leaching process reaches the plant stage, speed of analysis becomes more important without sacrificing accuracy.

The purpose of this report is to describe briefly the methods used at the Mines Branch for the chemical analysis of uranium in ores. These methods represent the results of investigations by a number of groups in the United Kingdom, the United States, and Canada. They

TYPICAL TEXTBOOK METHOD

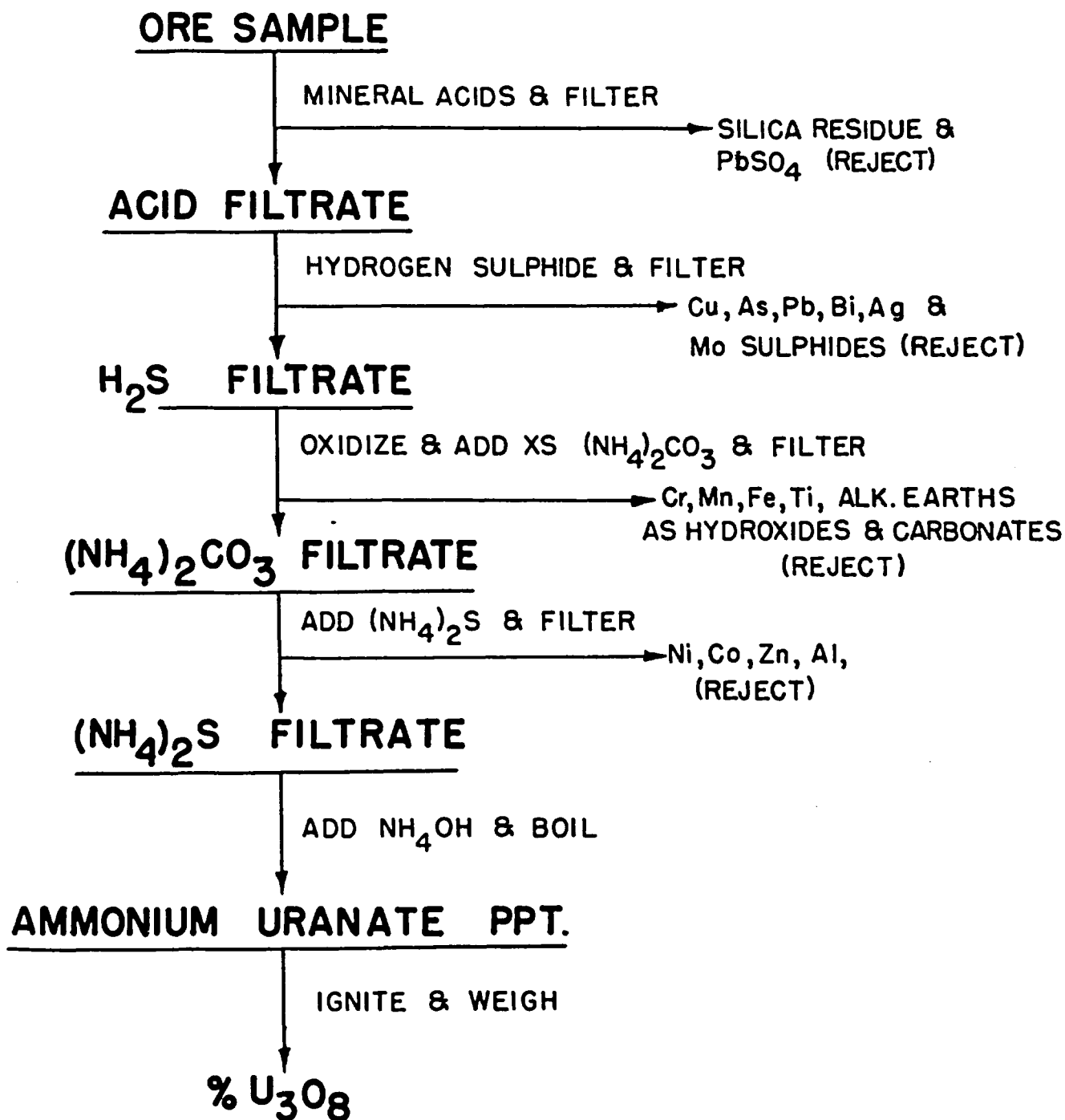


Figure 1

have been modified, where necessary, to be applicable to Canadian ores many of which are complex.

Four methods are outlined in the report. Method 1, the Typical Textbook method is of historical interest only. Method 2, the Mercury Cathode - Cupferron method, was formerly used in the Mines Branch but has now been replaced by Methods 3 and 4, the Cellulose Column and Microfluorimetric methods.

METHODS

Method 1 - Typical Textbook Method (Figure 1)

This method is very long and the accuracy and precision obtainable are poor as it is difficult to ignite ammonium diuranate to a residue of constant composition.

If vanadium is present an additional step is required in which the vanadium is separated as lead vanadate.

No special apparatus is required.

Method 2 - Mercury Cathode - Cupferron Method (Figures 2 and 3)

The detailed procedure for this method of uranium analysis has already been published in Mines Branch Memorandum Series No. 103 (Ref.1)

This is a general method for any type of uranium ore but it is time-consuming.

The accuracy and precision are good for ores containing 0.1 per cent U_3O_8 or better but colorimetric finish is not suitable because of the high concentration of salts present near the end of the analysis.

The only special equipment required is a set of mercury cathode cells. The type of cell used at the Mines Branch is illustrated in Figure 3.

2. MERCURY CATHODE - CUPFERRON METHOD (MEMORANDUM SERIES 103)

ORE SAMPLE (-150 MESH)

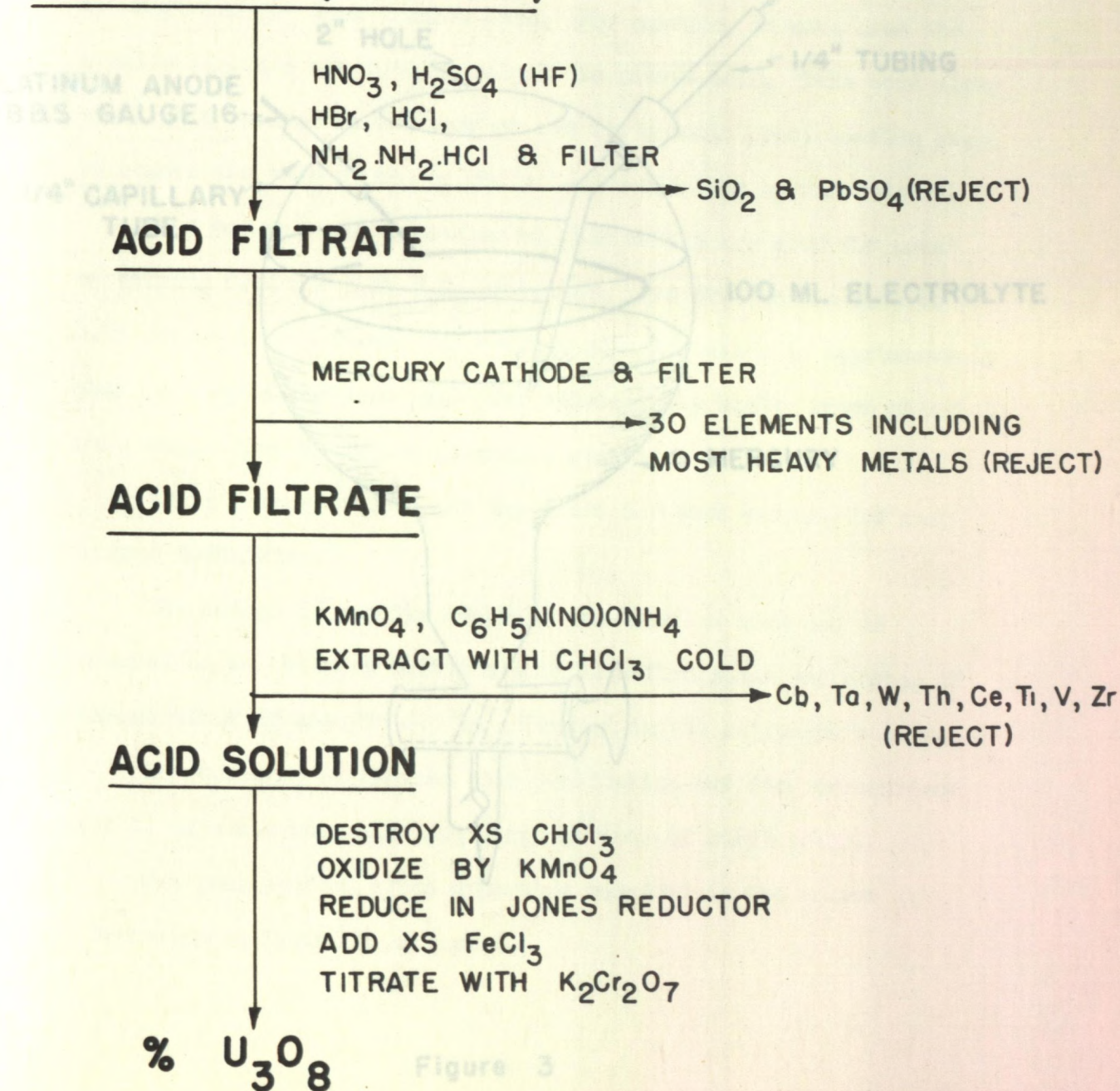


Figure 3

Figure 2

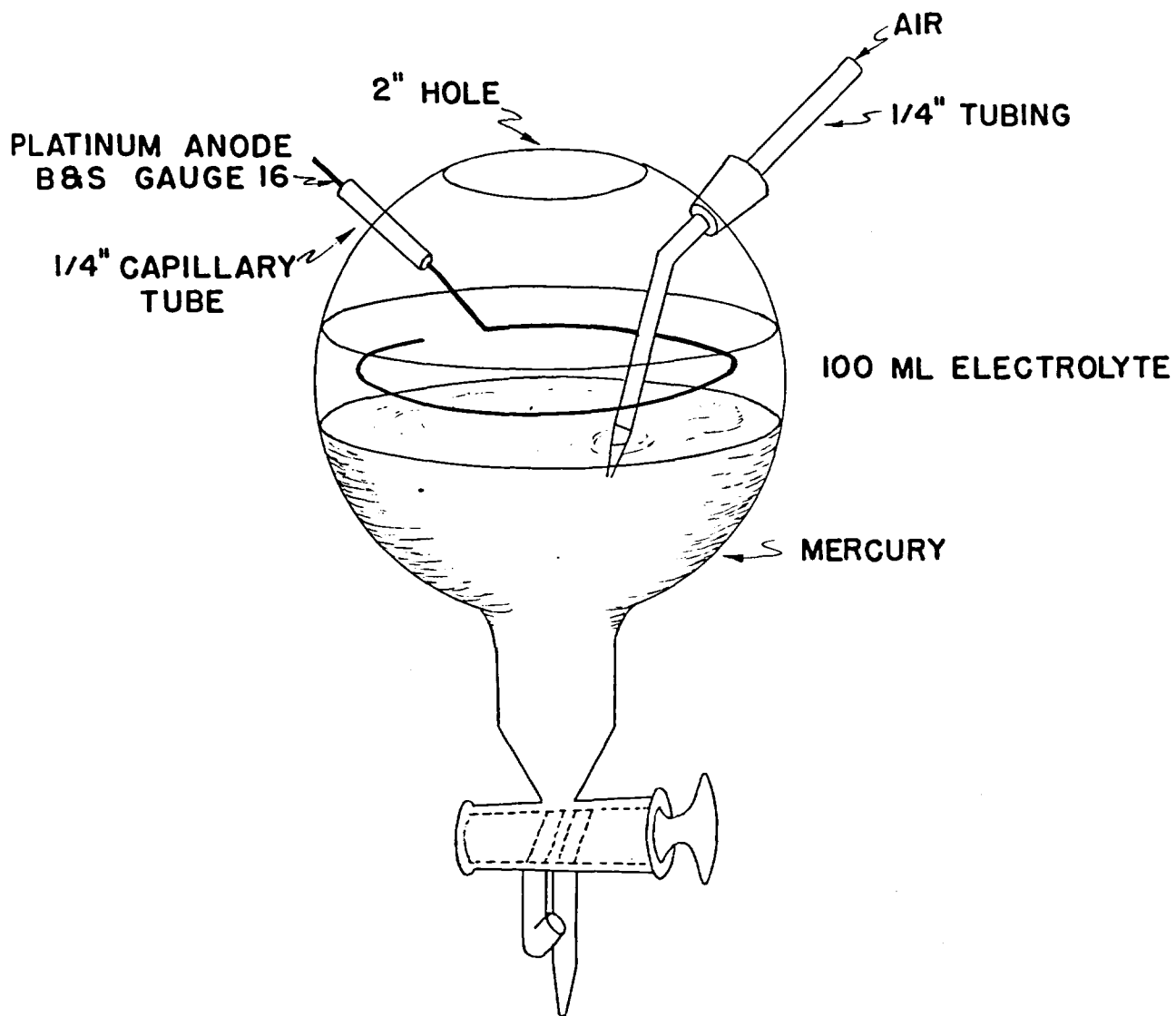


Figure 3

Method 3 - Cellulose Column Method (Figure 4)

Mines Branch Memorandum Series No. 105 (September, 1949) (Ref.2) contains a full description of this method of uranium analysis. It is based on the selective extraction of uranyl nitrate by ethyl ether, the other cations being absorbed by the cellulose. The procedure used at the Mines Branch is a modification of the one developed by the Chemical Research Laboratory, Teddington, England.

The procedure given is a general one for complex ores, but can be shortened for less complex ores. For example, in some ores the uranium minerals are readily soluble in nitric acid. This acid alone could then be used as the solvent and the ammonia precipitation step to remove the bulk of the sulphate ions would thus be unnecessary.

The accuracy and precision of this method are good for ores containing 0.01 per cent U_3O_8 or better. For ores in the 0.01 to 0.05 per cent U_3O_8 range, the average mean deviation is approximately plus or minus 8 per cent while for increasingly higher grade material the average mean deviation decreases steadily.

Eight determinations per day would be about average for one trained technician.

The method is readily adaptable for routine work and is recommended as the most suitable general method since any degree of concentration of uranium can be extracted in the cellulose column.

It should be emphasized that ventilation and fire precautions must be adequate when handling large amounts of ethyl ether.

The only special glass apparatus required is the column illustrated in Figure 5. on page 8.

3. CELLULOSE COLUMN METHOD
(MEMORANDUM SERIES 105)

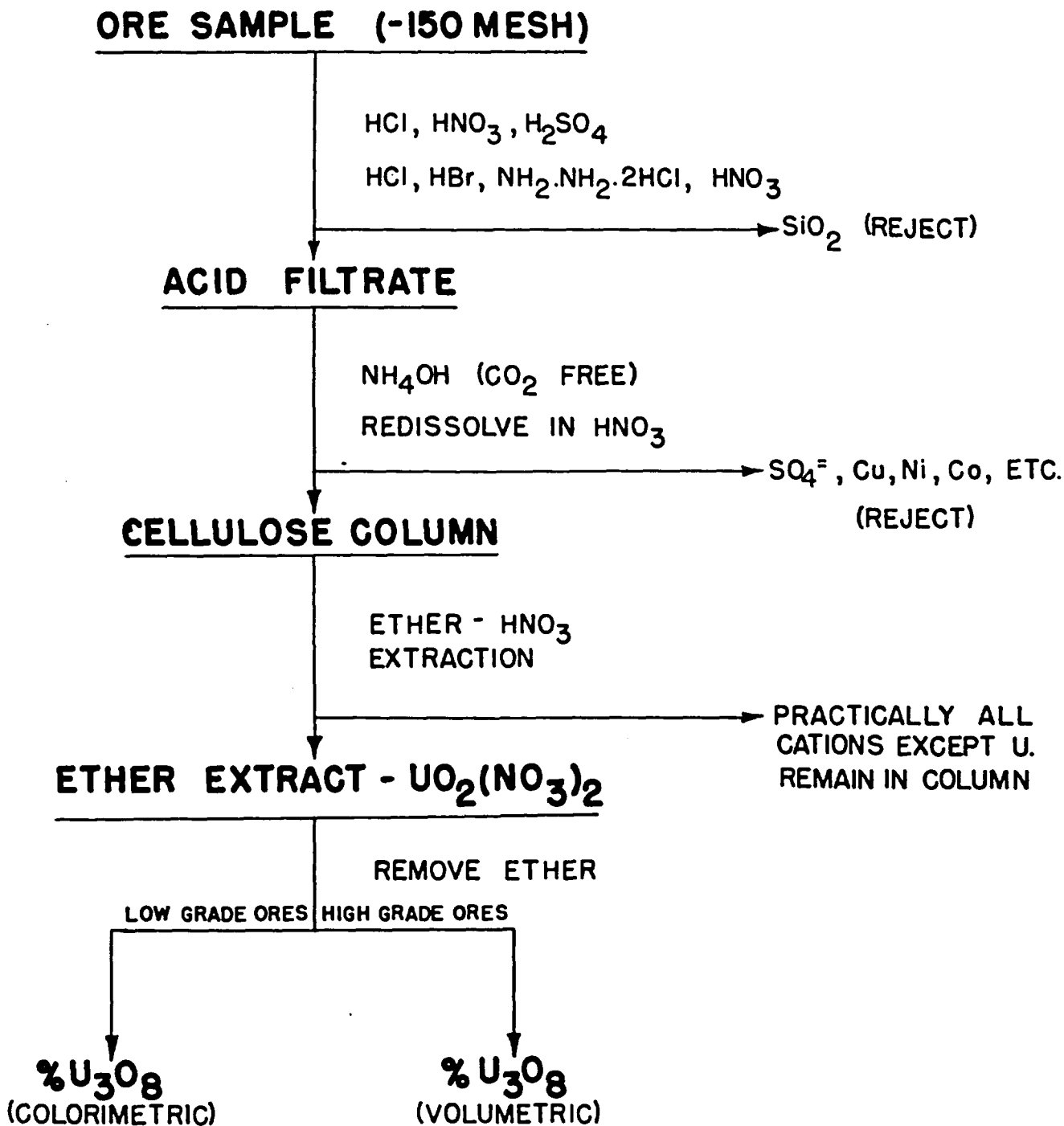
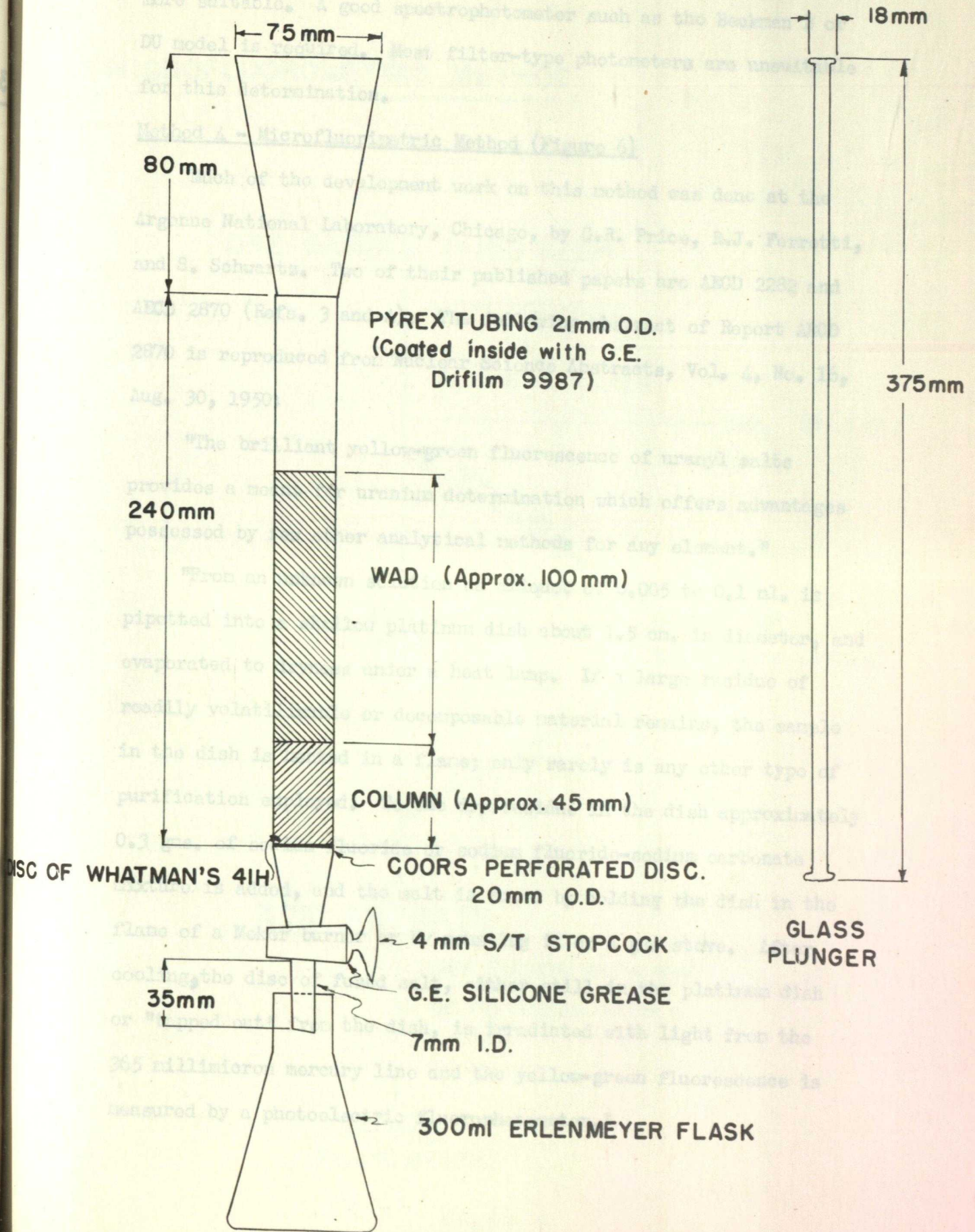


Figure 4

CELLULOSE COLUMN FOR EXTRACTION OF URANYL NITRATE



For ores below 1 per cent U_3O_8 a colorimetric determination is more suitable. A good spectrophotometer such as the Beckman B or DU model is required. Most filter-type photometers are unsuitable for this determination.

Method 4 - Microfluorimetric Method (Figure 6)

Much of the development work on this method was done at the Argonne National Laboratory, Chicago, by G.R. Price, R.J. Ferretti, and S. Schwartz. Two of their published papers are AEC-D 2282 and AEC-D 2870 (Refs. 3 and 4). The following abstract of Report AEC-D 2870 is reproduced from Nuclear Science Abstracts, Vol. 4, No. 16, Aug. 30, 1950:

"The brilliant yellow-green fluorescence of uranyl salts provides a means for uranium determination which offers advantages possessed by few other analytical methods for any element."

"From an unknown solution an aliquot of 0.005 to 0.1 ml. is pipetted into a shallow platinum dish about 1.5 cm. in diameter, and evaporated to dryness under a heat lamp. If a large residue of readily volatilizable or decomposable material remains, the sample in the dish is heated in a flame; only rarely is any other type of purification employed. To the dry residue in the dish approximately 0.3 gms. of sodium fluoride or sodium fluoride-sodium carbonate mixture is added, and the salt is fused by holding the dish in the flame of a Meker burner or by mounting it on a gas stove. After cooling, the disc of fused salt, either still in the platinum dish or "tapped out" from the dish, is irradiated with light from the 365 millimicron mercury line and the yellow-green fluorescence is measured by a photoelectric fluorophotometer."

"From the reading obtained for the fluorescence of the sample, the average value for the fluorescence of blanks is subtracted, and the difference is multiplied by a previously determined calibration factor to give the amount of uranium in the sample."

"If there is reason because of the presence of colour in the fused flux or from knowledge of the composition of the solution being analyzed, to suspect interference with the fluorescence, one can to a considerable degree remove this quenching by dilution, by employing a smaller aliquot, or can correct for it by "spiking" by adding a known amount of uranium to an identical aliquot in another dish."

"The useful range of the method is for a sample size of from about 10 to 0.0001 micrograms of uranium; work below 0.001 micrograms requires great care in avoiding contamination. Usually analyses are run in duplicate; for routine work the standard error of the mean of the pair is generally below 10 per cent except when the sensitivity is near its limit or when unusually large amounts of interfering substances are present, and by employing certain refinements in technique it is frequently possible to reduce the standard error to less than 5 per cent."

"No element besides uranium has been shown to produce detectable fluorescence under the conditions recommended in this paper."

This is a general method for ores containing 1 per cent U_3O_8 or less. The accuracy and precision obtainable are very good especially for low-grade ores. At the Mines Branch the average mean deviation for ores in the range 0.001 to 1.0 per cent U_3O_8 is approximately plus or minus five per cent. The method is rapid and is

well suited to routine work but is not suitable for ores containing over 1 per cent U_3O_8 . For this reason it is best used in conjunction with the cellulose column method.

The capital outlay for this method of uranium analysis is comparatively high. A suitable fluorimeter will cost between \$1500 and \$2000 while the investment in platinum dishes will range from \$500 to \$1000. In addition it is desirable to operate the fluorimeter in an air-conditioned room since it is important to control atmospheric dust and humidity carefully. On the other hand, the cost of analysis per sample is very low once the equipment has been set up.

Using this method an average output of ten ore samples or forty determinations can be obtained in an eight-hour day by a staff of two chemists.

References

1. "The Determination of Uranium in Ores - Modified Mercury Cathode - Cupferron Method", Memorandum Series No. 103, Mines Branch, Ottawa, August, 1949. (Free)
2. "The Determination of Uranium in Ores and Solutions - Cellulose Column Method", Memorandum Series No. 105, Mines Branch, Ottawa, September, 1949. (Free)
3. "The Microfluorimetric Determination of Uranium", United States Atomic Energy Commission Report No. AECG-2282. (15 cents)
4. "The Fluorophotometric Determination of Uranium", United States Atomic Energy Commission Report No. AECG-2870. (15 cents)

APPENDIX

Reporting of Uranium or Thorium Determinations

Under the Atomic Energy Regulations of Canada the results of an assay or analysis of a mineral that indicates a content of more than 0.05 per cent by weight of uranium or thorium are to be

reported forthwith to the Director of the Geological Survey, Department of Mines and Technical Surveys, Ottawa, for the Atomic Energy Control Board, together with full particulars relating to the material assayed or analysed, including the name and address of the person from whom such material was received, the purpose of the assay or analysis, and the origin of the material so far as known to the person making the report. This requirement does not apply to assays or analyses made for persons operating under orders of the Board which provide for periodical reports.

Copies of the Regulations may be obtained on application to the Secretary, Atomic Energy Control Board, Ottawa.

Atkins & Durbrow Limited

This company, formerly known as the B.C. Peat Company, excavates the peat hydraulically and dries it by mechanical means.

The company owns 1,000 acres on the Delta bog, near Ladner and the plant is at the western edge of the property. The present plant has been in operation since 1945, the previous plant built in 1938 having been destroyed by fire.

Figure 4 illustrates the method of operation. The peat, A, is excavated by a hydraulic monitor, B, supplied with water at 60 pound pressure. The force of the water loosens the peat and it flows in the form of a thin slurry along a ditch to the sump, C. Here the twigs and roots are screened out, and the peat and water mixture is pumped to the plant in a 12-inch pipe, E. Any remaining foreign matter is removed by the screens in the collecting box, F, and the mixture then flows on to the vibrating screen of a Fourdrinier paper machine. Here it is consolidated enough to pass over and around the rolls, from which it emerges as a blanket 70 inches wide and $\frac{1}{4}$ of an inch thick and containing about 70 per cent moisture. It passes through the shredder, J, into the three drying boxes, where it is further dried by passing along on a chain conveyor. These drying boxes, placed in parallel, are maintained at 210°F. by steam coils, and also under a slight vacuum by exhaust pump. The peat emerges with a moisture content of from 30 to 40 per cent. If required for horticultural purposes, it is further shredded in a hammer mill. The dried peat then goes by conveyor to the baling machines, is baled, and is then ready for shipment.

The main advantage of this process is that it can be operated if necessary 24 hours a day throughout the year; another being that much less labour is required. To maintain the plant in full operation, two 'monitors', requiring only two operators and two helpers, are necessary in place of the army of diggers, etc. required by the conventional system of operation. However, capital and operating costs are necessarily high. The paper machine and auxiliary equipment, boiler house, pumping machinery, etc. and the large amount of water used in the process are expensive.