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NEW METHODS FOR THE DETERMINATION OF TRANSURANICS, BORON, AND SILICON IN URANIUM HEXAFLUORIDE

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ABSTRACT

New methods for the analysis of boron, silicon, and transuranics in uranium hexafluoride have been developed. Extraction chromatography utilizing U/TEVA™ and TRU™ resins from EIChroM Industries, Inc. are used to separate the uranium from the analytes of interest and to further purify the fractions containing the analytes. The boron and silicon are then determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES), while the transuranics are determined by alpha spectroscopy. The boron and silicon method is rapid, precise, and less labor intensive than many of the spark spectrographic methods. The transuranic method is relatively rapid, generates less waste than more traditional methods, and allows for very low detection limits. Both methods allow the laboratory to ensure that the ASTM specifications for these analytes in uranium hexafluoride are not exceeded. Details of the separation chemistry involved, the measurement techniques, advantages and disadvantages of the new methods, and sample results are presented.

INTRODUCTION

The Portsmouth Gaseous Diffusion Plant enriches uranium hexafluoride for later conversion into fuel for use in commercial nuclear power plants. The product must be analyzed for various impurities as defined in ASTM C-996, the Standard Specification for Uranium Hexafluoride Enriched to Less Than 5% U^{235}.[1] The specification includes limits of 4 μg/g U for boron, 250 μg/g U for silicon, and 3.3 Bq/g U for neptunium and plutonium content. New methods were needed to shorten analysis times, decrease waste generation, and improve precision for these analyses.

SEPARATION CHEMISTRY (TRANSURANICS)

The separation chemistry for the analysis of trace levels of americium, neptunium, and plutonium in the presence of large amounts of uranium must be very selective for either the uranium or the transuranics at some stage within the procedure to afford very good decontamination factors of the uranium from the transuranics. The alpha decay pattern for Np^{237} is complicated, with major peaks at 4.771 MeV and 4.778 MeV. The major alpha decay energies for U^{234} are at 4.724 and 4.776 MeV. Furthermore, as U^{235} is enriched, the U^{234} levels increase also, resulting in relatively larger amounts of U^{234} than observed with natural uranium. The combination of the overlapping alpha energies of U^{234} and Np^{237}, the increased levels of U^{234} in the enriched uranium, and the high specific activity of U^{234} create the need for very large decontamination factors necessary to determine Np^{237} at low levels in UF_6. Furthermore, good separation of thorium and americium from plutonium are necessary to determine Pu^{238}, as Am^{241} and Pu^{238} have overlapping alpha energies, and the alpha energy of Th^{228} is very close to the alpha energies of Pu^{238} and Am^{241}.

The method for the separation of the transuranics involves conversion of the hydrolyzed UF_6 to an oxalic acid/nitric acid system, removal of the uranium with U/TEVA™ resin, destruction of the oxalate ion, extraction of the transuranics with TRU™ resin, and the subsequent elution of the transuranics.

An aliquot of hydrolyzed UF_6 sample is pipetted into a beaker. Appropriate chemical yield tracers (Am^{243} and Pu^{236} or Pu^{242}) are added and the sample is evaporated to dryness. The residue is then treated with concentrated nitric acid and evaporated to dryness to drive off fluorides. The resulting residue is then dissolved in 15 mL of 0.1M oxalic acid in 2M nitric acid. The column used to remove the uranium is a 12 mL polypropylene cartridge fitted with a 20 μm polyethylene frit. The column is packed with U/TEVA™ resin slurried with water to approximately the 10 mL mark. Figure 1 illustrates the sample preparation and U/TEVA™ column chromatography. The U/TEVA™ resin is selective for tetravalent and hexavalent actinides. Complexing agents such as oxalic acid have been shown to decrease the capacity of the U/TEVA™ resin for tetravalent actinides in nitric acid while having little effect on the retention of hexavalent species.[2] Therefore by loading the sample from 0.1M oxalic acid in 2M nitric acid, the trivalent americium, the complexed tetravalent plutonium and neptunium, and any pentavalent neptunium are not retained by the U/TEVA™ column, while the hexavalent uranium is extracted. After loading the sample onto the U/TEVA™ column, the column is rinsed with 15 mL of 0.1M oxalic acid in 2M nitric acid. The load and rinse solutions are combined and passed through a second U/TEVA™ column for the remaining uranium to be removed. The uranium may then be stripped from the U/TEVA™ column with either water or 0.1M ammonium oxalate, allowing reuse of the column. Experimental data indicate that the U/TEVA™ column may be reused up to five times.

The combined load and rinse solutions from the two passes through the U/TEVA™ columns are then evaporated to dryness. Two additions of concentrated nitric acid are made with subsequent evaporations to dryness. These steps are taken to sublime the oxalate ion, which can interfere with further extractions.

The sample residue is then dissolved in 15 mL of 3M nitric acid. A TRU™ resin column is used to extract the transuranics and then separate them. Figure 2 illustrates the column chromatography necessary to extract the transuranics and separate them. The TRU™ column is first conditioned with 5mL of 3M nitric acid. The oxidation states of plutonium and neptunium are then adjusted to the tetravalent state. The oxidation state adjustment may be done in two different ways. The first method is to add 2 mL of 10% (w/v) ascorbic acid and heat the sample very gently until a yellow color persists. This method relies heavily on the technique of the analyst. The second and more rugged method involves adding iron(III) to the sample, followed by addition of 2M nitric acid saturated with ascorbic acid until the blue color no longer appears. At this point, the neptunium will be tetravalent while the plutonium is trivalent. The sample is loaded onto the TRU™ column and the column is then rinsed with 5 mL 3M nitric acid. The column is then rinsed with 3M nitric acid that has had a small amount of sodium nitrite solution added. This step is to oxidize the plutonium to the tetravalent state. The column is then rinsed with 5 mI of 9M HCl, which serves as a crossover solvent.

The americium is then eluted from the TRU™ column with 15 mL of 4M HCl. The americium fraction is evaporated to near dryness and 15 mL 0.1M ammonium oxalate is added. The thorium is then stripped with 35 mL of 1.5M HCl. Finally, the plutonium and neptunium are eluted together with 15 mL of 0.1M oxalic acid in 1M HCl.

The americium fraction and the neptunium/plutonium fractions are precipitated as their respective fluorides, using neodymium as a carrier. This precipitation step was previously described by Sill.[3] The samples are mounted onto aluminum planchets with adhesive spray and counted by alpha spectroscopy.

SEPARATION CHEMISTRY (BORON AND SILICON)

The separation chemistry for the analysis of boron and silicon does not have to be nearly as rigorous as the above described method. The only separation requirements are adequate removal of the uranium so that the uranium lines do not interfere with the boron and silicon lines in the ICP-AES measurements and to prevent contamination of the instrument with uranium.

Figure 3 illustrates the column chromatography for the separation of the boron and silicon from uranium. A 10 mL packed U/TEVA™ column previously described is conditioned with 15 mL of 3M nitric acid. An aliquot of the hydrolyzed UF_6 sample equivalent to 0.25 g of uranium is pipetted into a Teflon beaker. Concentrated nitric acid is added to adjust the acid strength to 3M nitric acid. The sample is then loaded onto the U/TEVA™ column, and the load solution is collected. The column is then rinsed with 10 mL 3M nitric acid, and the rinse is collected together with the load solution. The sample is then analyzed for boron and silicon content by an ICP-AES equipped with a Teflon torch and sample introduction. Finally, the uranium may be removed from the U/TEVA™ column as previously described, allowing reuse of the column.

RESULTS (TRANSURANICS)

In the original study to validate the method, 30 samples of hydrolyzed UF_6 equivalent to 0.5 g of uranium were spiked at the 0.05 Bq/g U (1.35 pCi/g U) level with Am^{241}, Np^{237}, and Pu^{239}. The tracers used were 0.055 Bq (1.49 pCi) of Am^{243} and 0.046 Bq (1.24 pCi) of Pu^{242}. The Pu^{242} was used to correct for the chemical losses of neptunium, as well as plutonium, since the two are eluted and counted together.

Table 1 summarizes the results for the tracer recoveries and resolution of the peaks. Tracer recoveries were excellent, ranging from 75% to 90%. The resolution of the peaks was also good, with full widths at half maximum (FWHM) rivalling those reported for electroplated sources.

Table 2 summarizes the recoveries for Am^{241}, Np^{237}, and Pu^{239} in the thirty samples after correction for tracer recoveries. The results show good recoveries and precision at the 0.05 Bq/g U level.

Samples are now analyzed on a routine basis with this method. The only change in the procedure is the use of Pu^{236} as a tracer as opposed to Pu^{242}. This change was made because the Pu^{242} has alpha energies close to those of Np^{237}, while the Pu^{236} alpha energies are higher than those of the analytes of interest.

Finally, decontamination factors and detection limits were determined for the method. The decontamination factor was calculated by dividing the activity of the uranium originally in the sample by the detection limit for uranium in the transuranic fractions. The detection limit was used because no uranium was detected in the transuranic fractions. The decontamination factor was 1.5×10^8 for 0.5 g of 4.4% enriched uranium. Finally, though detection limits vary with sample size, tracer recovery, counting efficiency, and detector backgrounds, detection limits of 0.005 Bq/g U are easily achieved for 1000 minute counting times with this method.

RESULTS (BORON AND SILICON)

In the study to validate the boron and silicon method, 28 samples of hydrolyzed UF_6 equivalent to 0.25 g of uranium were spiked with boron at the 4.8 μg/g U level and silicon at the 90 μg/g U level and analyzed with this method. Table 3 summarizes the accuracy and precision of the method. The detection limits were established statistically using the precision and a t-table. The detection limits were 0.84 μg/g U and 15.4 μg/g U for boron and silicon respectively. Finally, the decontamination factor for the removal of uranium from the boron and silicon was determined to be 715, which was adequate for measurement of the boron and silicon.

SUMMARY

In conclusion, the boron and silicon method has the advantages of good precision and is very rapid. A batch of 12 samples is easily prepared in under one hour for measurement. Furthermore, the boron and silicon method has shown promise as a way to determine other metal impurities in UF_6, and further studies will be performed.

The transuranic method offers relatively shorter analysis times and excellent recoveries and detection limits. The method also generates a minimal amount of mixed waste, further lowering costs associated with the analysis.

TABLE 1

TRACER RECOVERIES AND RESOLUTION

TRACER	AVERAGE RECOVERY	AVERAGE FWHM (keV)
Am^{243}	88%	26
Pu^{242}	80%	34

TABLE 2

ACCURACY AND PRECISION (at 0.05 Bq/g U)

ISOTOPE	% RECOVERY	% RSD
Am^{241}	107	11
Np^{237}	101	10
Pu^{239}	95	16

TABLE 3

ACCURACY, PRECISION, AND DETECTION LIMITS FOR BORON AND SILICON IN UF_6

ANALYTE	% RECOVERY	% RSD	MDL (µg/g U)
B	96	6	0.84
Si	104	6	15.4

FIGURE 1: Flow chart illustrating the selective removal of uranium from UF_6 with U/TEVA™ resin.

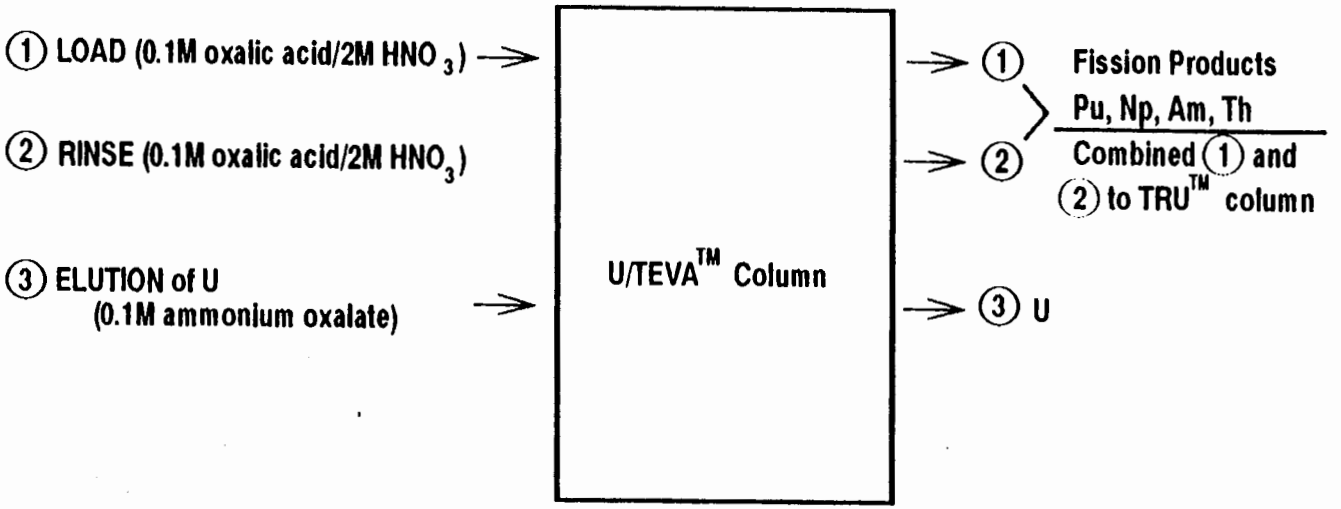


FIGURE 2: Flow chart illustrating the separation of thorium and transuranics with TRU™ resin.

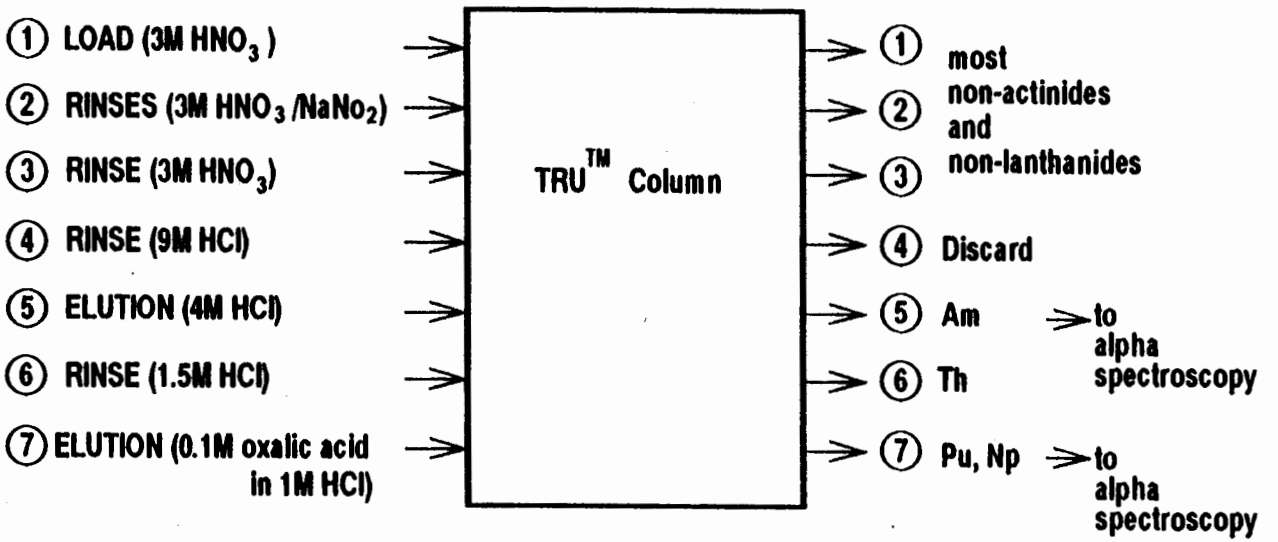
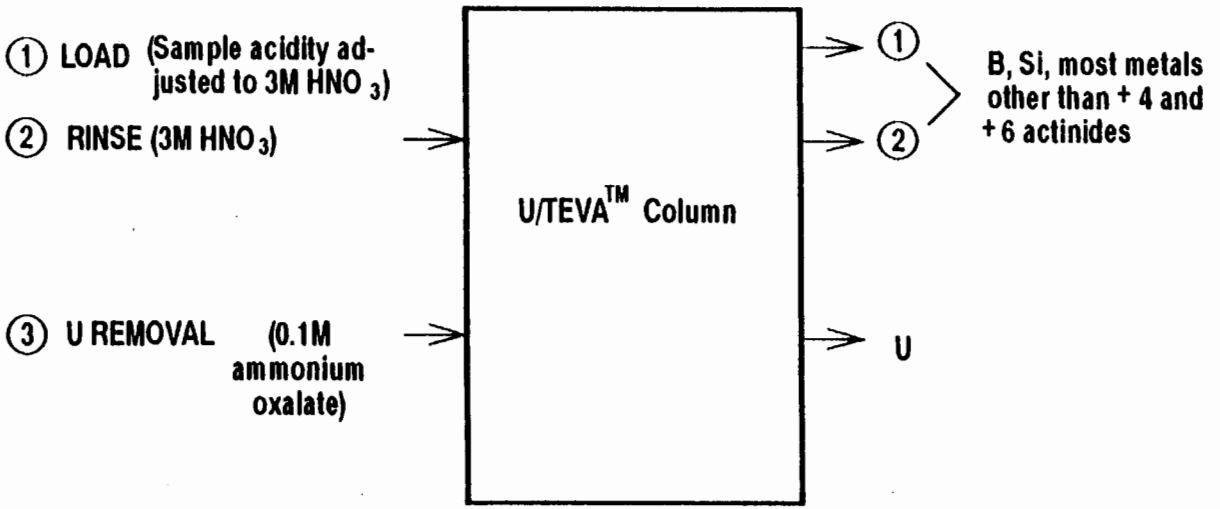


FIGURE 3: Flow chart illustrating the removal of uranium from UF_6 with U/TEVA™ resin for the analysis of boron and silicon.



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