TANAKA

LBMA A&R Conference 2023

Precise Quantification of Rh by Standard Bracketing Measurement in ICP-OES

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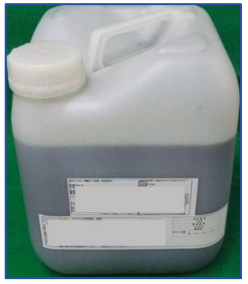
Introduction

Ichikawa plant



Rh-compound

Ir-compound

Ru-compound

INTERNATIONAL STANDARD **ISO 11494**

Third edition
2019-07

Jewellery and precious metals — Determination of platinum in platinum alloys — ICP-OES method using an internal standard element

Joaillerie et métaux précieux — Dosage du platine dans les alliages de platine — Méthode par ICP-OES utilisant un étalon interne

ISO 11494:2019

Title

Jewellery and precious metals - Determination of platinum in platinum alloys - ICP-OES method using an internal standard element

6 important points of ISO 11494

1) Y used as internal standard
2) Weigh 100 g of Y liquid accurately to 0.01 g
3) Bracketing measurement
4) 99.99% Pt is used as standard material for standard solution
5) Weigh Pt accurately to 0.01 mg
6) Complete dissolution with aqua regia

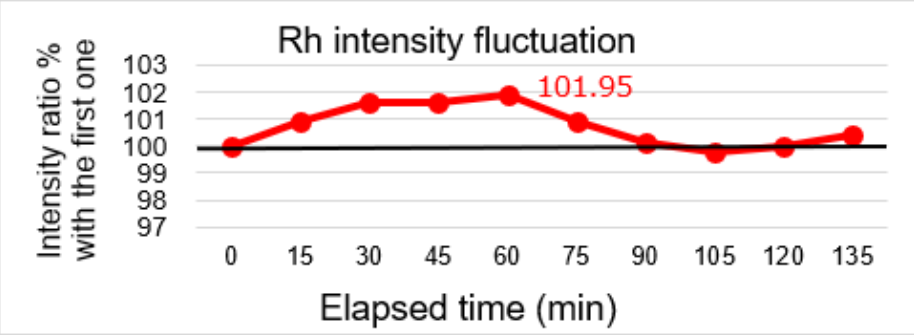
Effects of internal standard method

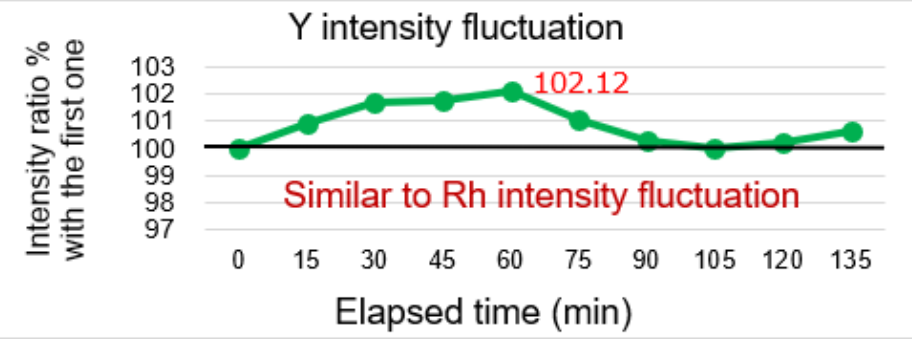
Internal standard method

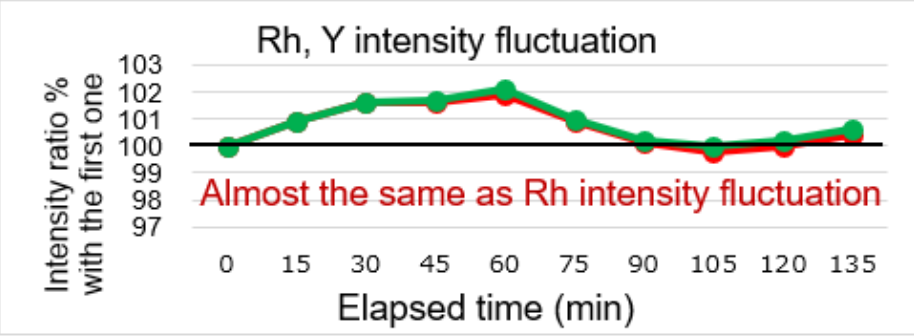
A method to reduce the fluctuation by using the intensity ratio with the element that fluctuates almost the same as Rh

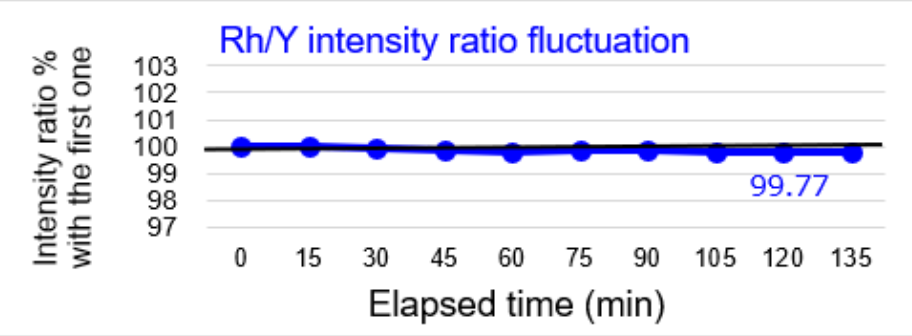
Compare Rh intensity fluctuation and Y intensity fluctuation

Rh 50 mg/L, Y 5 mg/L solution measured every 15 minutes for 2 hours









Problems of internal standard method

General internal standard element addition method

Add the same amount of internal standard element to all standard solutions and sample solutions to make the concentration constant

Actual addition method in Japan

Collect the volume of the internal standard solution with a volumetric pipette and pour it out

Problems of pipetting volume

Amount collected changes	Repetition and individual differences
Marked line has tolerance	10 mL tolerance ± 0.02 mL
Weight change with temperature	Change in density

For internal standard material, solid metal is better

Internal standard material

Ideal internal standard element

Terms	Y	In
Dissolvable	●	●
Intensity fluctuation is similar to Rh	●	?
Stable metal	×	●
High purity	●	●

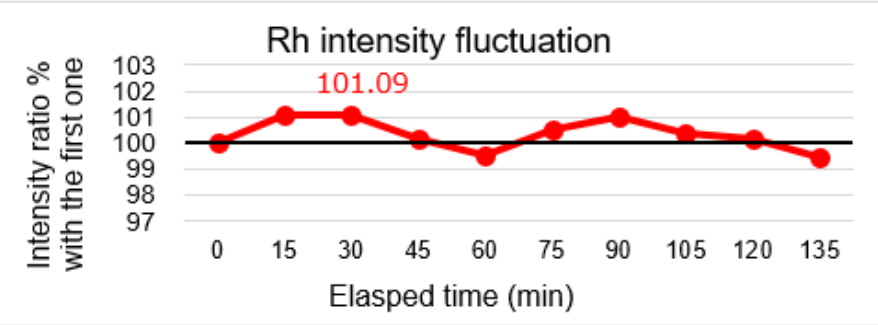
In metal is stable in the atmosphere

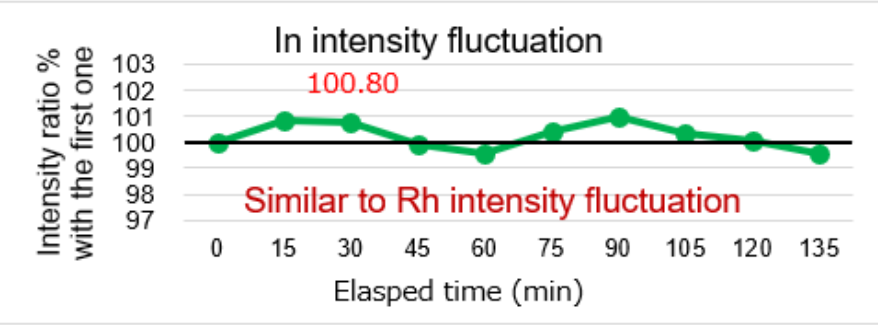
99.999% metal can be sourced

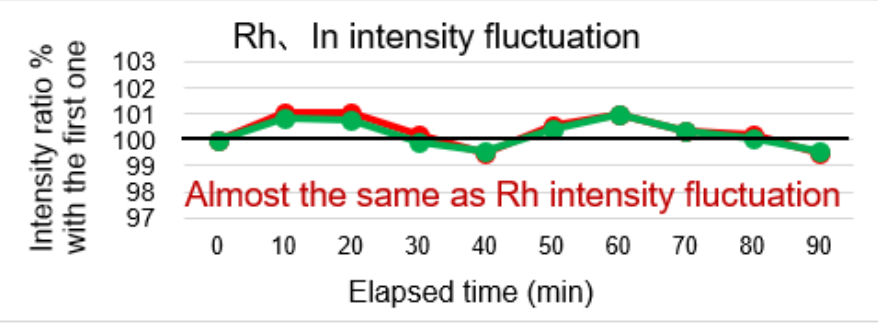
Effects of internal standard method by In

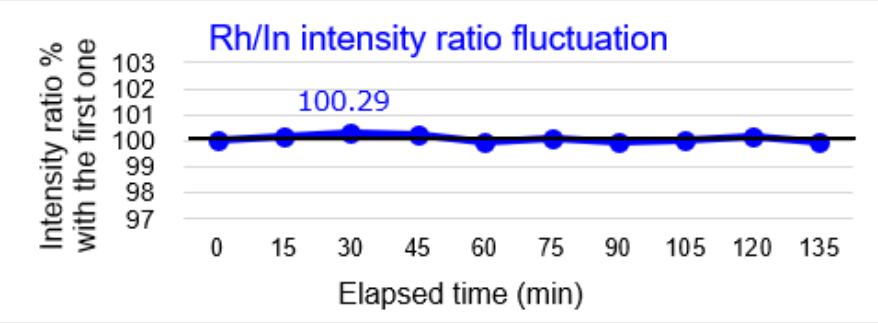
Compare Rh intensity fluctuation and In intensity fluctuation

Rh 50 mg/L, In 150 mg/L solution measured every 15 minutes for 2 hours









In intensity fluctuation is almost the same as Rh

99.999% In metal is stable in the atmosphere and can be sourced

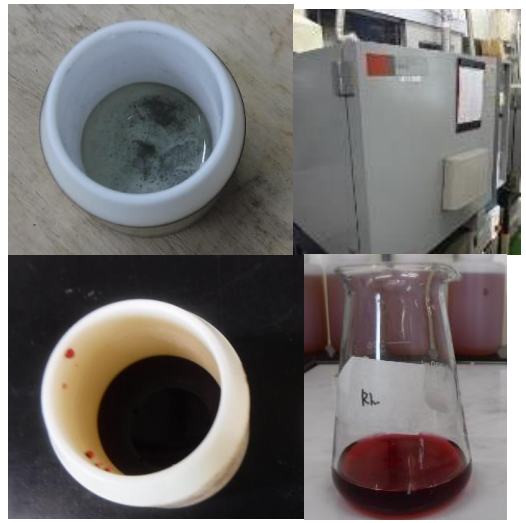
Rh standard material

Internal standard method

$$\frac{\text{Rh intensity}}{\text{In intensity}} : \frac{\text{Rh weight g}}{\text{In weight g}}$$

The last important parameter is the exact weight of Rh in the standard solutions

Element	Rh	Rh
Condition	solution	Sponge
Stability	●	●
Accuracy	×	●



Rh sponge dissolves in aqua regia under high temperature and pressure

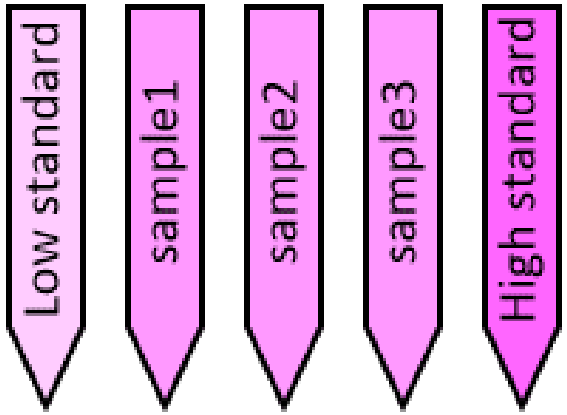
Experiment 1

Bracketing measurement of Rh pure solutions

- Purpose: Confirm accuracy of Rh Bracketing measurement
- Contents: The Rh recovery rate was determined by performing bracketing measurements for 10 days, bracketing a total of 3 samples (3 Rh pure solutions) between standard solutions

Solution preparation: weight ratio

Solution type	Rh mg	In mg
Low standard solution	70	300
High standard solution	130	300
①②③Rh pure solutions	100	300



Experiment 1 preparation of Rh pure solutions

Flow 1 Preparation of Rh/In weight ratio solutions

Analytical balance Mettler XP-26

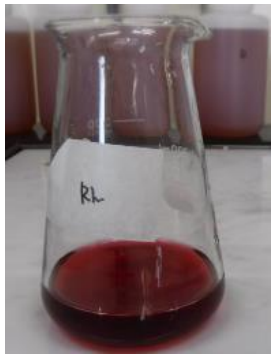
Weight measuring

100 mg 99.99 % Rh sponge

300 mg 99.999 % In metal

→

Dissolution



In aqua regia

In hydrochloric acid

→

Heat to expel the nitrogen oxides

→

❶❷❸

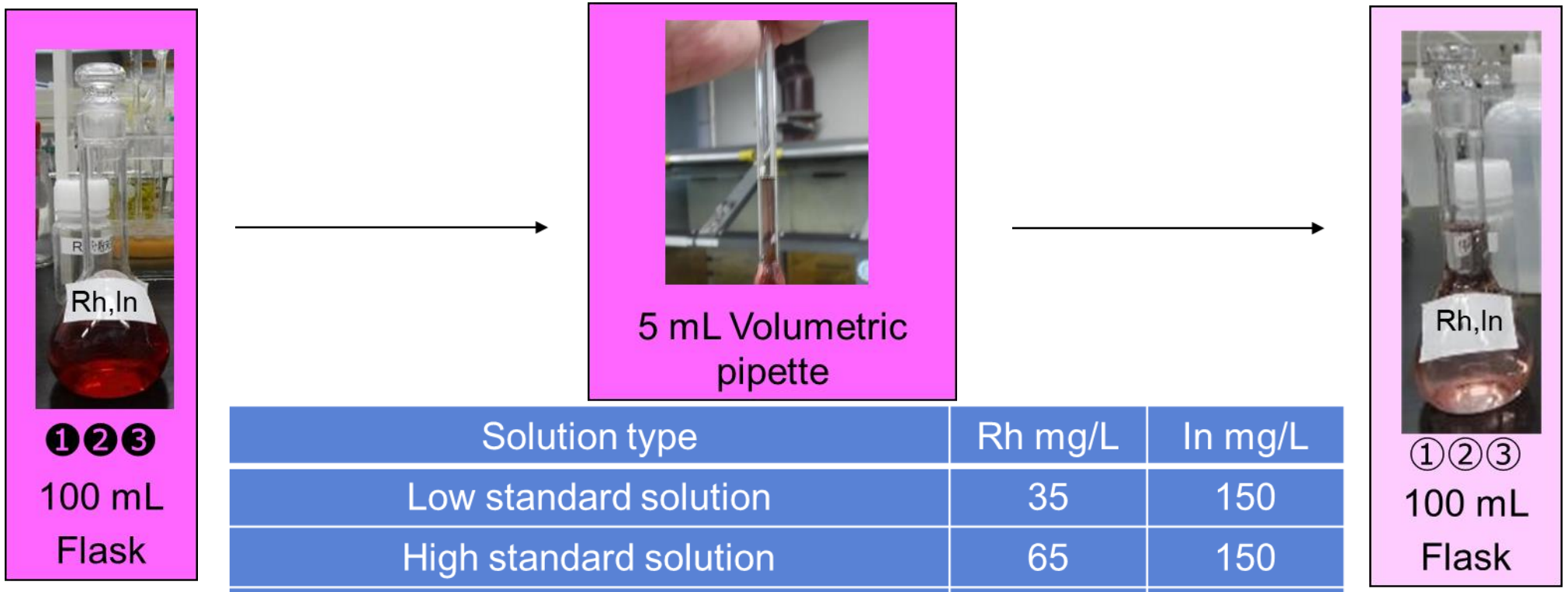
100 mL Flask

Transfer Rh solution and In solution in the same 100 mL flask

→ weight ratio: Rh 100 mg / In 300 mg

Experiment 1 preparation of Rh pure solutions

Flow 2 Preparation of ICP-OES measurement solutions



Solution type	Rh mg/L	In mg/L
Low standard solution	35	150
High standard solution	65	150
①②③Rh pure solutions	50	150

Rh/In weight ratio remains the same after dilution

Experiment 1 ICP-OES conditions

Equipment

Thermo Fisher Scientific iCAP6500

Torch vertical type

Radial view

Coaxial nebulizer

Tracey Spray Chamber

Auto Sampler

Wavelength

Rh 343.489 nm(I)

In 410.172 nm(I)

Measurement Conditions

RF output 1250 W

Plasma gas flow rate 12 L/min

NEB gas flow rate 0.65 L/min

AUX gas flow rate 0.5 L/min

photometry position 15 mm

Integration time 10 sec, 2 times

Sample replacement 100 rpm, 30 sec

Experiment 1 calculation

Pre - calculation

- Divide the In intensity (I(In)) by the In weight (W(In)) for each
  Q(In) = I(In) / W(In)
- Rh weight corrects with Rh sponge purity

Rh - Calculation

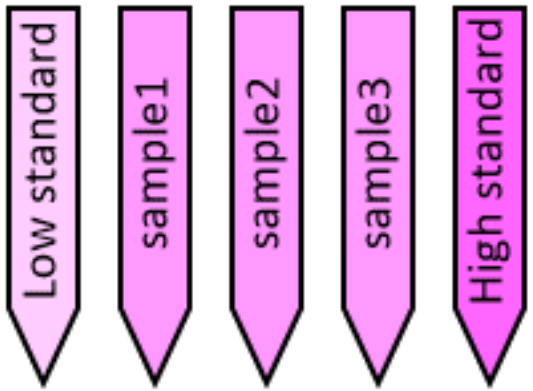
- $mRh1 = L + \frac{(H - L) \cdot (QCs1 - QCL)}{(QCH - QCL)}$

L : Low standard Rh weight mg
H : High standard Rh weight mg
QCL : Low standard Rh/In intensity ratio
QCH : High standard Rh/In intensity ratio
QCs1 : Sample1 Rh/In intensity ratio

Rh recovery rate - Calculation

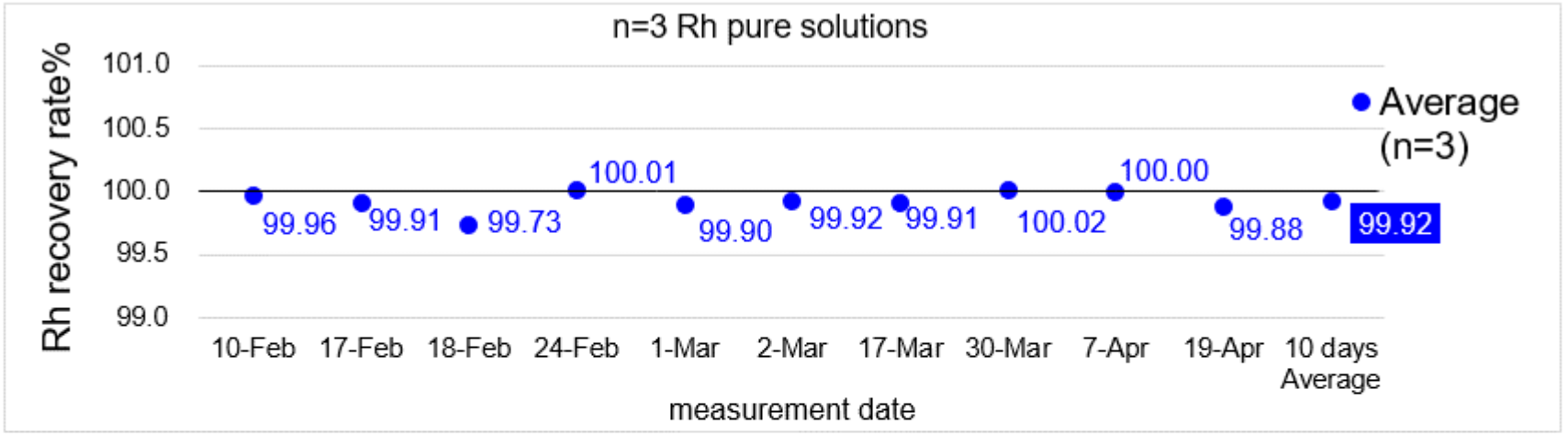
- Rh recovery rate % = $\frac{mRh1 \cdot 100}{Wsa1}$

Wsa1 : Sample1 Rh weight mg



Experiment 1 results

10 days data of Rh recovery rate



Rh pure solutions (n=3) 10 days Average **99.92**% RSD 0.10%

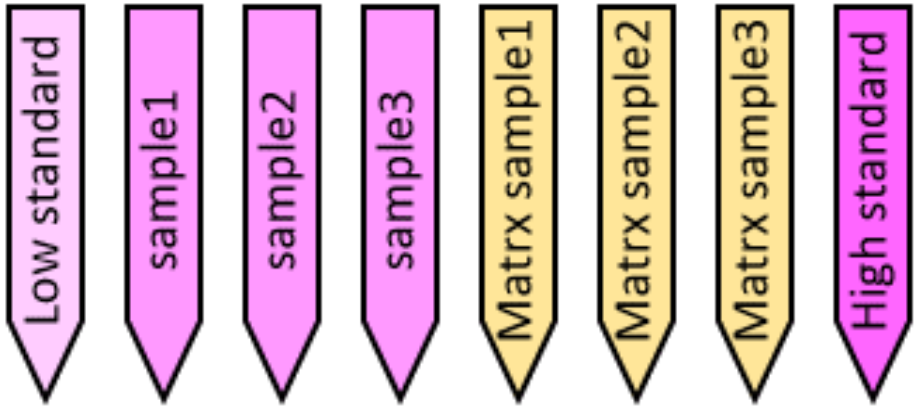
Experiment 2

Simultaneous bracketing measurement of Rh pure solution and Rh matrix solution

- Purpose: Confirmation of Fe, Mo, Ni matrix effects in Rh bracketing measurement
- Contents: The Rh recovery rate was determined by performing bracketing measurements for 2 days, bracketing a total of 6 samples (3 Rh pure solutions and 3 Rh matrix solutions) between standard solutions
- Solution preparation: Standard solutions L, H, and 3 sample solutions are the same as those used in experiment 1

- Composition ratio of Rh matrix solution
  Rh 100 mg : Fe 200 mg : Mo 40 mg : Ni 20 mg
  Synthetic Rh 278 ‰ alloy with Fe, Mo, Ni

Bracketing measurement procedure



Experiment 2 Preparation of Rh matrix Solutions

Flow 3 Preparation of ICP-OES measurement solutions

Dilution 20x

←

←

Pipetting

←

→

Pipetting

→

→

→

Dilution 20x

Rh pure solution from Experiment 1

Solution type	Rh mg/L	In mg/L	Fe mg/L	Mo mg/L	Ni mg/L
①②③Rh pure solutions	50	150	–	–	–
④⑤⑥Rh matrix solutions			100	20	10

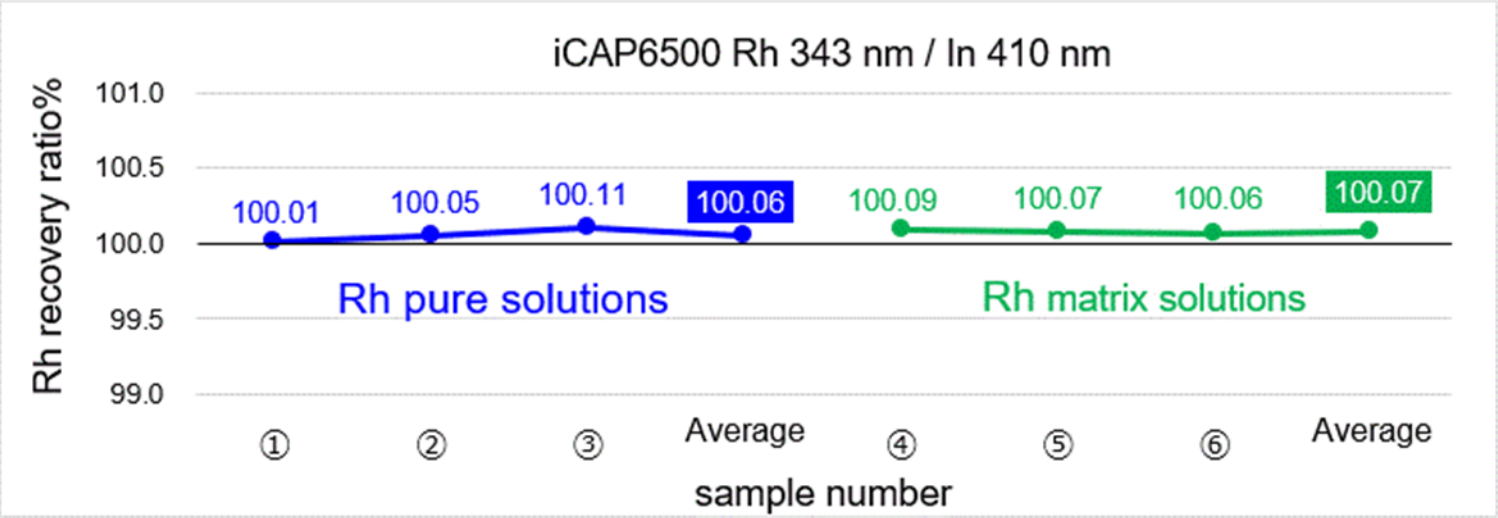
Rh matrix solution

The Rh/In weight ratio of Solution ① and Solution ④ are exactly the same

Experiment 2 Results 1

2-day average data of Rh recovery rate

Measured Rh amounts were corrected by Mo spectral interference amount



Rh recovery rate

Rh pure solution Average **100.06**% RSD 0.05%

Rh matrix solution Average **100.07**% RSD 0.02%

Change ICP-OES conditions

Equipment

Thermo Fisher Scientific iCAP-PRO-DUO

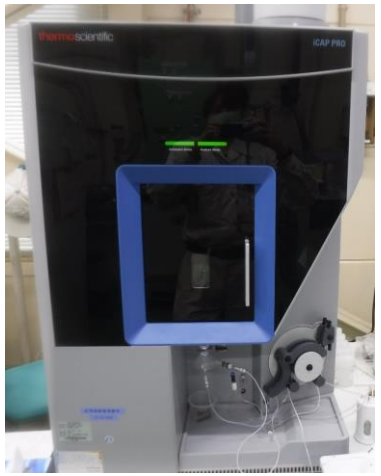
Torch vertical type

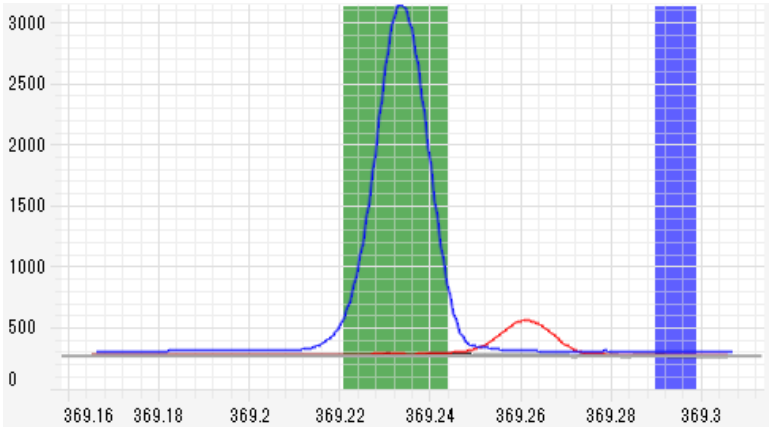
Radial view

Coaxial nebulizer

Twister Cyclonic Spray Chamber

Auto Sampler





Mo 20 mg/L

Rh 50 mg/L

Wavelength

Rh 369.236 nm(I)

In 303.936 nm(I)

Measurement Conditions

RF output 1250 W

Plasma gas flow rate 12 L/min

NEB gas flow rate 0.65 L/min

AUX gas flow rate 0.5 L/min

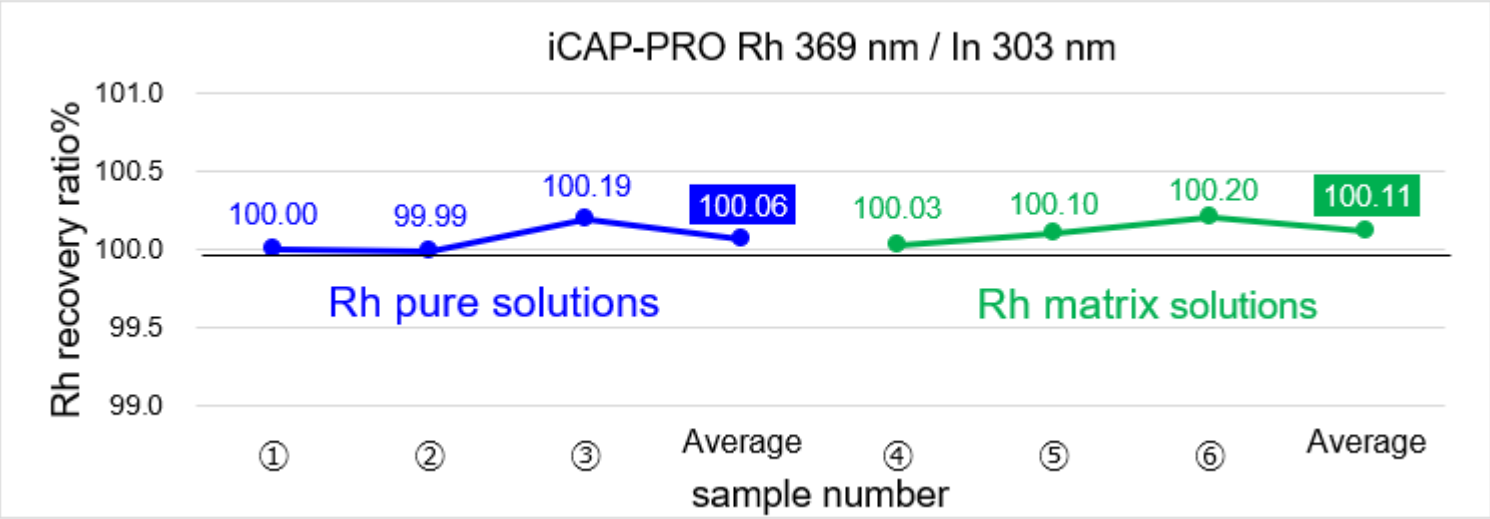
photometry position 15 mm

Integration time 20 sec, 3 times

Sample replacement 45 rpm, 60 sec

Experiment 2 results 2

2-day average data of Rh recovery rate



Rh recovery rate

Rh pure solutions Average **100.06**% RSD 0.11%

Rh matrix solutions Average **100.11**% RSD 0.09%

No matrix effect on Synthetic Rh 278‰ alloy with Fe, Mo, Ni

Summary

- We customized the bracketing method described on ISO 11494 for the determination of Rh, for which no international standard is available
- This new method allows Rh determination with high accuracy
- Matrix matching was not required in our case, but this should be checked for each analysis
- This method can also be applied for the determination of Ir & Ru

If you have any question, please contact me at m-amano@ml.tanaka.co.jp