Development of Primary Certified Reference Materials (PCRM™)

Primary SI Traceable Solution Standards For Iridium and Osmium

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INORGANIC VENTURES

What is a Primary Solution Standard?

Measured value is obtained by means of a **primary reference measurement procedure**. [1, 2]

Gravimetry, or measurement by weight, is a primary measurement procedure.

1. VIM_JCGM_200_2012, section 5.4
2. VIM_JCGM_200_2012, section 2.8

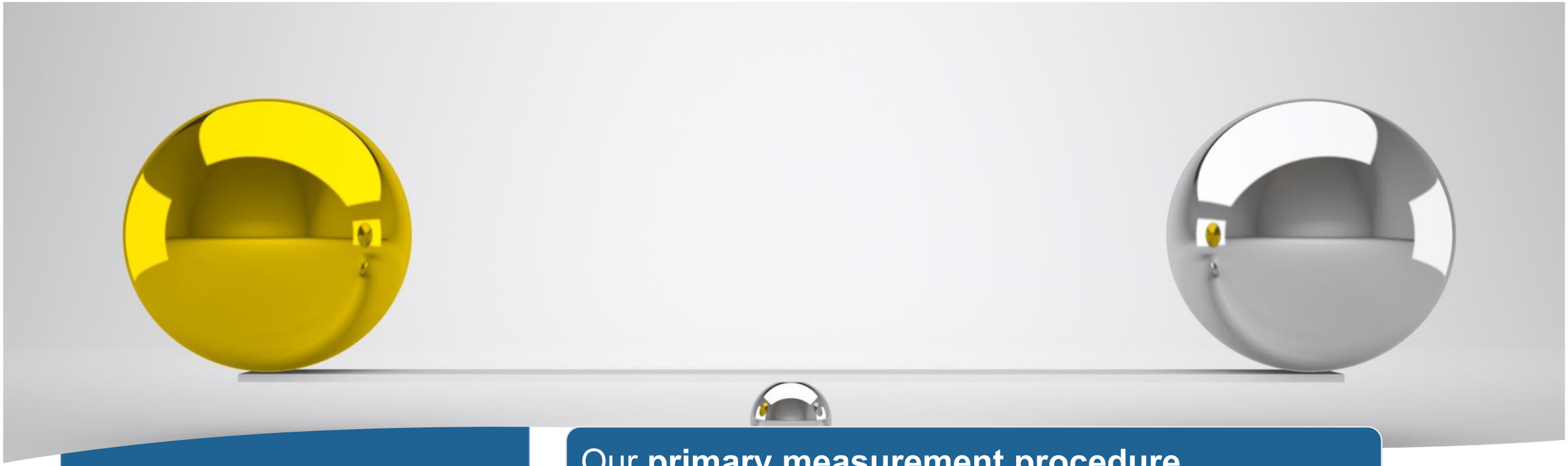
What is SI Traceability?

Your measured value is linked or traced to the International System of Units, the SI.

The SI was established in 1960.

There are 7 base units in the SI.[3]

Base Quantity	Base Unit	Symbol
Time	Second	s
Length	Meter	m
Mass	Kilogram	kg
Electric Current	Ampere	A
Thermodynamic Temperature	Kelvin	K
Amount of Substance	Mole	Mol
Luminous Intensity	Candela	cd



Establish SI traceability?

Our **primary measurement procedure** was **Gravimetry**, or measurement by weight.

The kilogram (kg) is one of the 7 base units of the SI.

Thus, we obtain traceability to the SI through the kg.

Why develop a primary SI traceable solution standard?

Ensure the accuracy of our Os and Ir Certified Reference Materials (CRMs).

No National Metrology Institute (NMI) has an SI traceable solution standards for Os and Ir.

Why develop a primary SI traceable solution standard?

- ISO is the International Organization for Standardization.
- Accreditation to the ISO 17034 and ISO 17025 standards is essential for a CRM manufacturer .
- Primary Requirement: Metrological traceability to the SI.

Requirements for SI traceability?

Primary Measurement Procedure

Purity Analysis of the candidate Starting Materials

Starting Materials

Candidate SI traceable starting materials

- Os and Ir salts:
  - Ammonium hexachloroosmate
  - Ammonium hexachloroiridate hydrate

High purity Os and Ir metal powders

Experimental Design

Followed the approach used by Beck, Salit et al. at NIST when they developed the Rh SRM. [1]

Determine the Os or Ir mass fraction in the candidate metal salt.

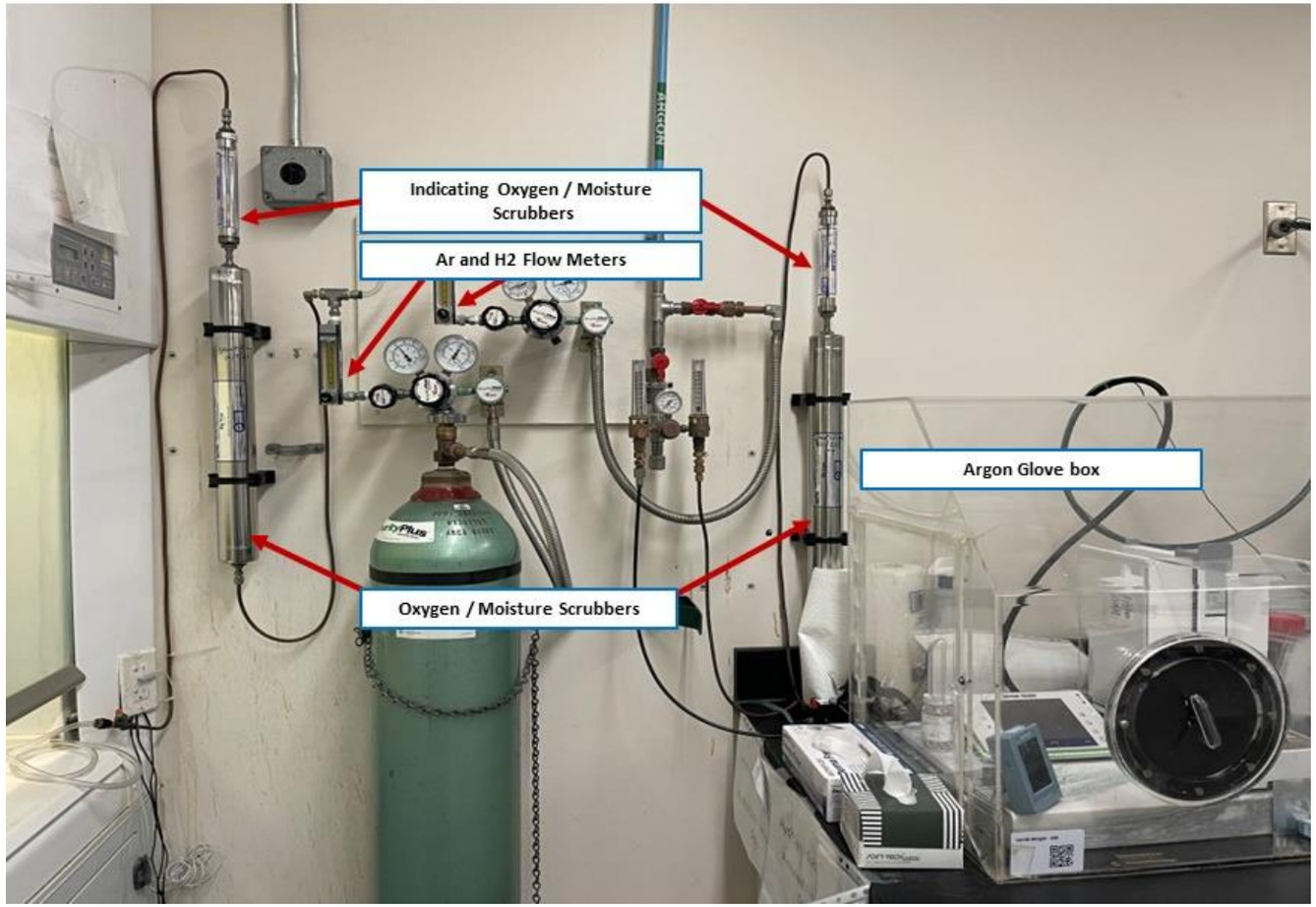
- Gravimetric Reductions of the salt to the metal
- Establishes SI traceability of the candidate starting material

High purity Os or Ir metal powder

- An independent source of Os or Ir
- Used as a standard for comparison

[1]Beck, C. M., II; Salit, M. L. Preparation and Certification of a Rhodium Standard Reference Material Solution. Anal. Chem. 1993, 65, 2899– 2902, https://doi.org/10.1021/ac00068a030

Eliminate Systematic Errors

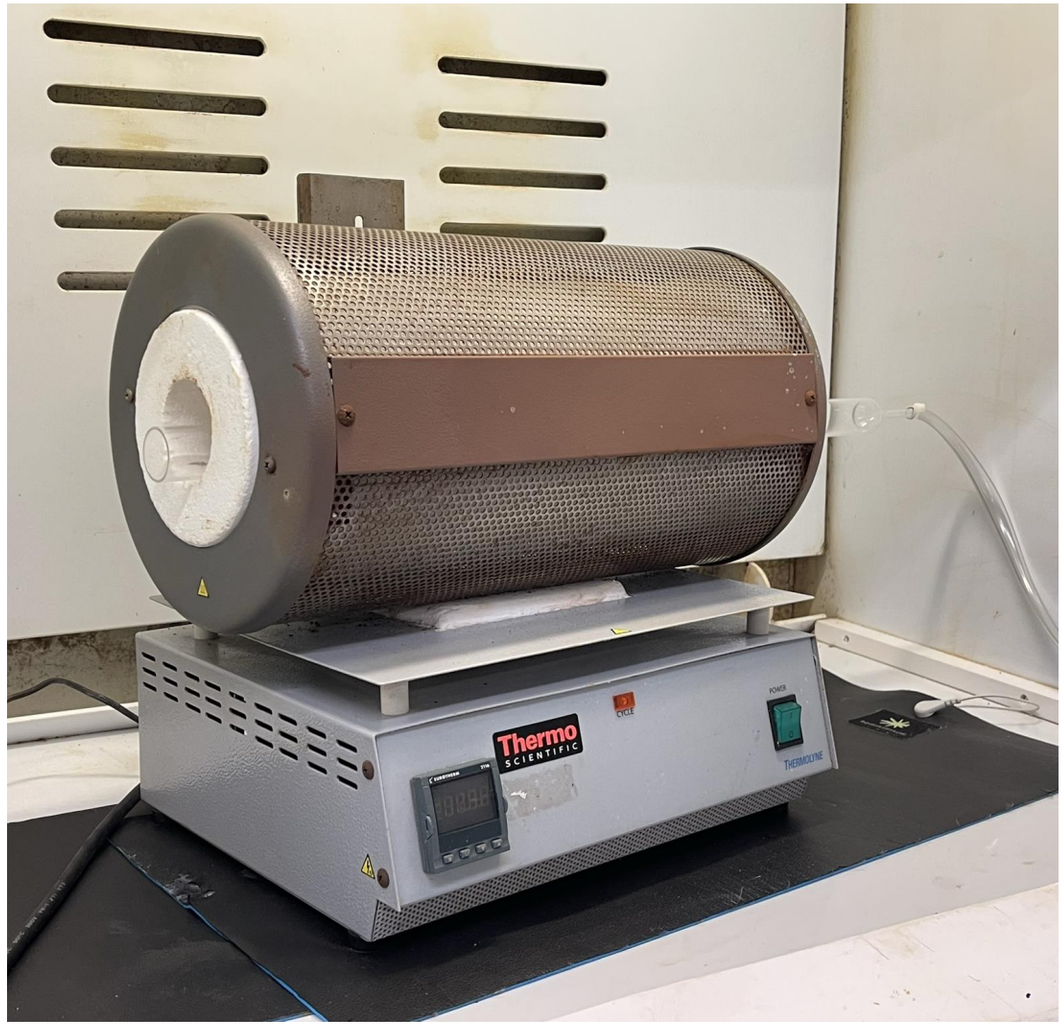


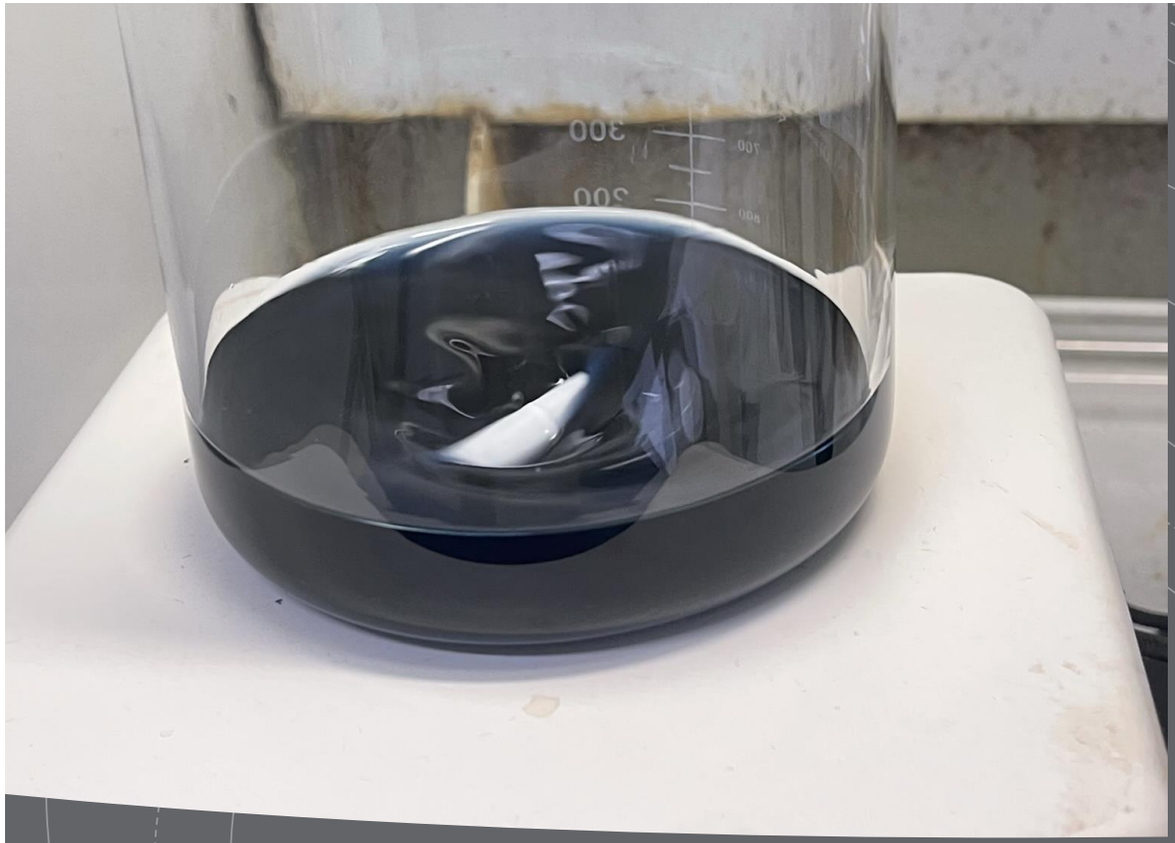
Major Systematic Errors

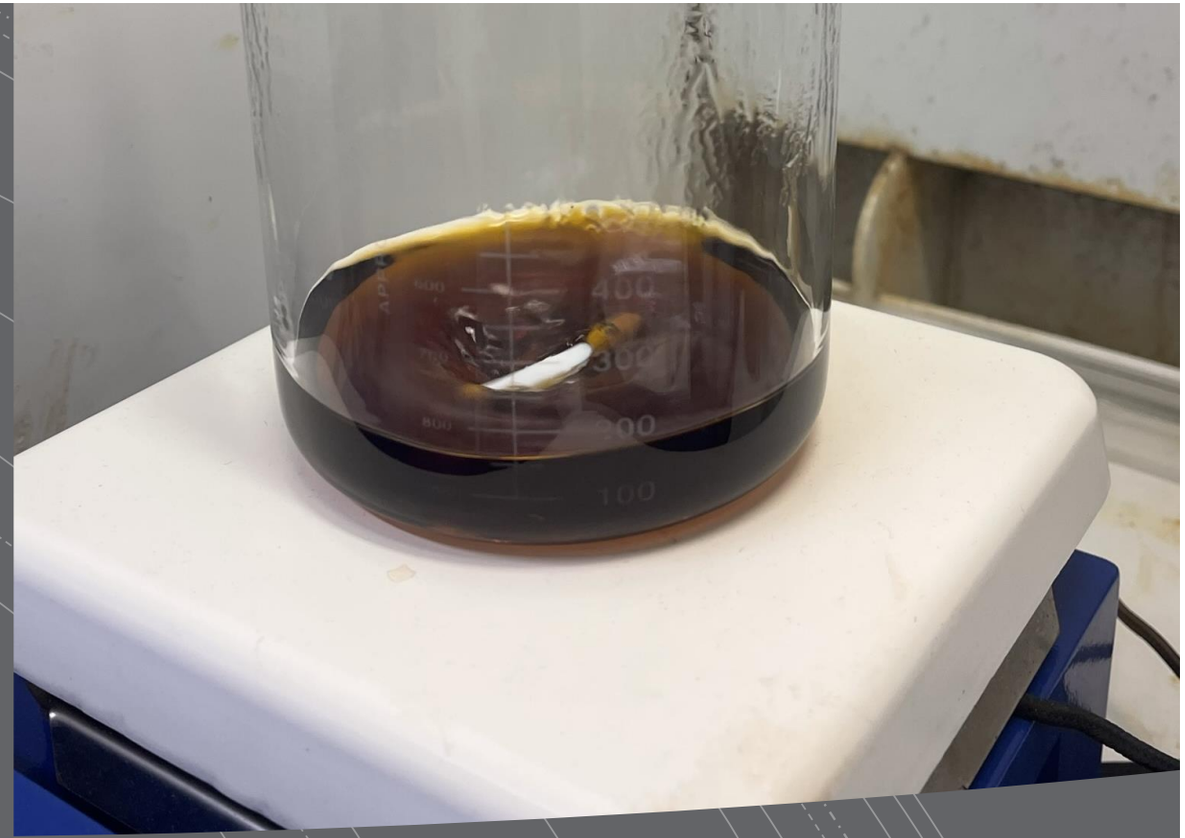
- Exposure to air/moisture
- Static

Gravimetric Reduction

- Reduce the starting material, Os or Ir salts, to Os or Ir metal under H_2 at high temperature.
- Weighing, gravimetry, is the primary measurement procedure.
- SI Traceability: through weighing the salt and metal gravimetric reduction products.
- Determine the mass fraction of metal in the salt.

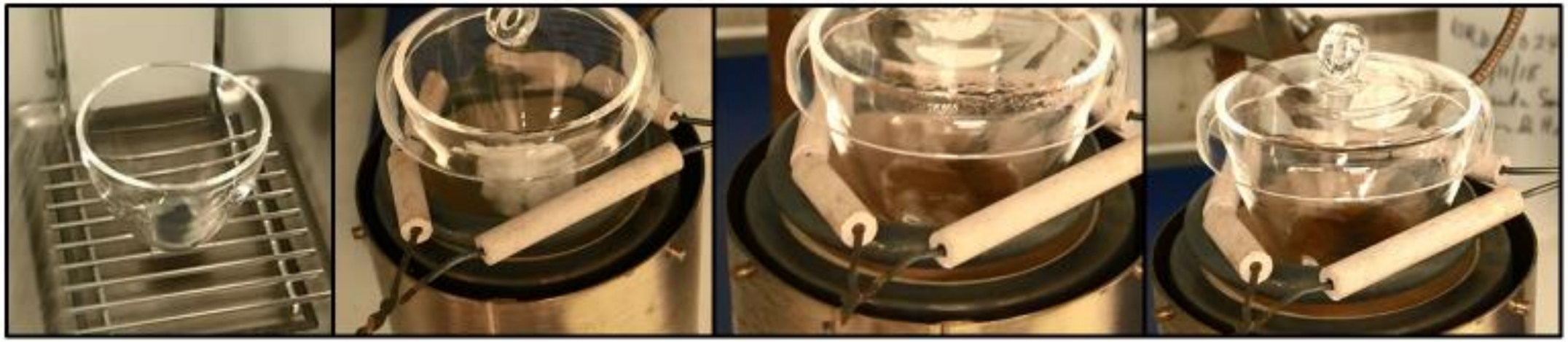






Dissolution of the Metal

$NaOH$ / $NaNO_3$ Fusion



Sample Os^0 weighed into quartz crucible

$NaOH$ and $NaNO_3$ added on top of the sample

$NaOH$ and $NaNO_3$ almost completely melted

$NaOH$ and $NaNO_3$ completely melted, metal fully dissolved

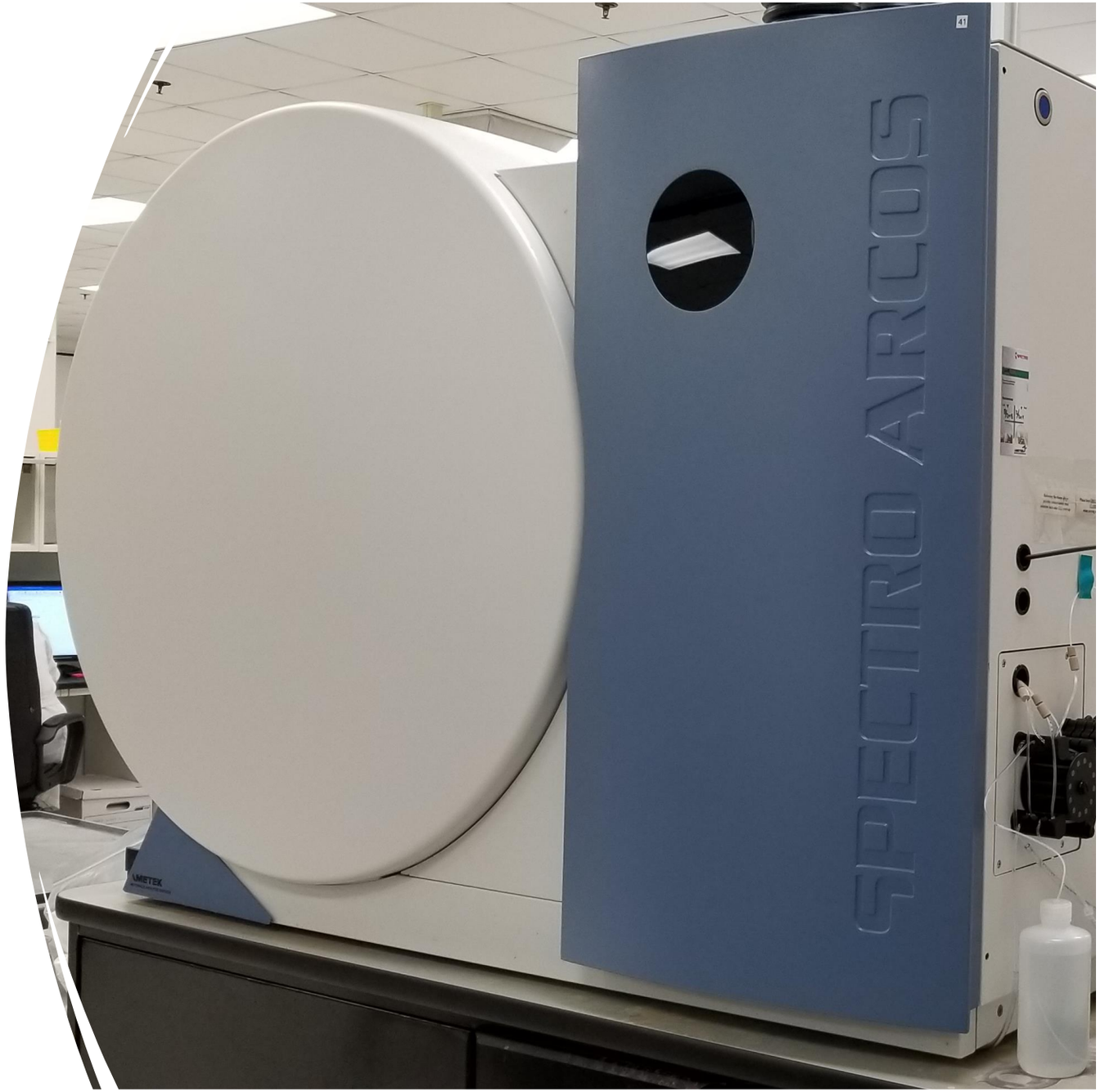
Purity Analysis:
Requirement for Establishing SI Traceability

- Trace metallic Impurities (TMI) analysis was performed on solutions of the candidate SI traceable salts
- Inert Gas Fusion analysis was performed to determine estimates of the O, N, and H impurities.
- The combined impurities from TMI and IGF analysis were applied as corrections to the mass fraction of Ir or Os in the starting material

ICP-OES Comparison

The metal mass fraction in the salts was found by Gravimetric Reduction.

- Highly reproducible results
- The accuracy of the results must be confirmed.

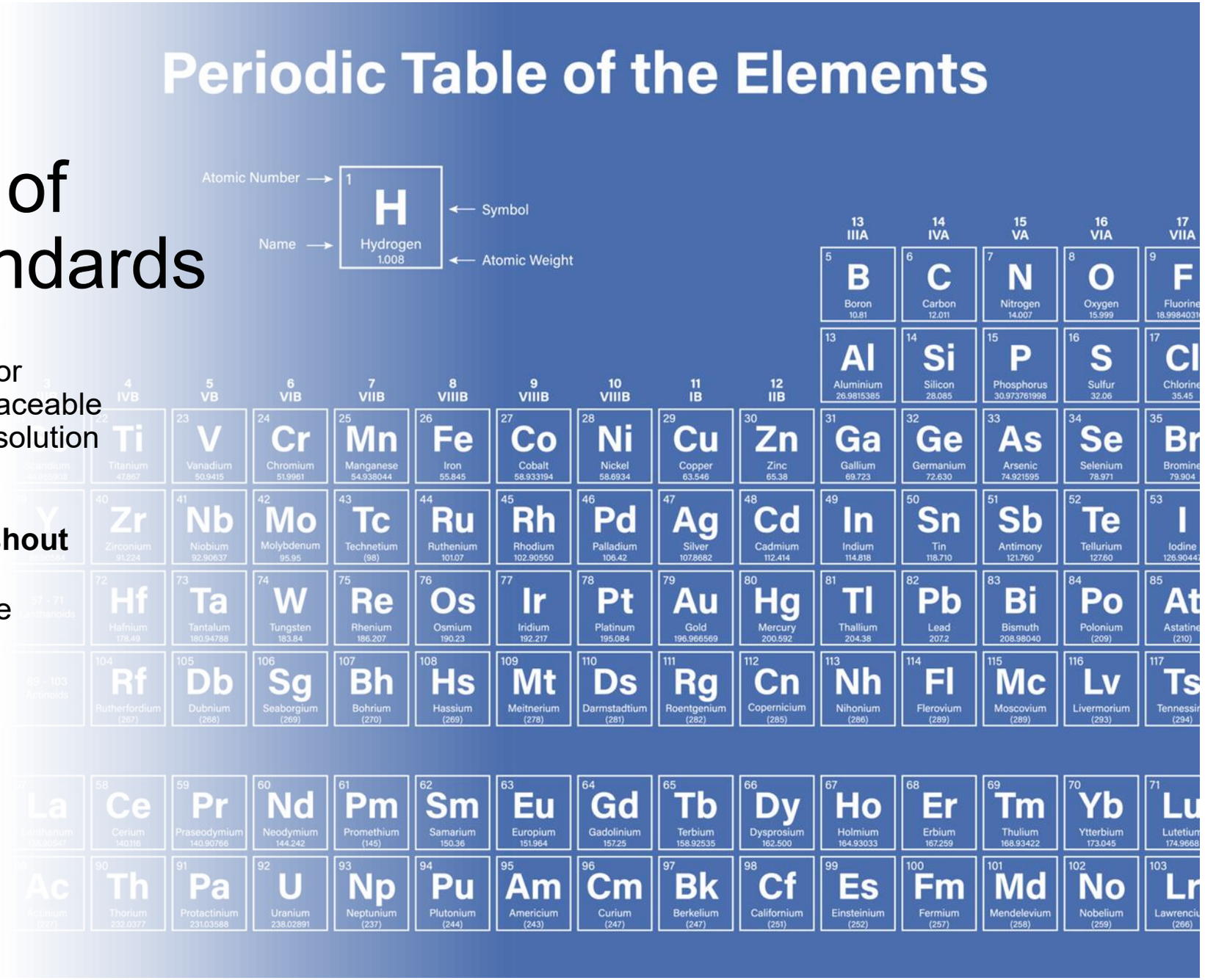


ICP-OES Comparison of Solution Standards

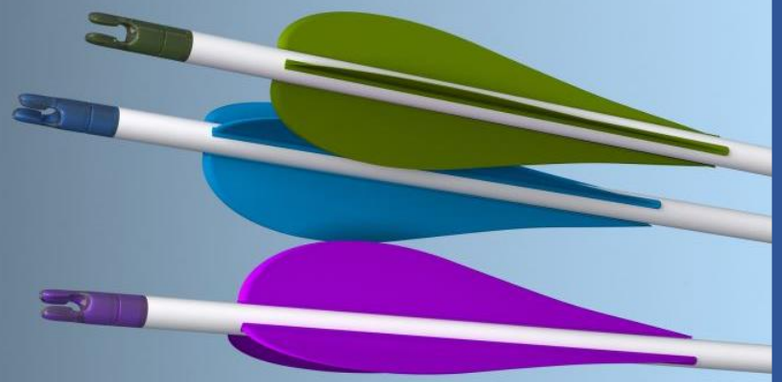
Solution standards are made from the two independent starting materials.

- Solution standards are made from the candidate SI traceable salt.
- The comparison solution standard is made from the dissolved high purity Ir or Os metal powders.

ICP-OES Comparison of Solution Standards



- **Accurate matrix matching** and/or **internal standardization** of SI traceable solution standard to comparison solution standard
- Careful **monitoring** of metal **washout**
- **Natural aspiration** function of the nebulizer
- Large number of replicates
- Bracketing of samples



ICP-OES Comparison Results

- Results for candidate SI solution standards were < 0.1% from the calculated values.
- Demonstrated the accuracy of the candidate SI traceable solution standards.
- The high precision of the analysis lowered the ICP-OES uncertainty.

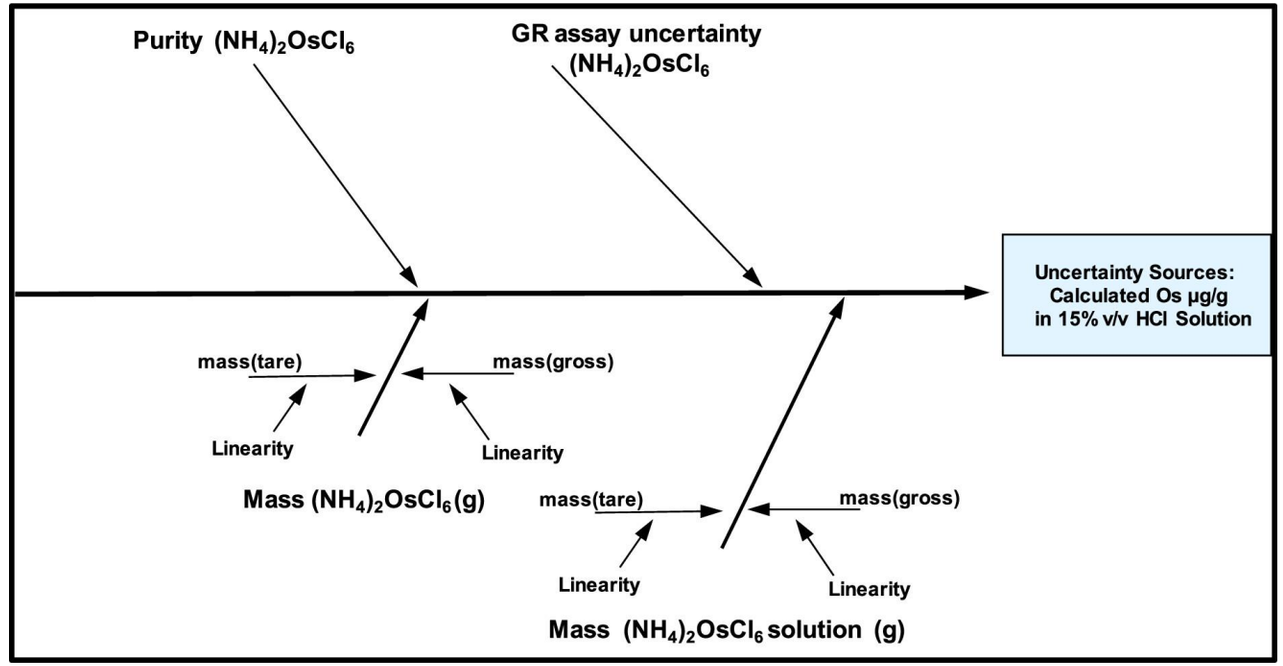
Uncertainty Estimates

- ISO 17034 and ISO 17025 accreditation requires reporting the uncertainty in a certified value
- Make uncertainty estimates using:
  - Cause and Effect diagrams
  - Error budget analysis.

Uncertainty Estimates

Cause and Effect diagram

Uncertainty sources in the preparation of the Os Solution standard in 15% v/v HCl.



Uncertainty Estimates

Error Budget Analysis

	Error Budget Contributions: Preparation of Os Solution Standard in 15% v/v/ HCl	Individual Uncertainty Contributions (u_x)	Value (X)	Relative Uncertainty = $(u_x / X)^{\wedge 2}$
GR assay uncertainty $(NH_4)_2OsCl_6$	Precision of GR assay			1.27E-06
Purity $(NH_4)_2OsCl_6$	Purity	0.0002	0.9979	4.02E-08
Mass $(NH_4)_2OsCl_6$ (g)	Weight of $NH_4)_2OsCl_6$	0.0001g	1.16g	4.95E-09
Mass $(NH_4)_2OsCl_6$ solution (g)	Weight of $(NH_4)_2OsCl_6$ solution	0.02g	500g	1.07E-09
	CRU = Combined Relative Uncertainty = $(\sum(u_x/x)^{\wedge 2})^{\wedge 0.5}$			1.15E-03
Expanded Uncertainty of Characterization	Expanded Uncertainty = 2 * Os (µg/g) * CRU = 2*1000*0.00115			2
	Os (µg/g) Calculated			1000

Error Budget for the Preparation of the Os Solution Standard in 15% v/v HCl

In Summary

Primary SI traceable solution standards for Os and Ir

Certified Value (µg/g)
± Expanded Uncertainty (µg/g)

Low uncertainties:
fit for purpose as
Calibration Standards

ISO 17034 and ISO 17025 accreditation