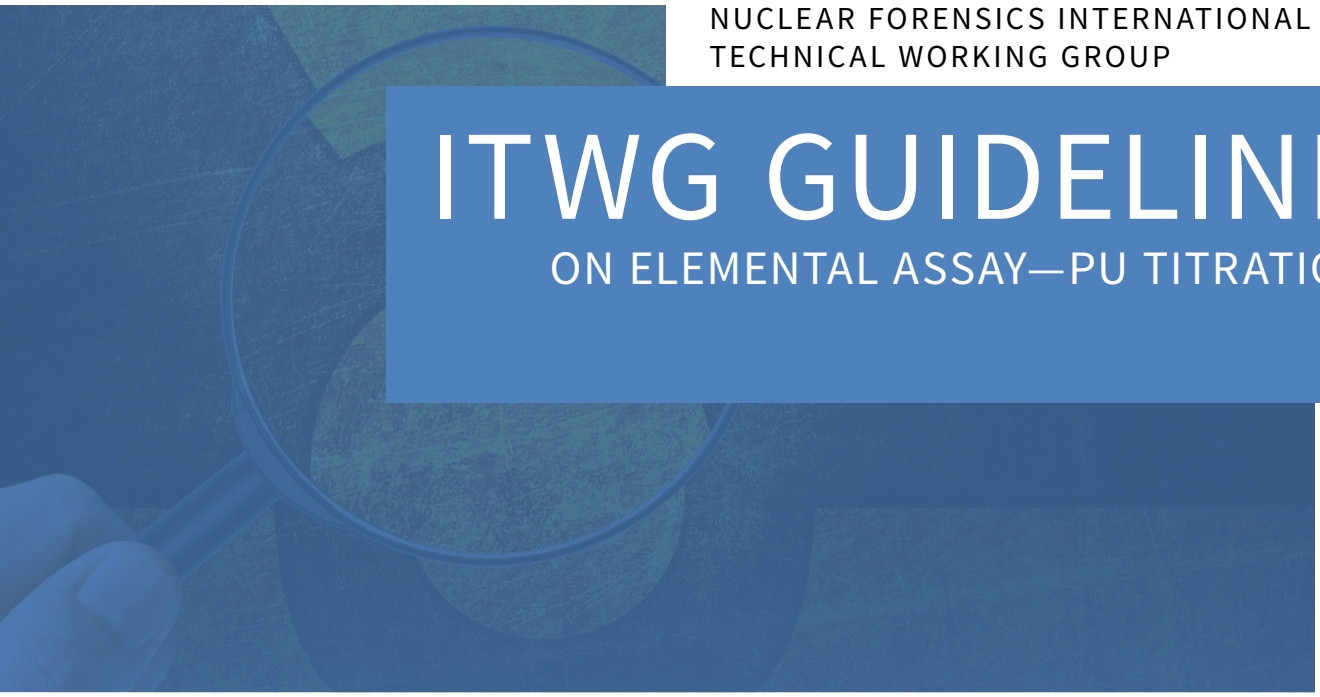

NUCLEAR FORENSICS INTERNATIONAL
TECHNICAL WORKING GROUP

ITWG GUIDELINE

ON ELEMENTAL ASSAY—PU TITRATION

EXECUTIVE SUMMARY

In this guide, plutonium (Pu) assay through titration refers to a methodology determining the Pu content in material where Pu is the major constituent. Pu 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 Pu assay techniques commonly used across the nuclear industry include coulometric titration, spectrophotometry of Pu (III) or Pu (VI) and ignition gravimetry. 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 Pu assay, but are also discussed in different ITWG documents. All these Pu 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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1. INTRODUCTION

Chemical titration is a standard method for the determination of the Pu 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. Titration methods are designated, inter alia, according to the mode of detection of the end point, e.g. potentiometric and spectrophotometric titrations.

This method is an oxidative titration of Pu(III) to Pu(IV) with an oxidant such as Ag (II), Cr(VI), or Ce (IV). The method quantitatively establishes Pu in the (III) oxidation state then titrates with a standardized oxidant solution by volume to a slight excess, then back titrates with a standardized Fe (II) solution utilizing an automated titrator. The end point can be electrochemically detected using a potential break as the excess oxidant is titrated. The back titration allows for an enhanced precision as only a slight excess of oxidant is used. A couple variations of this methodology have been used by various nuclear laboratories including use of a ferroin colorometric endpoint with the Ce titrant after the Pu has been oxidized. A simple automated system is shown in Figure 1.

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.

3. SAMPLE REQUIREMENTS

- The sample/standard requirement is about 250 mg Pu/titration. This method is not appropriate for Pu as a minor sample component. The analysis will use the entirety of the dissolved sample with none left over for other analyses. Some laboratories have developed methods that require less than 250 mg/titration, however larger sample sizes are more typical.
- Main interferences for this method are from Fe, U and Np as the titration will simultaneously and quantitatively oxidize these elements. However, the assay can be easily corrected for small amounts of these interferences using the relative atomic weight

Fig.1. Automated system using Metrohm titrators used for Pu assay at Los Alamos National Laboratory.

and electron charge for each element. This will require additional analyses of the material to be completed for trace elements.

- When large amounts of these elements are present such as with a mixed oxide nuclear fuel material, other methods are a better choice.

- Given the relatively large sample size this method typically requires, use for materials with significant quantities of Pu-238 is not recommended due to formation of radiolysis products as well as radiation exposure risks to analysts.

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

Pro's:

- This method is capable of the best uncertainty for pure metals (0.05% expanded uncertainty, k = 2) of all the Pu assay methods. For most Pu materials the International Target Value (ITV) uncertainty is 0.21%, k = 2.

- The method is very robust with the fewest steps and transfers of materials and requires less laboratory technical skills than coulometry (see separate ITWG guideline).

- Inexpensive, commercially available instrumentation available.

- This method has the potential to be automated.

Con's:

- The method has a large number of interferences and is best used on pure Pu metal or known alloys. Very pure Pu oxides may also be analyzed, but salts, carbides, nitrides, etc. are not recommended for this method as they often contain larger amounts of impurities that will react with the titrants.

- Uses large amounts of material for standards, control materials and sample in comparison with other available assay techniques.

- This analysis will use the entirety of the dissolved sample with none left over for other analyses.

5. FAQ

- Good, commercially available instruments are available in the US$10,000–$20,000 range.

- A group of 4 samples can be analyzed in 2–3 days from receipt, dissolution through final data reporting.

- Routine analysis of a control material is recommended.

- Best practice requires 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 weighing, dissolution, aliquoting, or other handling of the sample.

- Best practice requires that all processing be gravimetric because of the high accuracy and low uncertainty achievable for this method.

- This method requires CRM/SRM plutonium assay standards.

- This method is best utilized for pure Pu metals or known alloys, but can be adapted to accommodate oxide materials with the proper reduction of the Pu prior to titration.

- Pu titration provides the best uncertainty of Pu assay methods for pure metals.

6. REFERENCES

1. ASTM C1206 – 02 (Reapproved 2010) Standard Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration.

2. Zendel M., Donohue D.L., Kuhn E., Deron S., Biro T., *Handbook of Nuclear Chemistry*, chpt. 63, section 63.4.5.3, Plutonium Titration, pp. 2973–2974, 2011.

DOCUMENT REVISION HISTORY

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