

NUCLEAR FORENSICS INTERNATIONAL TECHNICAL WORKING GROUP



EXECUTIVE SUMMARY

In this guide, the assay of uranium through titration refers to a methodology determining the U content in material where U is the major constituent. U assay through titration is a well-tested and well-understood method developed over the last 50 to 60 years as part of nuclear safeguards verification in different nations. Other U assay techniques commonly used across the nuclear industry include ignition gravimetry and X-ray fluorescence. These methods are described in separate ITWG guideline documents. Mass spectrometric techniques such as thermal ionization mass spectrometry (TIMS), isotope dilution mass spectrometry (IDMS), or inductively coupled plasma mass spectrometry (ICP-MS) with multi collector, can also be used for U assay, but are also discussed in different ITWG documents. All these U assay methods are considered primarily destructive assay techniques and leave the sample in a form which may or may not be useful for other analyses.

The analysis time quoted for the method assumes a standard eight hour day and 5 day work weeks. Times will be different if shift work schedules are available. Uncertainties are expressed using GUM terminology expressed in relative percent. Uncertainties from ASTM/ISO methods, the 2010 International Target Values (ITV), and/or documented historical knowledge are reported.

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ITWG Guidelines are intended as consensus-driven best-practices documents. These documents are general rather than prescriptive, and they are not intended to replace any specific laboratory operating procedures.

1. INTRODUCTION

Chemical titration is a standard method for the determination of the U concentration of nuclear fuel material for accountability measurements or accountability verifications. In chemical titration, the sample is made to react with an exactly measured amount of a selective reagent of known composition, leading to the completion or characteristic end point of a well-known stoichiometric reaction.

Uranium titration can occur under a large variety of conditions using many different reagents; however, the most commonly used and accepted technique is based on a method developed by Davies and Gray in 1964. This method can determine precise uranium assay values with minimum interferences and without requiring separations prior to the assay of uranium materials. A system using computer controlled titrator and an automated sample system is seen below (Fig. 1).

The uranium is reduced to U(IV) by excess Fe(II) in strong phosphoric-sulfamic acid, and excess Fe(II) is selectively oxidized by nitric acid in the presence of a Mo(VI) catalyst. Then the U(IV) is titrated by a dichromate solution or by cerium sulfate solution with a potentiometric titration using vanadyl as electrochemical enhancer. The overall process for the dichromate titration is:

$$Cr_{2}O_{7}^{2} + 3U^{4+} + 2H^{+} = 2Cr^{3+} + 3UO_{2}^{2+} + H_{2}O_{2}^{2+}$$

To determine the mass fraction (C_{U}) of uranium in a sample,

$$C_{II} = WT(m_s/2m_s)$$

where:

W	= the relative atomic mass of the uranium in
	the sample

- T = the titer of the dichromate solution in equivalent/gram
- m_c = the mass of dichromate solution used to reach the endpoint in gram
- m_a = the mass of sample aliquant used in the titration, in grams

2 = the electron change in U

2. USE FOR NUCLEAR FORENSICS

There are many techniques available to apply to a bulk nuclear forensic sample depending on the precision desired, instrumentation availability, expected impurities/ interferences, access to sufficient quantities of standards or reference materials, and the amount of sample provided for assay. The Davies and Gray technique is robust and precise, making this the method of choice for U assay when sufficient material is available.

3. SAMPLE REQUIREMENTS

- Sample/Standard requirement: 25 mg/titration. However, preparation of samples/standards containing 250 mg of U are needed to meet the uncertainty of 0.1%, k = 2. The remainder of the sample may be used for other analyses. This method is not appropriate for U as a minor sample component.
- This method is applicable to the determination of uranium in uranium metal, uranium oxides and nitrides, uranium-plutonium oxides, carbides, and nitrides, and to solutions containing uranium and plutonium. The method can be used to



Fig. 1. Automated titrator set up in a fume hood at Atomic Weapons Establishment for uranium assay in the United Kingdom.

determine uranium in mixed oxides in which the uranium:plutonium ratio varies from 20:1 to 2:1 and in mixed carbides and nitrides containing uranium and plutonium in a ratio of 4:1 or greater.

• This method is generally free from interferences seen, however, the following elements that are not normally present in uranium materials could interfere when at mg or higher levels: Ag, V, Pt, Au, Ru, Os, I, Sn, As, Sb, Mo, and Mn. Elements that interfere but are removed by fuming a sample prior to analysis are F, Cl, and Br.

4. PRO'S AND CON'S OF THE TECHNIQUE

Pro's:

- Several laboratories are known to produce accurate results with uncertainties at or below 0.10% for samples containing 20–30 mg of uranium. International Target Value uncertainties range from 0.14% to 0.28%, k = 2 depending on the material analyzed.
- This method is considered the 'gold standard' for uranium assay.
- This method can be automated. See Figure 1 above.
- The manual method does not require special instrumentation and can be used when sample numbers are small and infrequent.
- Method can handle a broad range of materials with little to no interferences. Pure metals, alloys, oxides, salts, carbides, and nitrides do not pose any difficulty once the sample is dissolved.
- Material is left over for other analyses.

- Method does not typically need any chemical separations, as little will interfere with the assay.
- Titrants are very stable and can be calibrated versus a number of available uranium assay CRM/SRMs.

Con's

- Chemical separations could be required if unexpectedly large impurities are present.
- Large amount of material required for initial dissolution to achieve low uncertainties for the method.

5. FAQ

- Good, commercially available instruments are available in the \$10,000-\$20,000 range. However, the method can be set up for <\$5000 using a manual weighing burette, voltmeter, analytical balance, and stir plate.
- A group of 4 samples can be analyzed in 1 week, less if the method is automated.
- Routine analysis of a control material is recommended.
- Best practices require true replicates of sample (unique sampling leading to each analysis). This allows one to determine if a material is homogenous or not at the sampled level as well as prevent erroneous data due to errors during weighting, dissolution, aliquoting, or other handling of the sample.
- This method requires chemical assay CRM/SRM.

- Care must be taken in the preparation of the materials and standards being analyzed as the method is sensitive enough to detect even small losses of material.
- It is recommended that approximately the same amount of sample, standard and control material be analyzed every time. This ensures similar chemical conditions apply for all analyses and helps keep the uncertainty associated with the analysis low.
- Calibration must be done each day that the measurement is performed.
- Some of the regents used may have limited shelf life and can require weekly preparation. If reagents are prepared and not used in the same week, their effectiveness is reduced and some reactions used to force or maintain the U in the desired oxidation state will not go to completion causing bias and uncertainty to increase.
- If using Ce(IV) titrant, care must be taken to prevent the burette tip from touching the solution. If this happens, the Ce(IV) can precipitate in the tip and clog the delivery of the titrant.
- If using Ce(IV) titrant, care must be taken when approaching the endpoint of the titration as the potential break is very sharp and easy to over titrate as compared to titrating with the Cr₂O₇ titrant.

6. REFERENCES

 Davies, Gray W., A Rapid and Specific Titrimetric Method for Precise Determination of Uranium Using Iron(II) Sulfate as Reductant, *Talanta* 11, 1964, 1203.

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DOCUMENT REVISION HISTORY

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