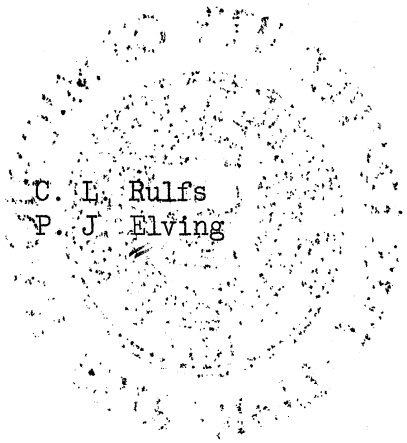
ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

Quarterly Status Report No. 5

ISOLATION AND DETERMINATION OF SUBMICROGRAM QUANTITIES OF THE HEAVY ELEMENTS FROM GROSS FISSION PRODUCTS

February 15, 1955 to May 14, 1955



Project 2228

ELECTRONICS RESEARCH DIRECTORATE
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ABSTRACT

The techniques for the separation and determination of submicrogram quantities of uranium-233 have been concerned mainly with simultaneous electroreduction of the uranium with assay by plating and alpha counting. The investigation of the extraction of uranium (VI) by 8-quinolinol has practically been completed, and work has been started on the isolation of U-233 from mixtures containing gross fission products.

OBJECTIVE

The project is concerned with the isolation and determination of microgram and submicrogram quantities of heavy elements, in particular uranium, when present in admixture with fission products. Emphasis is being placed on the separation of uranium by extraction of the chelates which it forms with organic molecules. Measurement is being made through the use of uranium-233 tracer and alpha counting.

I. INVESTIGATIONS IN PROGRESS

Activity during the past quarter has involved the application and refinement of the techniques described in previous quarterly status and research reports for the separation and determination of submicrogram quantities of uranium-233. These studies have involved the simultaneous electroreduction and extraction of the uranium with assay by plating and alpha counting. The investigation of the extraction of uranium(VI) by 8-quinolinols has been essentially completed. Work has been started on the isolation of uranium-233 from mixtures containing gross fission products. Work on the critical review of the current status of the analytical chemistry of uranium has continued.

A. OXINE EXTRACTION

Another worker has confirmed the results previously obtained (Quarterly Status Report No. 4) on the extraction of U(VI) from aqueous solution by chloroform solutions of 8-quinolinol (8-hydroxyquinoline or oxine), 5,7-dichloro-8-quinolinol, and 5,7-dibromo-8-quinolinol, using 2.1-mg quantities of uranium. A few extractions were carried out at intermediate pH regions which had not been covered previously, thus establishing a complete picture of the extraction curves. The extraction curves have been redrawn on the basis of two sets of results and the value of K_D recalculated in a few cases where the new data slightly changed the curve slopes in regions of low percentage extraction of uranium.

The manuscript, in the form of a scientific paper which was prepared as a summary of the work on the extraction of uranium by 8-quinolinols, has been approved for release for publication by the Air Force Cambridge Research Center and by the University of Michigan Engineering Research Institute. The manuscript has been submitted to the journal, Analytical Chemistry, for consideration for publication.

B. CUPFERRON SEPARATION

A number of runs have now been made involving the complete process

for uranium isolation based on simultaneous electrochemical reduction and cupferron extraction of the uranium followed by re-extraction of the uranium, destruction of organic matter, and electrodeposition of the uranium for alpha counting. The runs have involved amounts of uranium-233 of the order of 10^{-8} g in initially 30 ml of solution, to which is added as carrier 20 micrograms of natural uranium. The recovery or yield based on comparison of the alpha count of the U-233 taken and of that of the final plate obtained has been 90%. A series of experiments indicated that the recovery in the plating process was 98% or better. The 10% loss which is consequently involved in the processes of reduction and extraction and of preparation of the extracted uranium for plating has been traced to a loss of about 5% in the residual aqueous layer after extraction and a loss of about 3 to 4% in the residual ether layer after extraction with nitric acid.

Considerable difficulties which were at first encountered in obtaining satisfactory cupferron extraction of amounts of uranium-233 of the order of 10^{-8} g have now been overcome by improvements in the procedure. The whole operation at present takes about 4 hours. It is significant to note that an average recovery of 95% was obtained using milligram quantities of uranium-238; the recovery was checked by colorimetric oxine and ferrocyanide methods. Use of milligram additions of carrier uranium can not be tolerated due to the self-absorption of alphas that would occur in counting a milligram plate of uranium.

The manuscript on uranium(III) cupferrate which was approved for release for publication by the Air Force Cambridge Research Center and by the University of Michigan Engineering Research Institute, has been submitted to the Journal of the American Chemical Society.

C. SEPARATION OF URANIUM FROM FISSION PRODUCTS

Orientation studies have been begun on the behavior of the mixture of fission products (U. S. Atomic Energy Commission Sample FP-P-1 consisting of a mixture of fission products, present as nitrates in nitric acid solution and prepared by separation from heavy metals which have been exposed for 40 to 60 days in the reactor and cooled only a short time). The fission products have been subjected to the same electroreduction and cupferron extraction, and plating and counting procedures used for uranium. The discussion of these experiments will be deferred until more work has been done.

D. ANALYTICAL CHEMISTRY OF URANIUM

Work has been progressing on the critical survey of the analytical chemistry of uranium mentioned in Status Report No. 4. A literature survey of

the methods reported since 1947 for the determination of uranium has been made, based on reports in Nuclear Science Abstracts and Abstracts of Declassified Documents. About three hundred abstracts were found. The work up to 1947 has been well covered in Rodden's book, Analytical Chemistry of the Manhattan Project, and in other publications resulting from the Manhattan Project.

All the major areas, with the exception of radiometric techniques, have been covered, including gravimetric, titrimetric, electrometric, and photometric methods. The techniques of separation and preparation of uranium for measurement have also been surveyed with special attention to the isolation of uranium from microgram and submicrogram amounts of complex mixtures of fission products, and to techniques, such as extraction, which lend themselves to automatic or semiautomatic remote-control manipulations involving a minimal introduction of reagents and solvents. The literature has been classified and a synthesis is now being prepared.

II. RESEARCH PLANS

Work will be continued on the attempt to make the electrochemical reduction-cupferron extraction-re-extraction process for uranium isolation at the microgram level approach a recovery of 95% or better. The present recovery of 90% is reproducible enough for use as the basis for a correction factor but it would be preferable, if possible, to be able to use a smaller correction factor. It will also be desirable to investigate each unit operation in the overall process not only from the viewpoint of 100% recovery but also from the standpoint of decreasing in so far as feasible the time required for that process.

At the same time investigation will be continued on the application of the procedure discussed in the previous paragraph to the separation of uranium from mixed fission products. Radiochemical contamination by active nucleides should provide a sensitive measure of the efficiency of the separation scheme.

Work will be started on an investigation of the properties of the chelate formed by uranium(III) with cupferron from the viewpoint of the isolation and measurement of micro and submicro amounts of uranium.

The survey of the current status of the analytical chemistry of uranium will be continued with preparation of the critical systematic review.

III. PERSONNEL AND ADMINISTRATION

One part-time research assistant (Mr. Robert Stenger) will terminate work as of May 25 due to the end of the main academic year. Dr. De continues to work full time on the project while the authors and Mrs. Kochanny are working part time on it.

During the summer, beginning about June 10, two graduate students, Mr. Daniel J. Macero and Mr. Herman Wissenberg, who are majoring in analytical chemistry and electrochemistry, will work half time on the project.

IV. FISCAL INFORMATION

As of April 31, 1955, there was an approximate unexpended balance of $8,700; most of this sum is encumbered by salary committments.

There were no important acquisitions during the past quarter. However, the U. S. Atomic Energy Commission has approved our receiving another 20 micrograms of uranium-233.