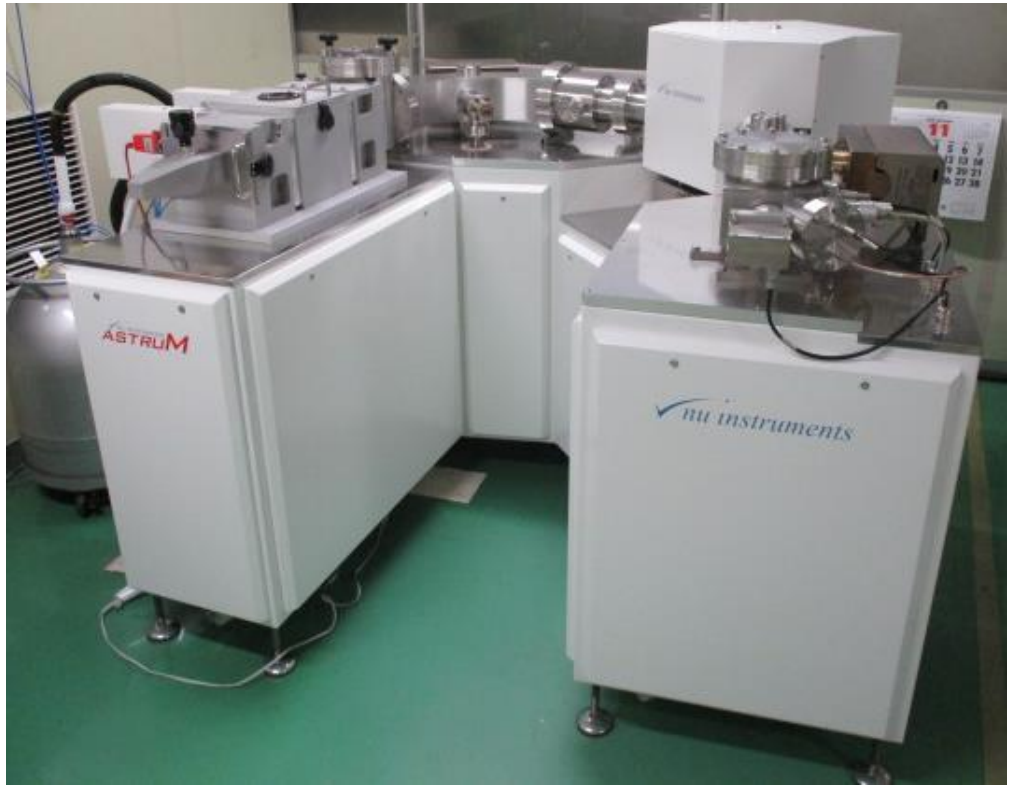
A Study on a Verification of Trace Elements in Precious Metals analyzed by GD-MS



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Agenda

1. Status of GD-MS use in TANAKA
2. Characteristics of GD-MS
3. Configuration of GD-MS AstruM
4. Measured values by GD-MS
5. Comparison of measured values in GD-MS
6. Verification results using CRM
7. Fineness evaluation
8. Summary

1. Status of GD-MS use in TANAKA

- GD-MS (VG9000) installed in 1997, analyzing trace elements in various precious metals and their alloys.
- GD-MS (AstruM) made by Nu Instruments installed in 2015
- Spark-OES, Spark-ICP, and GD-MS utilized for trace element quantitative analysis of solid samples.
- At the beginning in-house standards prepared were used, then in 2009 CRMs from LBMA and LPPM were available for GD-MS analysis.

2. Characteristics of GD-MS（1/2）

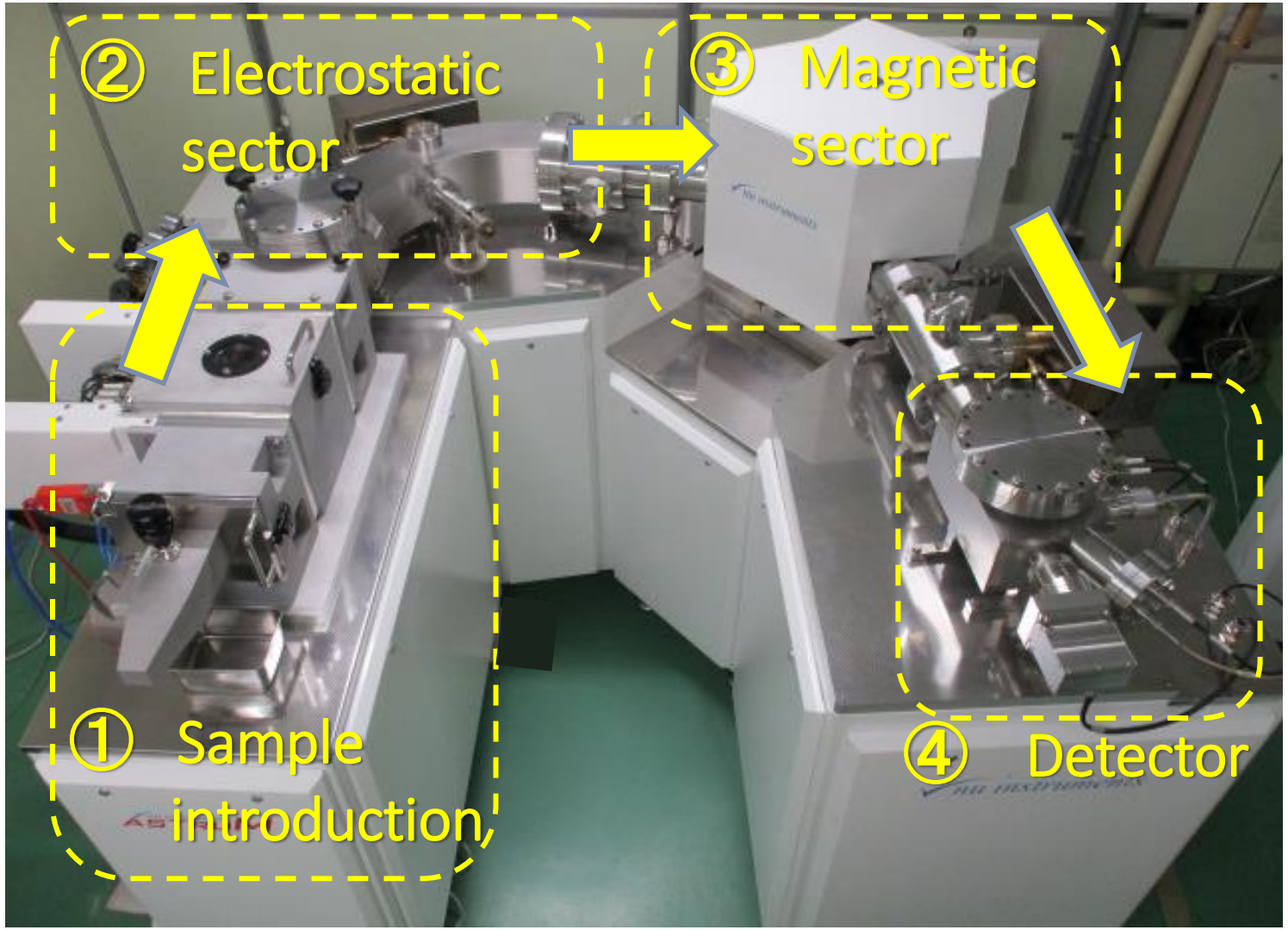
Comparison with Spark-OES

	Spark-OES	GD-MS
Sample	Flat plate	Flat plate or Pin
Intensity	Depend on element even at the same concentration.	Less dependent on element. (Depend on isotope abundance.)
Detection Limit	Approx.　1 mg/kg	Approx.　0.01 mg/kg
Elements	Fix wavelength when installed Analyzed elements are limited	Choose mass when measured Can measure 60 elements
Interference	Hard to analyze alloys because of spectrum interferences	GD-MS in the market adopt double focus system. Few mass interferences makes alloys analyzed.
Time	Approx. 1 min/sample	1~2 hour/sample
Price	Relatively low	Expensive
Application	Daily analyses for single matrix materials	Development. Support analysis for another analysis results.

Characteristics of GD-MS（2/2）

- Approx. 0.01 mg/kg level can be detected in a solid sample.
- Intensity is less dependent on at the same concentration element.
- Without standards, intensity ratio (analyzed/ matrix element) can be treated as approx. concentration.
- Compared to optical analyses, mass analysis has less interference, and isotopes facilitate to find the cause of interferences.

3. Configuration of GD-MS AstruM



4. Measured values by GD-MS

(1) Ion Beam Ratio
(2) Semi Quantitative Value
(3) Fully Quantitative Value

▶ (1) Ion Beam Ratio (IBR)

The ratio of the intensity of the analyzed elements to that of the matrix element, considering isotope abundance.

$$IBR = (I_x/Abd_x)/(I_{Matrix}/Abd_{Matrix})$$

Ix: Intensity of analyzed element
I_{matrix}: Intensity of matrix element
Abd_x: Abundance of analyzed element
Abd_{matrix}: Abundance of matrix element

Sometimes, treated as the approximate concentration.

Relative Sensitivity Factor (RSF)

Actually,

IBR must be corrected for the accurate analysis by RSF.

RSF is defined as below.

$$\frac{C_x}{C_{matrix}} = RSF * IBR$$

$$= RSF \frac{Ix * Abd_x}{I_{matrix} * Abd_{matrix}}$$

Ix: Intensity of analyzed element
I_{matrix}: Intensity of matrix element
Cx: Concentration of analyzed element
C_{matrix}: Concentration of matrix element

▶(2) Semi Quantitative Value： $Value(Semi)=IBR \times RSF_{Semi}$

In the absence of a standard sample,

RSFs for various matrices are sometimes calculated from known Fe-based RSF supplied by the manufacturer and the paper*. (→ RSF_{Semi}),

$$RSF_{semi} = \frac{RSF_{Analyze\ EL\ on\ Fe\ Base}}{RSF_{Matrix\ EL\ on\ Fe\ Base}}$$

*:Relative sensitive factors in glow discharge mass spectrometry (W.Vieth et.al, Spectrochimica Acta, 1991, 46B, 137-153)

A quantitative value obtained by using RSF(semi) and IBR is called Semi Quantitative value or Value(semi).

▶(3) Fully Quantitative Value : $Value(Full)=IBR \times RSF_{Full}$

To determine ***the relative sensitivity factor*** , the best way is measuring the Certified Reference Materials. (→ RSF_{Full})

RSF_{Full} = *(Certified value of CRM)/ IBR*

The concentration of an analyzed element is determined by the IBR observed and RSF_{Full}.

5. Comparison of measured values in GD-MS

The measured values for each matrix will be compared from the following pages.

- Measured CRM

Au:	LBMA	Au	RM1, RM2, RM3
Ag:	LBMA	Ag	RM1, RM2
Pt:	LPPM	Pt	RM1, RM2
Pd:	LPPM	Pd	RM1, RM2

- Compared Result

IBR

Value (Semi) : $IBR \times RSF_{Semi}$

Value (Full) : $IBR \times RSF_{Full}$

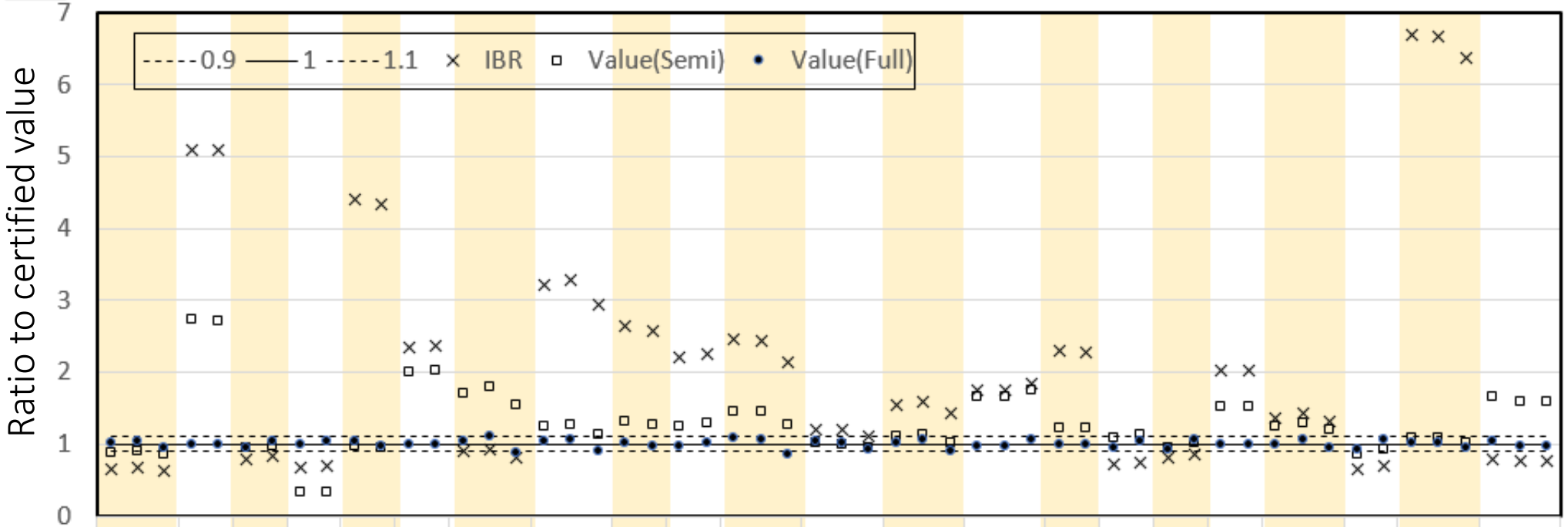
Note: Quantitative values from RM1 were derived from the calibration curve from RM2, and vice versa.

- Criteria : Ratio should be within 0.9 and 1.1.

6. Verification results using CRMs

Comparison by ratio to Certified values

Au LBMA RM1, RM2, RM3



Certified Value (mg/kg)

	Ag	Al	As	Bi	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Pd	Pt	Rh	Sb	Se	Si	Sn	Te	Ti	Zn
RM1	20.0	9.6	14.5	30.4	9.6	9.4	13.5	10.6	30.1	9.7	9.8	9.8	9.7	10.3	7.3	35.7	11.8	9.4	9.7	40.7	10.5	10.3
RM2	99.6	28.3	47.1	9.7	28.0	27.7	31.6	30.1	9.9	28.2	29.2	28.9	29.2	30.2	39.6	11.3	37.4	28.0	29.4	12.0	31.6	31.4
RM3	4456						317.0	21.0			13.4	23.6	25.8	25.4					12.2		7.8	12.6

IBRs (×) deviate from the certified values.

The Value(semi) (□) is closer than IBR, but still far.

The Value(Full) (●) within 0.9 to 1.1.

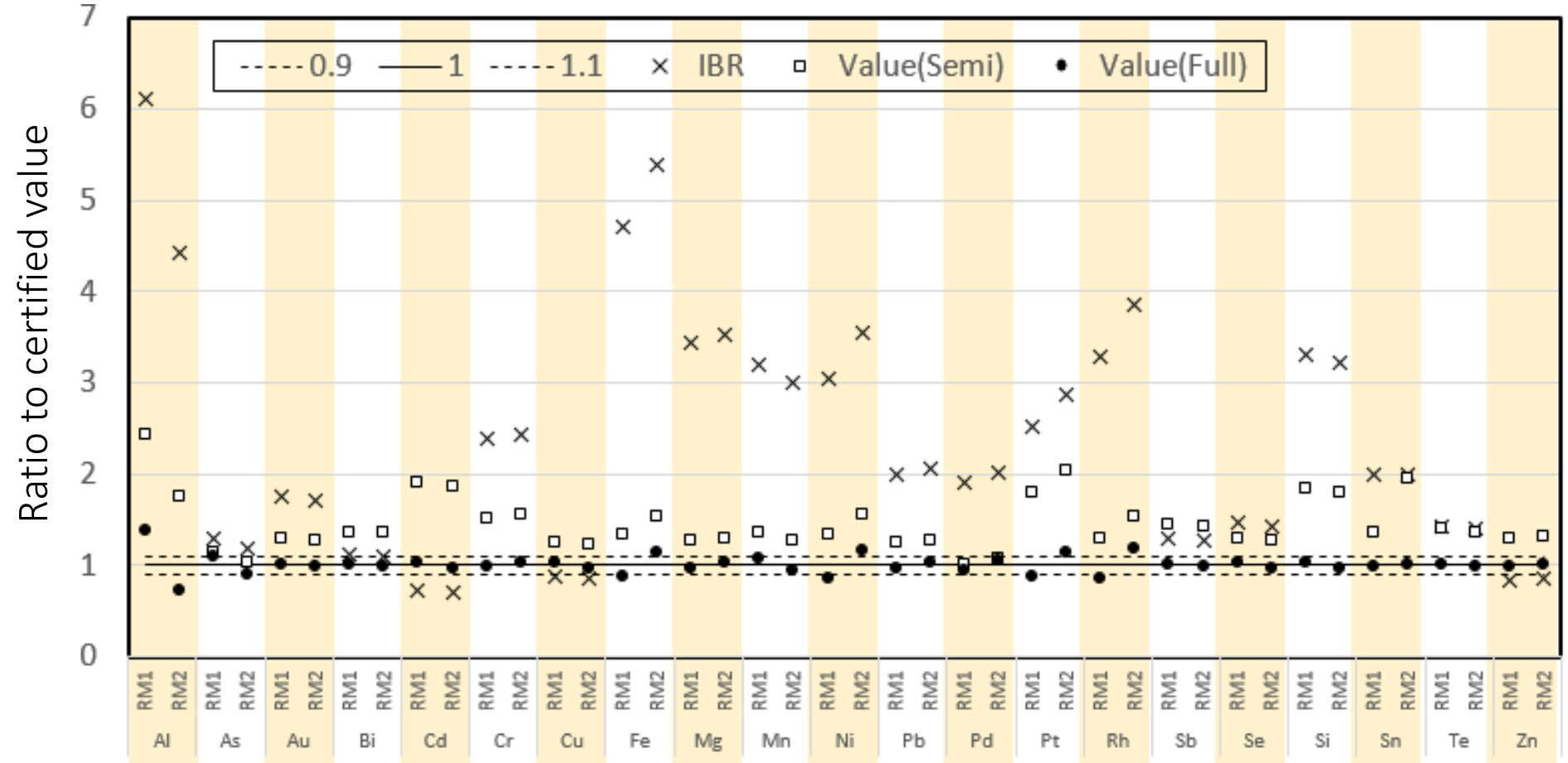
Selected Elements in **Au** by GD-MS

Concentrations from different calibration methods, mg/kg

Element	RM	IBR, X	Value(Semi), □	Value(Full), ●	Certified
Ag	RM1	13.1	17.6	20.1	20.0
	RM2	66.5	89.5	103.6	99.6
	RM3	2,808	3,780	4,255	4,456
Cu	RM1	12.1	23.1	14.0	13.5
	RM2	29.6	56.5	34.8	31.6
	RM3	256	489	280	317
Rh	RM1	16.7	8.9	7.3	7.3
	RM2	90.3	48.3	39.6	39.6

Comparison by ratio to Certified values

Ag LBMA RM1, RM2



Certified Value (mg/kg)	Al	As	Au	Bi	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Pd	Pt	Rh	Sb	Se	Si	Sn	Te	Zn
RM1	7.9	19.0	6.1	7.3	8.0	62.9	30.2	22.4	13.9	8.9	66.1	37.5	5.2	5.5	13.4	4.5	23.0	10.0	49.2	4.7	26.9
RM2	61.8	5.5	26.2	40.8	23.5	8.8	110.5	15.7	49.3	16.1	10.6	5.6	23.1	20.9	4.6	23.6	8.6	54.6	4.5	38.1	5.2

The Value(semi) tends to be high in the Ag matrix.

Selected Elements in **Ag** by GD-MS

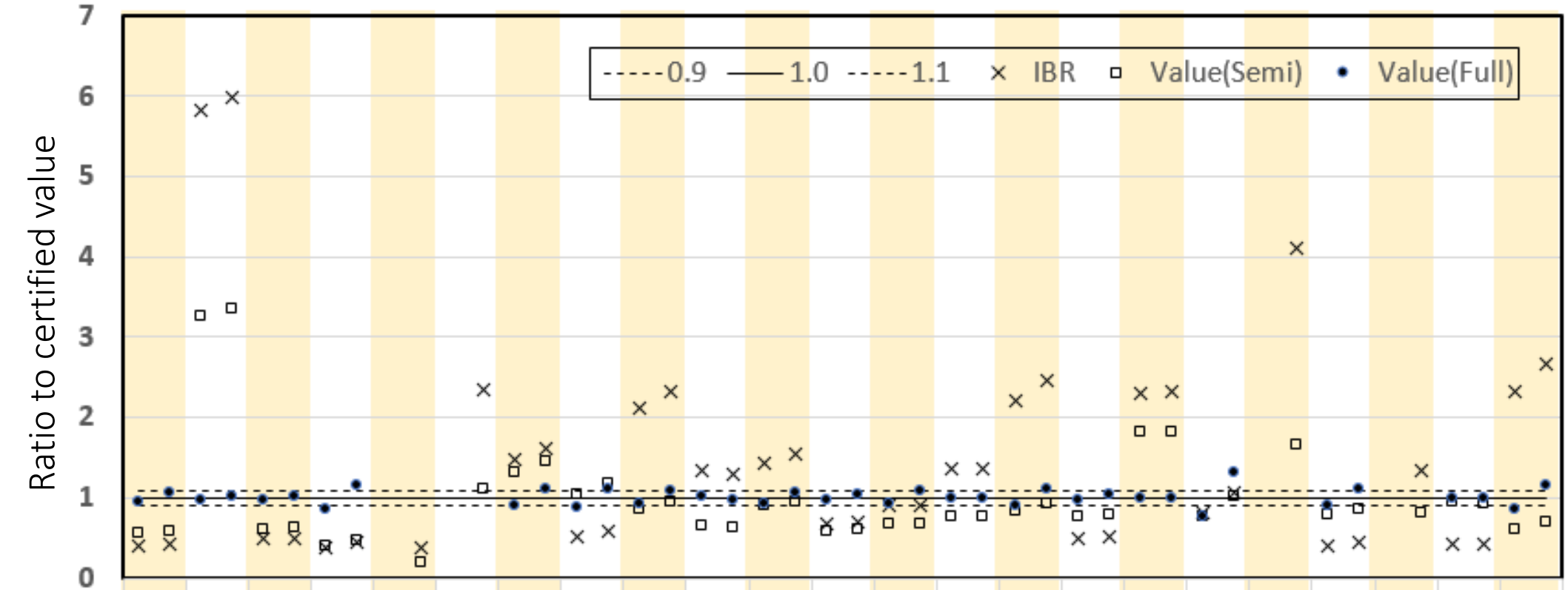
Concentrations from different calibration methods, mg/kg

LBMA GOOD DELIVERY REFEREE

Element	RM	IBR, X	Value(Semi), ☐	Value(Full), ●	Certified
Au	RM1	10.6	7.9	6.2	6.1
	RM2	44.9	33.4	25.7	26.2
Cu	RM1	26.7	37.9	30.9	30.2
	RM2	95.6	135.5	107.9	111
Pt	RM1	13.9	9.8	4.8	5.5
	RM2	60.0	42.5	23.8	20.9
Rh	RM1	43.9	17.4	11.4	13.4
	RM2	17.7	7.0	5.4	4.6

Comparison by ratio to Certified values

Pt LPPM RM1, RM2



Certified Value (mg/kg)

	Ag	Al	As	Au	Bi	Co	Cr	Cu	Fe	Ir	Ni	Pb	Pd	Rh	Ru	Sb	Si	Sn	Ti	Tl	W	Zn	Zr
RM1	13.9	93.9	58.3	11.7	–	–	9.3	26.1	12.4	204.0	11.1	12.3	10.5	13.3	11.4	19.5	47.5	47.6	–	6.2	–	44.9	1.2
RM2	44.8	34.7	28.7	51.9	18.6	19.5	47.2	90.8	85.4	59.2	41.4	33.3	95.3	101.6	51.5	49.9	13.1	7.0	11.8	39.2	20.2	9.5	36.5

The Value(semi) tends to be low in the Pt matrix.

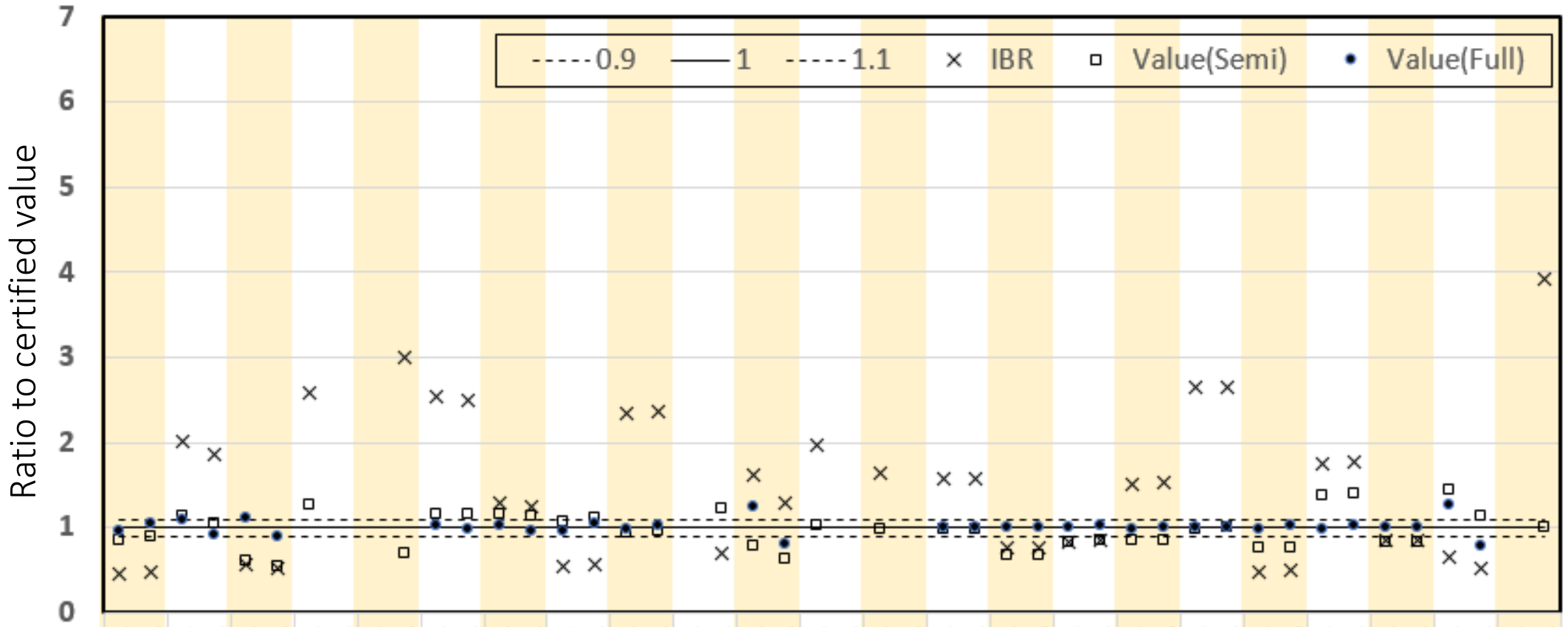
Selected Elements in **Pt** by GD-MS

Concentrations from different calibration methods, mg/kg

Element	RM	IBR, X	Value(Semi), ☐	Value(Full), ●	Certified
Ag	RM1	5.5	7.8	13.1	13.9
	RM2	18.8	26.5	47.5	44.8
Au	RM1	4.5	4.7	10.1	11.7
	RM2	22.8	23.9	60.0	51.9
Cu	RM1	13.7	27.5	23.3	26.1
	RM2	53.6	107.1	101.7	90.8
Rh	RM1	18.1	10.2	13.4	13.3
	RM2	137.5	77.0	100.9	101.6

Comparison by ratio to Certified values

Pd LPPM RM1, RM2



Certified Value (mg/kg)

	Ag	Al	Au	B	Ca	Co	Cr	Cu	Fe	Ga	Ir	Mg	Mn	Ni	Pb	Pt	Rh	Ru	Sb	Si	Sn	Zn	Zr
RM1	11.1	12.4	99.2	2.5		8.8	45.5	11	11.1		9.7	22.3	23.8	54.4	13.2	54.4	56.3	10.3	9.2	50	12.3	9.5	
RM2	95.5	5	16		9.5	17.5	9.3	92.1	45.1	18.6	43.4			10.1	66	228	13.3	45.1	42.8	119	44.4	17.4	10.8

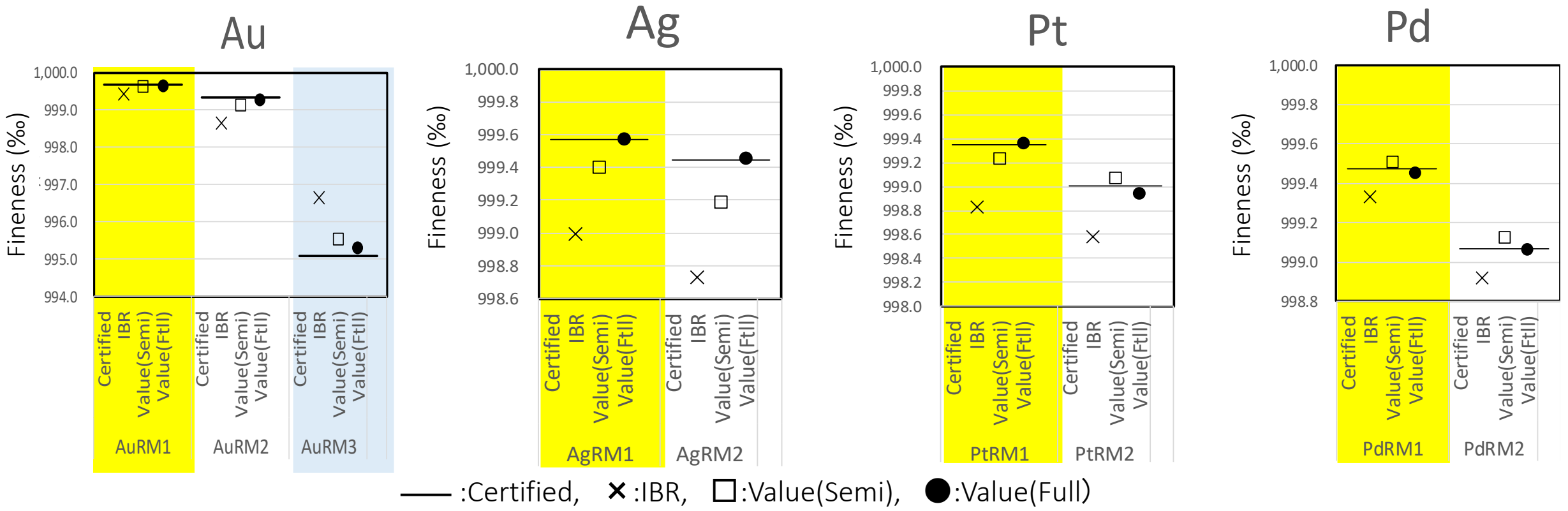
The deviation of Value(semi) in the Pd matrix is tend to be smaller than that in other matrices.

Selected Elements in **Pd** by GD-MS

Concentrations from different calibration methods, mg/kg

Element	RM	IBR, X	Value(Semi), ☐	Value(Full), ●	Certified
Ag	RM1	5.0	9.4	10.6	11.1
	RM2	45.3	84.7	100.3	95.5
Au	RM1	56.7	59.4	110.2	99.2
	RM2	8.2	8.6	14.4	16.0
Cu	RM1	5.8	11.7	10.6	11.0
	RM2	50.9	101.8	95.8	92.1
Rh	RM1	84.4	47.3	55.5	56.3
	RM2	20.2	11.3	13.3	13.3

7. Fineness evaluation



- The fineness from IBRs (×) was deviated from that from the certified values.
- The fineness from Value(semi)(□) approached to that from the certified values, but not enough.
- To determine the accurate fineness, we must use the concentrations from the Value(Full)(●) obtained by measuring the *Reference Materials.*

8. Summary

- The measurement results by GD-MS detected at low concentration has been verified.
- Au and Ag CRM (LBMA) and Pt and Pd CRM(LPPM) were contributed for verification.
- The measured values obtained by the RSF(Full) were the most accurate.
- The ratios of the measured values obtained by the RSF(semi) were frequently out of range from 0.9 to 1.1.

The CRMs provided from LBMA and LPPM are suitable to verify your analysis methods.

For requiring more assured values, it is recommended to acquire these CRMs.

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Thank you for your attention.
Please do not hesitate to send any inquiries to
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