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ANALYTICAL PROGRAM FOR PROCESSING
STAINLESS STEEL URANIUM DIOXIDE REACTOR FUEL ELEMENTS

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by

G. A. Huff

Date

September 18, 1959

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
Idaho Falls, Idaho
Contract AT(10-1)-205

IDAHO OPERATIONS OFFICE
U. S. Atomic Energy Commission

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A B S T R A C T

Analytical programs have been described for uranium recovery processes for aluminum-uranium and zirconium-uranium reactor fuel elements. It is the purpose of this paper to describe the analytical program for the uranium recovery process involving stainless steel-uranium reactor fuel elements.

The recovery process consists of a two step dissolution and the regular liquid-liquid solvent extraction using TBP in kerosene. Sulfuric acid is used to dissolve the stainless steel. As a result of the sulfuric acid dissolution the uranium is converted to a slurry. The uranium slurry is then dissolved in nitric acid. After the nitric acid dissolution the feed material is compatible with the extraction columns used at the Idaho Chemical Processing Plant for other type fuel elements previously described.

In order to analyze samples of dissolver solutions for constituents necessary for plant operation, three new analytical methods were developed. These methods are a rapid method for determining uranium, one for nitrate and one for sulfate.

Methods are described for uranium, acidity, specific gravity, nitrate and sulfate in the dissolver solution; also for small amounts of uranium in the extraction column raffinates.

Samples of dissolver solution and first cycle aqueous raffinate contain large amounts of fission products. These samples require shielded facilities for analytical work.

The remote analytical facility described by Dykes and his co-workers was used for this work.

Precision and accuracy data are given for the analytical methods described.

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ANALYTICAL PROGRAM FOR PROCESSING
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INTRODUCTION

Analytical programs have been described for uranium recovery processes for aluminum-uranium⁽¹⁴⁾ and zirconium-uranium⁽¹³⁾ reactor fuel elements. It is the purpose of this paper to describe the analytical program for the uranium recovery process of stainless steel-uranium dioxide reactor fuel elements.

Figure I shows a simplified flowsheet of the recovery process used. The scheme consists of a two step dissolution and the conventional liquid-liquid solvent extraction using tributylphosphate in kerosene. Sulfuric acid is used to dissolve the stainless steel. As a result of the sulfuric acid dissolution the uranium dioxide is converted to a slurry. The uranium dioxide slurry is then dissolved in nitric acid. After the nitric acid dissolution the feed material is compatible with the extraction columns used at the Idaho Chemical Processing Plant for other type fuel elements previously described.

SAMPLES ANALYZED

The more important routine samples, constituents determined, and analytical techniques are summarized in Table I.

In order to analyze samples of dissolver solutions for constituents necessary for plant operation, three new analytical methods were developed. These methods are a rapid method for determining uranium, one for nitrate and one for sulfate.

Samples of dissolver solution and first cycle aqueous raffinate contain large amounts of fission products. These samples require shielded facilities for analytical work. The remote analytical facility described by Dykes and his co-workers⁽⁵⁾ was used for this work.

TABLE I

Important Routine Samples, Constituents
Determined and Analytical Techniques

<u>Sample</u>	<u>Composition</u>	<u>Constituent Determined</u>	<u>Analytical Technique</u>
Dissolver	Sp. Gr. 1.263 Mg. 0.109M Fe 0.406M Cr 0.112M Ni 0.078M U 14.97 g/l U(VI) H ⁺ 4.71M So ₄ ⁻ 3.08M No ₃ 0.496M	Uranium Uranium Nitrate	Isotope Dilution Mass Spectrometer Spectrophotometric Spectrophotometric
Dissolver Wash	H ₂ O < 0.01M NO ₃ ⁻	Nitrate	Acid-Base Titration & Spectrophotometric
Coarse Feed	As dissolver, but diluted about 7 fold & 3.13M NO ₃ ⁻	As dissolver plus Specific Gravity Acidity Sulfate Fission Products	Falling Drop pH Titration with Oxalate Complexing Amperometric Total β and Gamma Counting
First Cycle Extraction Column Feed	As coarse feed but diluted by nitric acid adjustment NO ₃ ⁻ 3.00M	Nitrate	Spectrophotometer
First Cycle Extraction Column Raffinate	As first cycle feed but with less than 1 x 10 ⁻³ mg./ml. of U(VI)	Uranium	Pellet Fluorophotometric
First Cycle Extraction Column Product	1M U(VI) nitrate 0.81M HNO ₃	Uranium Specific Gravity Fission Products	Isotope Dilution Mass Spectrometer Falling Drop Total β and Gamma

ANALYTICAL METHODS

Uranium in Dissolver, Coarse Feed, First Cycle Extraction Column Feed, and First Cycle Extraction Column Product.

From the composition listed in Table I, it can be seen that these samples, with exception of the first cycle extraction column product, contain constituents which interfere with analytical procedures. Liquid-liquid solvent extraction has been used successfully in separating uranium from fission products and other interfering impurities. After separation samples readily lend themselves to the isotopic dilution mass spectrometric method. This technique was proposed by Ingram⁽¹¹⁾ and further developed for uranium by Duffy and Tingey⁽²⁾ and Goris and Tingey⁽⁹⁾. This is an excellent method since quantitative recovery from the extraction is not required and concentration as well as isotope ratio are obtained at the same time. This method is used for the plant input measurement.

The separation procedure is as follows.

To a test tube is added 0.5 ml. of a 1.0 mg. per ml. uranium-233 standard solution and 4.0 ml. of 1N^B, 2.0M aluminum nitrate salting solution. The test tube is transferred to the remote facility (Figures 2 and 3) where 0.5 ml. of the sample is added from a remote pipetter (Figures 4 and 5). This pipetter was discussed at the Second Conference on Analytical Chemistry in Nuclear Reactor Technology in 1958. Details on the apparatus are given by Dykes⁽⁴⁾. The test tube is then stoppered and the aqueous solution is mixed by shaking to obtain homogeneity. A manipulator (Figure 6) is used to shake the tube. Two ml. of organic extractant, hexone, are added and the mixture is stoppered and shaken for one minute. As much of the organic as possible is poured into a clean centrifuge tube. The tube is transferred from the remote facility to the conventional laboratory. The uranium is simultaneously stripped from the organic phase and precipitated as the peroxide by contacting with 1 ml. of 30% hydrogen peroxide.

After centrifuging and decanting the precipitate is washed with 1 to 1 water-acetone mixture and transferred to the Mass Laboratory.

The peroxide is dissolved in a minimum amount of nitric acid and evaporated on a tantalum filament. Details of the operation of the mass spectrometer and of the determination are given by Duffy, Wheeler and Morgan⁽³⁾. Results are reported for total uranium concentration and percentages of each isotope.

The isotopic dilution mass spectrometric method is time consuming and is not a method to be used if production schedules are critical. In order to obtain rapid data for uranium concentration a spectrophotometric method was developed. The procedure is as follows.

To a test tube is added 6 ml. of 2.8M aluminum nitrate (2N^B, 0.025M in TPAN) and 3 ml. of hexone. The tube is transferred to the remote line where 0.750 ml. of sample is added. A polyethylene stopper is used to stopper the tube and it is transferred to the special tumbler (Figure 7) and mixed for 3 minutes. As much of the organic as possible is poured off and transferred to the conventional laboratory. The sample is centrifuged and as much of the organic as possible is transferred to a 1-cm. Corex absorption cell. The spectra of the material is scanned from 500 to 400 mμ on a Cary Model 14 recording spectrophotometer at a scan speed of 5A per second.

Details on this method are given by Maeck, Booman, Elliott, and Rein⁽¹²⁾.

Uranium in First Cycle Extraction Column Raffinate.

These samples are very low in uranium ($< 1.0 \times 10^{-3}$ mg. U per ml.) and pellet fluorophotometry is used to analyze them. They contain large amounts of fission products which create radiation problems. Also they contain foreign ions which quench fluorescence. In order to separate the uranium from fission products and other interfering ions a liquid-liquid extraction is made in the Remote Analytical Facility. The uranium, which is contained in the organic, is transferred to the conventional laboratory where pellets are prepared and read.

The procedure is as follows.

To a test tube is added 0.5 ml. of sample, 1.5 ml. of solution 1.5M in aluminum nitrate, 5% in citric acid, 1M in nitric acid, and 2 ml. of 1% tributyl-phosphate in n-hexane. After extracting for 1 minute, as much of the organic as possible is transferred to the conventional laboratory. Sodium fluoride pellets are prepared in platinum dishes and 0.2 ml. aliquots are pipetted onto each pellet. The pellets are dried under infrared lamps, fused in a gas-air flame and the fluorescence is measured in a high sensitivity fluorophotometer. Uranium concentration is then read from a working curve prepared from processed standards.

Acid in Coarse Feed.

The coarse feed sample contains hydrolyzable ions which require complexing before acidity is measured. A pH titrimetric method is used to determine free acid (or base) in solutions of this nature. Oxalate, as the potassium salt is used as the complexing agent. The potassium oxalate is adjusted to a reference pH of 5.80. This pH minimizes hydrolysis in a stainless steel matrix. The method is described by Booman et. al.⁽¹⁾

The procedure is as follows.

Fifteen ml. of an 8% potassium oxalate solution adjusted to a pH of 5.80 is added to a 50 ml. beaker. If the sample is known to be near neutral or slightly basic an acid spike is added. The beaker is transferred to the remote analytical facility where 0.200 ml. of sample is added by the pipetter. The beaker is then transferred to a titration apparatus (Figures 7 & 8) and allowed to digest for two hours. This digestion time is required for chromium to complex. After digestion the sample is titrated with standard 0.2N sodium hydroxide until the exact reference pH is obtained. Acidity is calculated from the base titer, sample volume and volume and normality of acid spike.

Specific Gravity in Coarse Feed and First Cycle Extraction Column Product.

These samples contain fission products, therefore they require remote handling. Specific gravity is determined by the falling drop method. A small, known volume of sample is dropped through an immiscible organic liquid (a mixture of O-nitrotoluene, α -chloronaphthalene and α -bromonaphthalene) and the time for the drop to travel a known distance is determined. The remote apparatus used for this measurement is shown in Figures 9 & 10.

The procedure requires that a 0.005 ml. drop be formed on the pipet tip while submerged in the liquid. The drop is released as the pipet tip breaks the surface of the liquid as it is withdrawn. The time for the drops to fall a measured distance is obtained. An average time for five drops is obtained. Specific gravity is then read from a working curve prepared from known standards.

Total Beta and Gamma Activity in
Coarse Feed and First Cycle Extraction
Column Product.

Gross beta and gross gamma activities are reported on these samples as a complete fission product analysis is costly and time consuming. Activities from one stream are compared to the other in order to determine the effectiveness of the decontamination process. Dilutions of these samples from 100 to 10,000 fold are prepared using 0.1N HNO₃ as a diluent. Original dilutions are prepared in the Remote Analytical Facility and transferred to the conventional laboratory for further work.

The gross beta measurement is very simple. An aliquot of the diluted sample is pipeted onto a 1-inch watch glass and evaporated to dryness under infrared lamps. The watch glass is covered with cellophane tape and mounted on a paper card. The sample is counted on a proportional counter at 10% geometry and reported as counts per minute per milliliter.

The entire dilution is used in the gross gamma measurement. The sample is deposited into the thimble of a high-pressure ion chamber and read at 100% geometry. Since the sample contains a large number of gamma energies and decay schemes are unknown, results are reported in terms of radium equivalents per milliliter.

Sulfate in Coarse Feed.

Since sulfuric acid is used in the first dissolution step, sulfate data are necessary in obtaining material balance checks over the feed end. A rapid titrimetric method is used. The method involves the amperometric titration of sulfate ion with lead nitrate at -1.2 volts versus the saturated calomel electrode with a dropping mercury cathode. The technique was proposed by Elving and Grodzka⁽⁶⁾ and further developed by the Analytical Development Group at the Idaho Chemical Processing Plant. Remote apparatus for this method is shown in Figures 11 & 12.

The procedure is as follows.

To a 150-ml. beaker is added 10 ml. of absolute alcohol. A volume of distilled water is added to give a total aqueous phase of 25 ± 1 ml. This final volume also includes the sample aliquot to be added. Five drops of brom thymol blue indicator and stirring bar are added. An aliquot of sample containing from 0.25 to 0.65 millimoles of sulfate is added to the beaker. The beaker is placed on a magnetic stirrer and 0.5N sodium hydroxide is added to the brom thymol blue end point (yellow to blue). The sample is scrubbed with nitrogen for 5 minutes. After scrubbing, the sample is swept with nitrogen during titration.

The sample is then titrated with standard lead nitrate solution using 0.5 ml. increments. Data are plotted on coordinate graph paper, galvanometer readings versus volume of lead nitrate. The best straight line is constructed through points on either side of the break. The intercept of 2 lines is the end point. Molarity of the sample is determined from the lead nitrate titer and sample volume.

Nitrate in Dissolver, Dissolver Wash, and
First Cycle Extraction Column Feed.

In order to dissolve stainless steel-uranium fuel elements with sulfuric acid, it is necessary to have the dissolver tank free of nitrate ion. Nitrate present renders the elements passive to sulfuric acid. After the nitrate acid dissolution step the dissolver is washed with water until the nitrate concentration is 0.01M. In order to determine the nitrate content of the dissolver a sample of the wash material is analyzed for total hydrogen ion. A simple, rapid, acid-base titration using phenolphthalein as an indicator is the method involved. If an answer of 0.01M is obtained the dissolver is assumed to be clean. If an answer of 0.01M is obtained it may be due to hydrogen ion indicating nitrate content or to hydrolyzable ions being titrated with base. In this case a more accurate check of nitrate content is obtained by the "Colorimetric Determination of Nitrate." The acid-base titration is generally a sufficient check.

The "Colorimetric Determination of Nitrate" is the method used to determine nitrate concentration on dissolver and first cycle extraction column feed material. This method is dependent upon the purple complex of ferrous nitrosyl sulfate. The technique is one reported, Feigl⁽⁸⁾, English⁽⁷⁾, Elving and Grodza⁽¹⁵⁾, and further developed by the Analytical Development Group at the Idaho Chemical Processing Plant. The Remote colorimeter is shown in Figures 13 and 14.

The procedure is as follows.

To a 50-ml. glass centrifuge tube is added 1 ml. of ferrous sulfate solution. Twenty-five ml. of 15M sulfuric acid is added into the tube. A volume of distilled water is quantitatively added to give a total aqueous phase of 29.0 ml. This final volume should include the sample aliquot to be added later. The tube is then cooled in an ice bath until its content is less than 5°C. While the tube is still in the ice bath, an aliquot of sample containing from 0.007 to 0.16 millimoles of nitrate is added. The tube is removed from the ice bath and the color is allowed to develop. The absorbance of the sample is read on a spectrophotometer at a wavelength of 530 mμ. Because of the transient nature of the color, the absorbance measurement is made between 35 and 45 minutes after removal of the tube from the ice bath. Millimoles of nitrate corresponding to the sample absorbance is read from a standard curve.

QUALITY CONTROL AND RELIABILITY OF THE METHODS

A quality control program similar to those described for the analytical programs on aluminum-uranium⁽¹⁶⁾ and zirconium-uranium⁽¹⁷⁾ fuel processing was maintained on the analytical program for stainless steel-uranium fuel processing. Also, all analysts were trained and tested on the methods used according to the training and testing program described by Huff and Tingey⁽¹⁰⁾.

Bench standards were used to check performance of apparatus and reagent purity from shift to shift. Control samples for each method were submitted to the laboratory and analyzed at a rate of 8 per method per month. Where practical bench standards and controls were prepared in matrix similar to process samples.

The reliability data listed in Table II were calculated from the results of control samples.

TABLE II
Precision and Accuracy of Methods Under
Routine Operating Conditions

<u>Analysis</u>	<u>Range</u>	<u>Precision</u> ^(A)	<u>Bias</u> ^(B)
Uranium Concentration by Isotopic Dilution Mass Spectrometry	1.8 mg./ml.	0.04 mg./ml.	None
Uranium Isotope Distribution	50% U-235 1 to 6% U-236	0.08% ^(C) 0.02% ^(C)	None None
Uranium Spectrophotometric	2.20 to 14.80 mg./ml.	0.04 to 0.18 mg./ml.	+0.03 to 0.04 ±0.03 mg./ml.
Uranium Extraction Fluorophotometric	8.0×10^{-5} to 9.0×10^{-2} mg./ml.	37.48%	None
Nitrate Spectrophotometric	0.008 to 3.0M	0.016M	None
Specific Gravity Felling Drop	1.15 to 1.34	0.006	None
Acidity-pH Titration With Oxalate Complexing	1.44N ^B to 4.44N ^A	0.10N	0.05 ± 0.02N
Sulfate Amperometric	2.60 to 5.80M	0.21M	None

- A. Precision is expressed as 95% limits of uncertainty for a single determination.
- B. Precision of the bias is also expressed as 95% limits of uncertainty.
- C. Expressed in absolute percentage units.

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FIGURE 1

STAINLESS STEEL FUEL DISSOLUTION AND EXTRACTION COLUMN FEED PREPARATION

Figure 2. Operating Aisle of Remote Laboratory

Figure 3. Remote Line

Figure 4. Remote Analytical Facility
Model "B" Pipet Box Installation

Figure 5. Remote Analytical Facility
Model "B" Pipetter

Figure 6. Remote Analytical Facility
Manual Extraction Apparatus

Figure 7. Remote Analytical Facility.
Mechanical Extraction Apparatus

Figure 8. Acid Titrator

Figure 9. Falling Drop Specific Gravity
Apparatus Box Installation

Figure 10. Falling Drop
Specific Gravity Apparatus

Figure 11. Remote Sulfate Titrator
Box Installation

Figure 12. Remote Sulfate Titrator

Figure 13. Remote Colorimetric
Nitrate Box Installation

Figure 14. Remote Colorimetric
Nitrate Apparatus