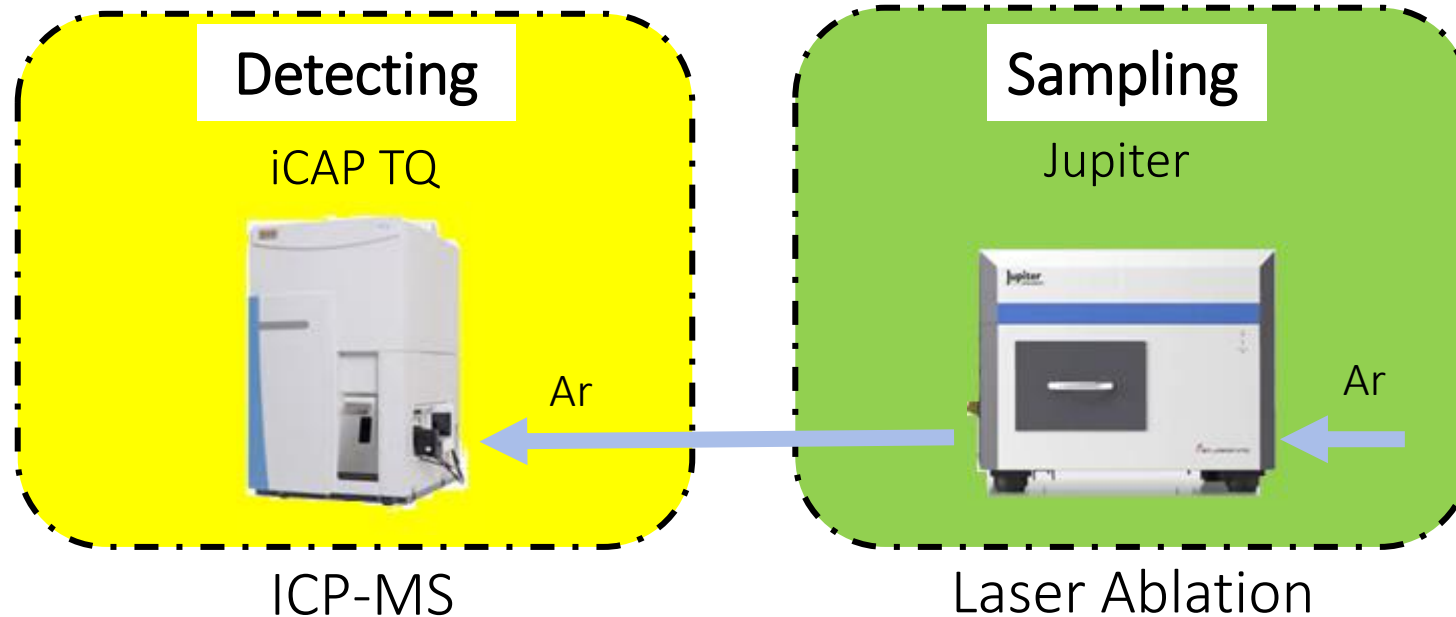


Application of LA-ICP-MS to the analysis of trace elements in precious metals



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Agenda



1. Problems of trace element analysis in precious metals
2. Application to analysis of trace elements in precious metals
3. Application to analysis of trace elements in precious metal alloys
4. Summary



1. Problems of trace element analysis in precious metals

- ▶ Problems in solution analysis
 - ✓ Long dissolution time.
 - ✓ Necessity of securing dedicated equipment for liquefaction.
 - ✓ Requirement for advanced knowledge (about interference).
 - ✓ Effect on the environment and human body due to the use of acid.
 - ✓ Possibility of insoluble.

- ▶ Problems in solid analysis
 - ✓ Difficulty in procuring Reference materials.
 - ⇒ Alloys are more difficult to procure.
 - ⇒ Difficulty to apply solid analysis to alloy products.

Need for analysis technic that can cover a wide range with limited amount of solid reference materials.

LA-ICP-MS can solve many of these problems !

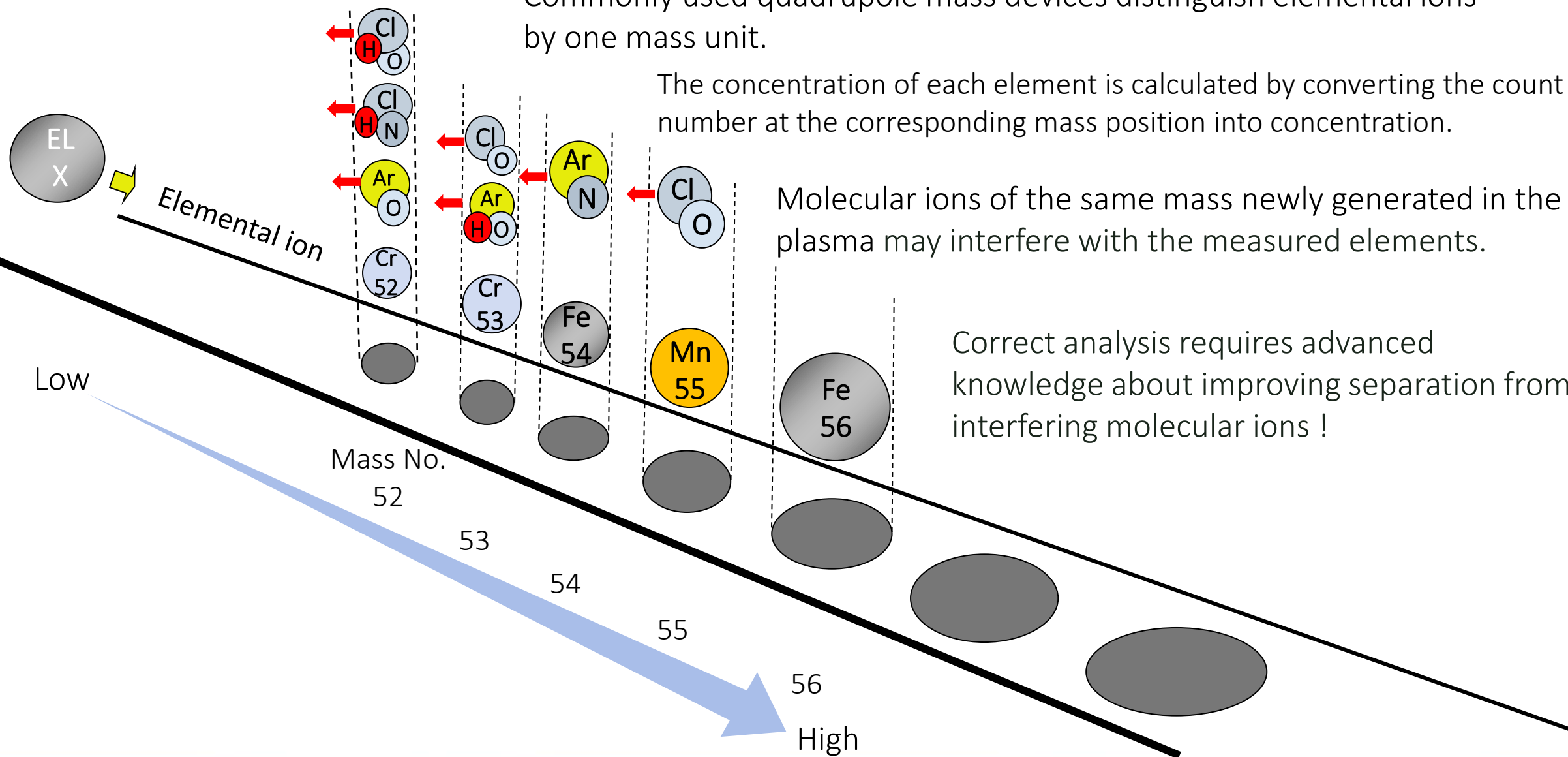
Detection issues in ICP-MS analysis

Commonly used quadrupole mass devices distinguish elemental ions by one mass unit.

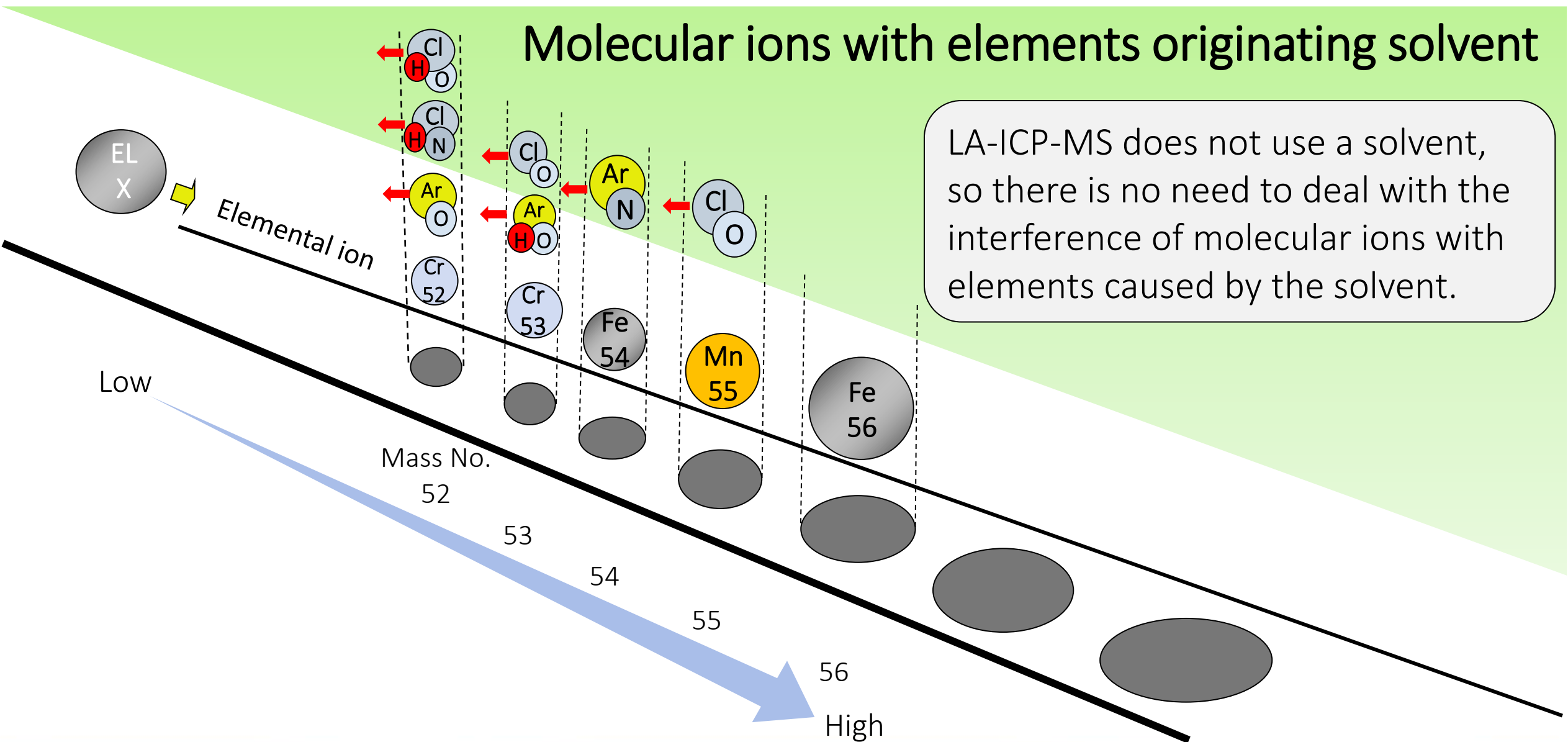
The concentration of each element is calculated by converting the count number at the corresponding mass position into concentration.

Molecular ions of the same mass newly generated in the plasma may interfere with the measured elements.

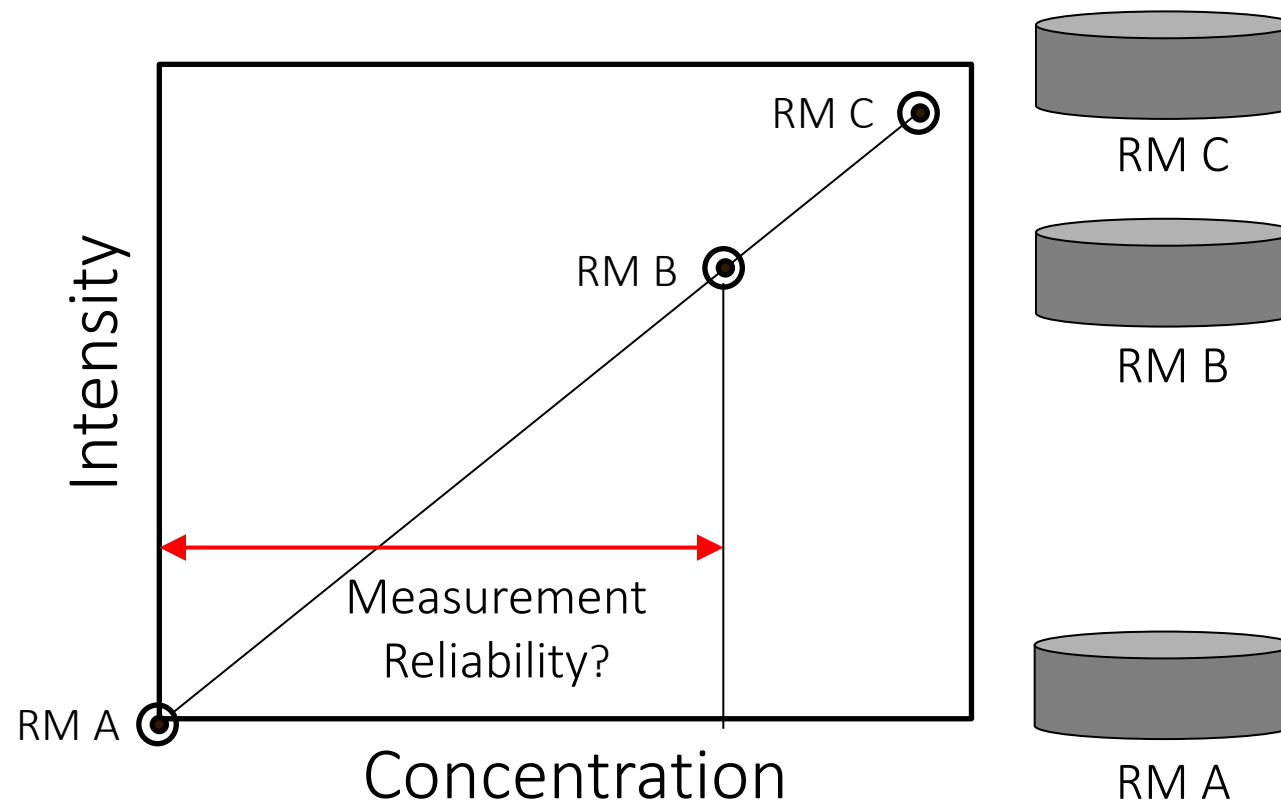
Correct analysis requires advanced knowledge about improving separation from interfering molecular ions !



Detection advantages of LA-ICP-MS



Problems with the calibration curve of general solid measuring devices



Problems

- 1 It is difficult to ensure the measurement reliability in the wide concentration.
- 2 Additional plots require newly prepared reference materials.
However, there is a problem that it takes time and money to manufacture.

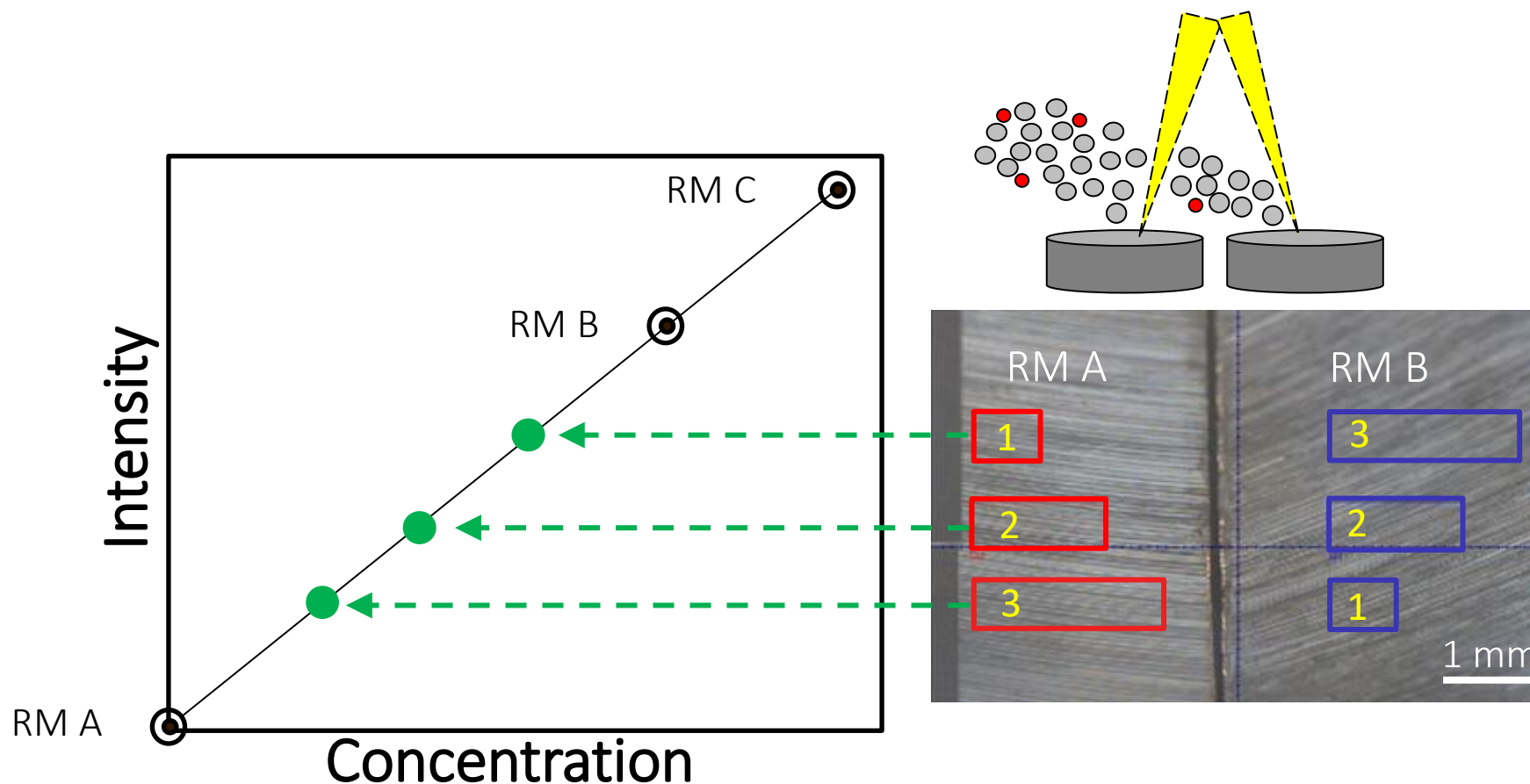
2. Application to analysis of trace elements in precious metals

2-1 Measurement principle with
high-speed multiple spot laser ablation.

2-2 Measurement results in the Pd system.

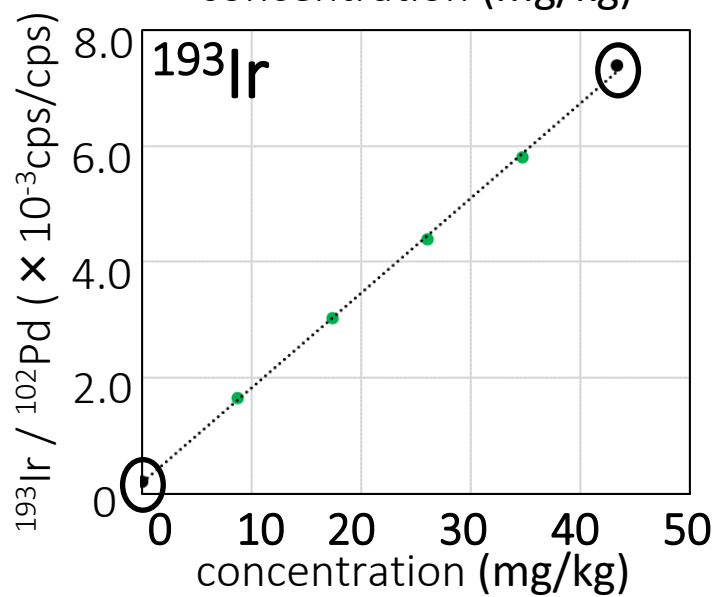
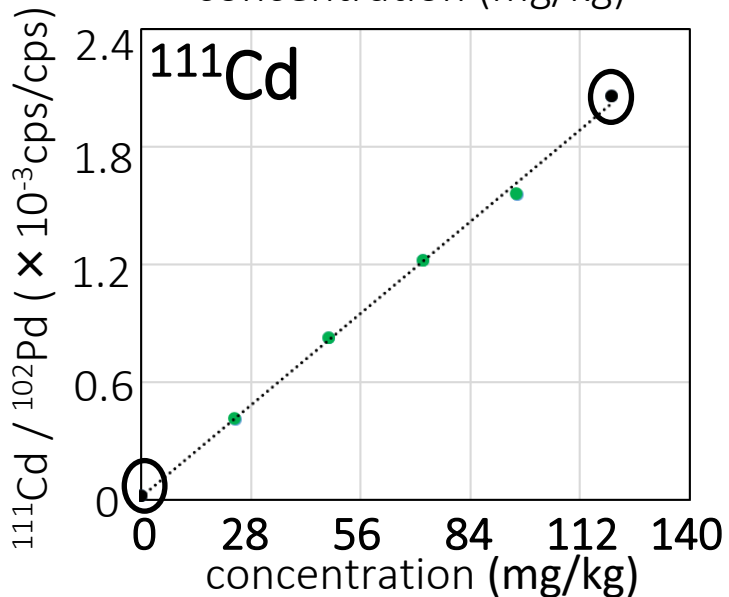
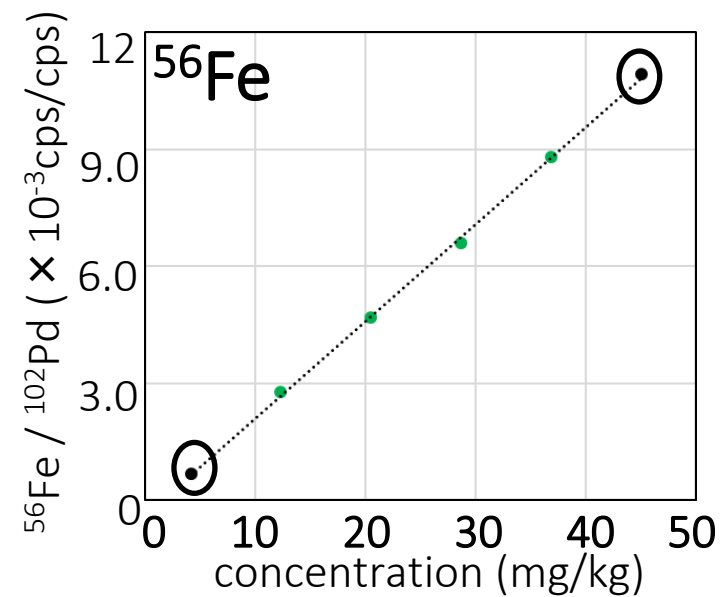
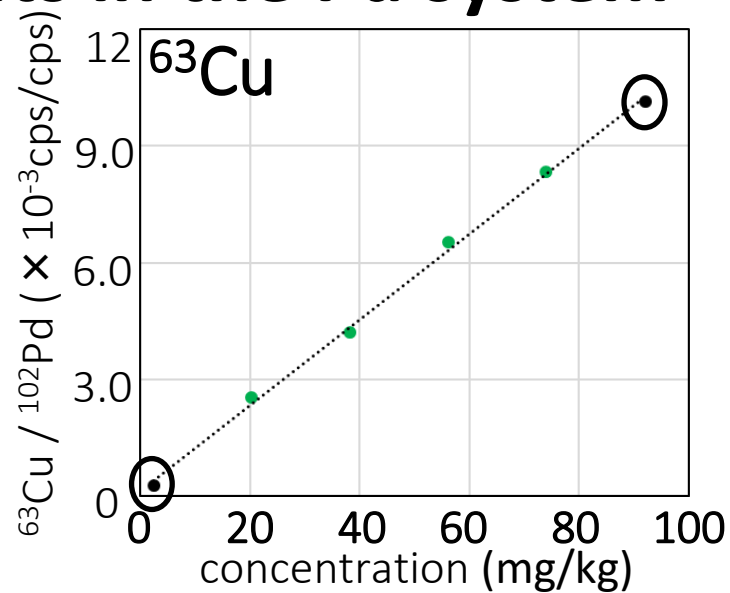
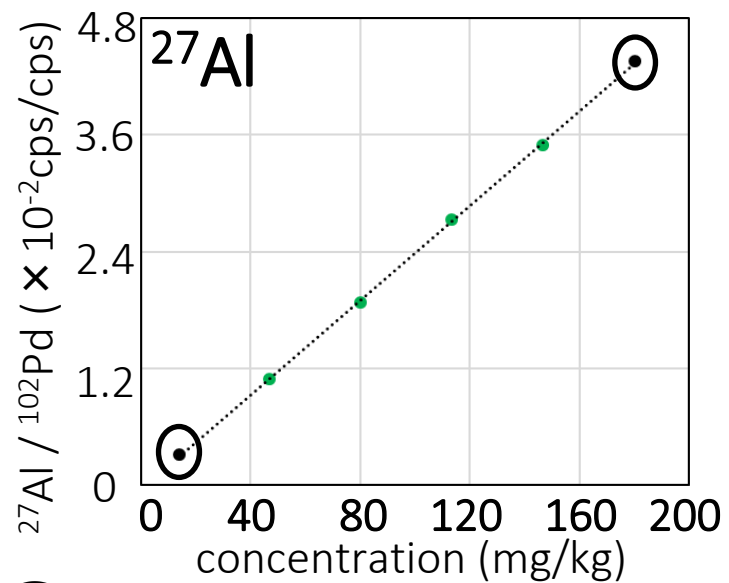
2-3 Verification by LPPM-CRM.

2-1 Measurement principle with high-speed multiple spot laser ablation



- ▶ Simultaneous ablation to different Reference materials.
- ▶ Adjust the concentration of trace elements by changing the ablation ratio of each RM.

2-2 Measurement results in the Pd system



● Point for irradiation of each RM

● Points for mixed irradiation

The green points are arranged linearly between the black circle points.

2-3 Verification by LPPM-CRM

| Pd RM1 | | | (mg/kg) | | |
|--------|-----------------|----------------|---------|-----------------|----------------|
| | Certified value | measured value | | Certified value | measured value |
| Ag | 11 | 11 | Mn | 24 | 22 |
| Al | 12 | 10 | Ni | 54 | 56 |
| Au | 99 | 100 | Pb | 13 | 13 |
| B | 3 | 1 | Pt | 54 | 48 |
| Co | 9 | 7 | Rh | 56 | 57 |
| Cr | 46 | 37 | Ru | 10 | 9 |
| Cu | 11 | 12 | Sb | 9 | 9 |
| Fe | 11 | 11 | Si | 50 | 46 |
| Ir | 10 | 8 | Sn | 12 | 11 |
| Mg | 22 | 22 | Zn | 10 | 9 |

| Pd RM2 | | | (mg/kg) | | |
|--------|-----------------|----------------|---------|-----------------|----------------|
| | Certified value | measured value | | Certified value | measured value |
| Ag | 96 | 85 | P | 20 | 20 |
| Al | 5 | 3 | Pb | 66 | 80 |
| Au | 16 | 17 | Pt | 228 | 224 |
| Ca | 10 | 0 | Rh | 13 | 16 |
| Co | 18 | 16 | Ru | 45 | 46 |
| Cr | 9 | 9 | Sb | 43 | 43 |
| Cu | 92 | 97 | Si | 119 | 130 |
| Fe | 45 | 45 | Sn | 44 | 42 |
| Ga | 19 | 17 | Zn | 17 | 19 |
| Ir | 43 | 43 | Zr | 11 | 13 |
| Ni | 10 | 10 | | | |

⇒ Measured values agree with certified values.

High-speed multiple laser ablation is effective for trace element analysis.

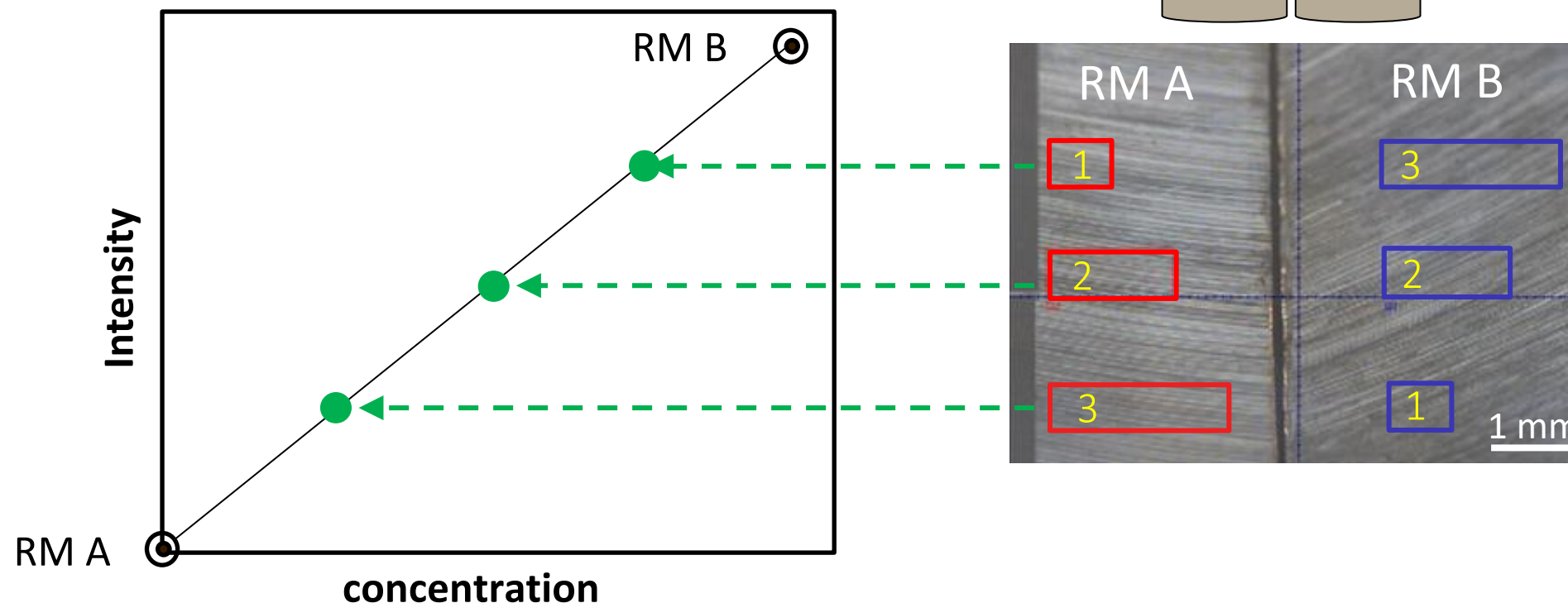
3. Application to analysis of trace elements in precious metal alloys ^{11/18}

3-1 Calibration curve using alloy RMs.

3-2 Calibration curve using combining RMs of dissimilar metals.

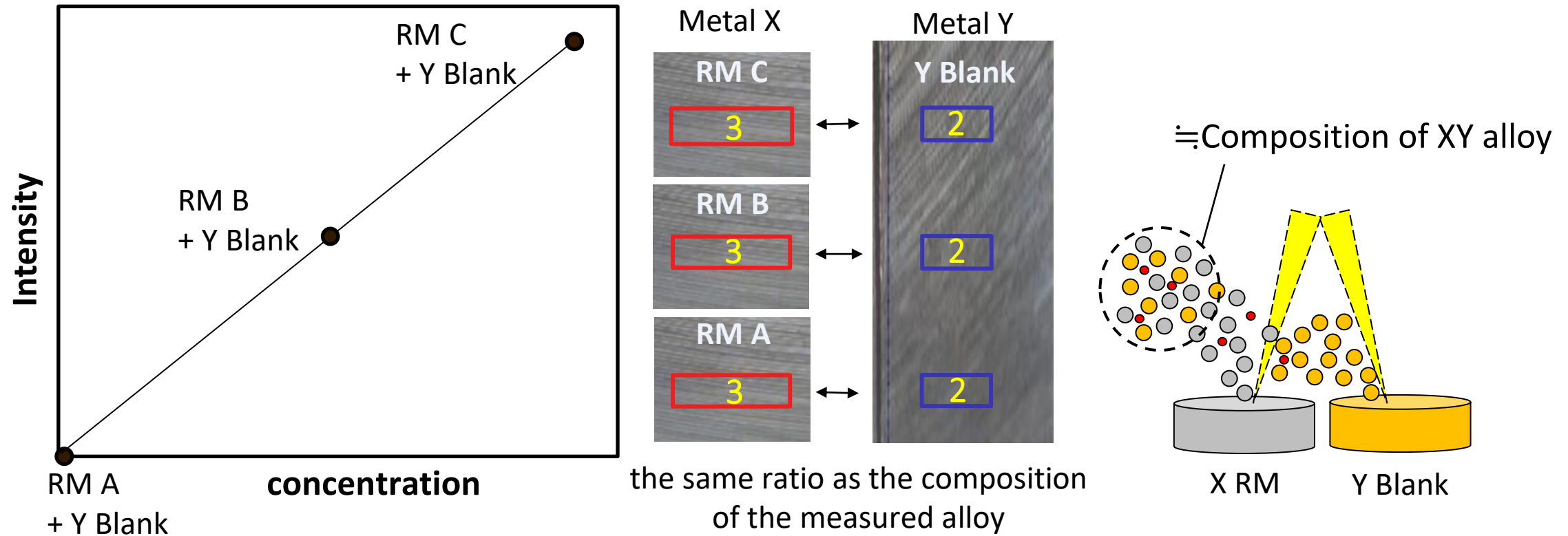
3-3 Comparative verification of measurement results with Pd alloy.

3-1 Calibration curve using alloy RMs



- ▶ Creation of calibration curve by high speed multi-spot laser ablation for two alloys with different concentrations of RM.
- ▶ The concentration of trace elements is changed by the ablation ratio.

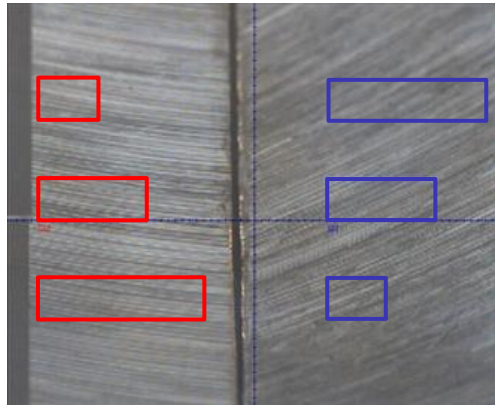
3-2 Calibration curve using combining RMs of dissimilar metals



- ▶ Approximate alloy conditions by ablating two materials at the same ratio as the composition of the measured alloy.
- ▶ Mixed on transport path (Aerosol composition is the same as XY alloy) .
- ▶ Changing concentration by replacing with X RM of different concentration.

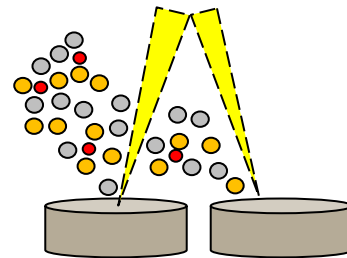
Calibration curve using alloy RMs

Alloy XY



RM A

RM B



RM A

RM B

≠
or
=

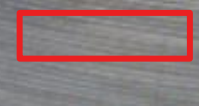
Calibration curve using combining RMs of dissimilar metals

Metal X

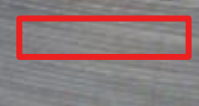
RM C



RM B

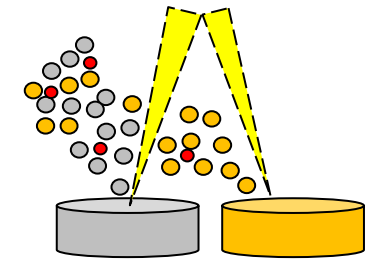
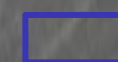
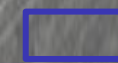


RM A



Metal Y

Y STD

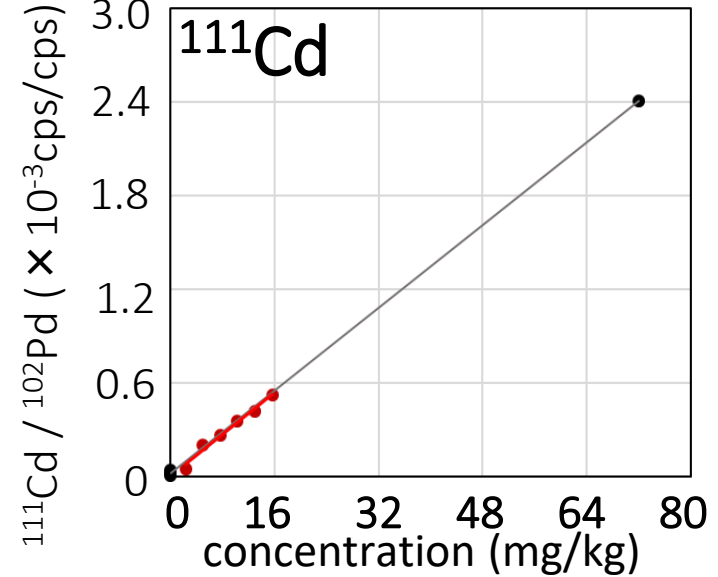
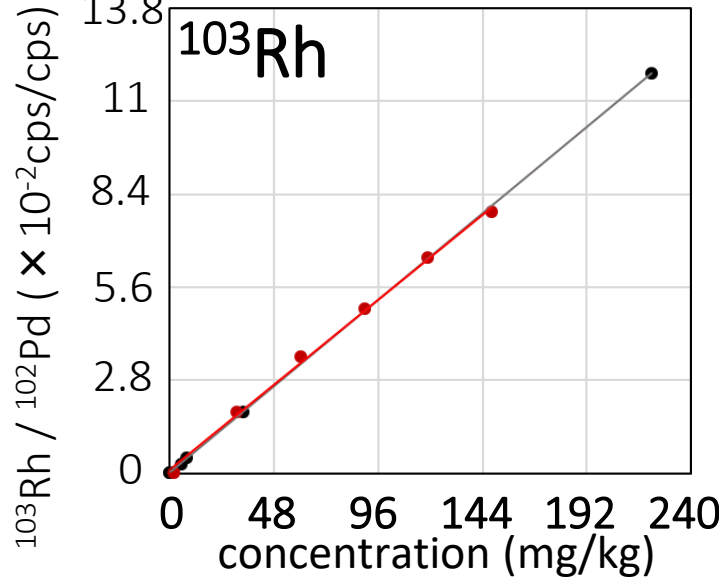
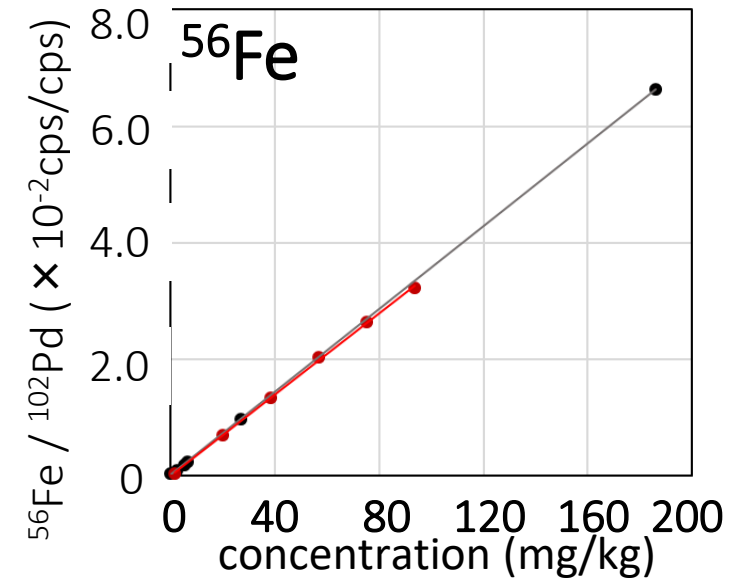
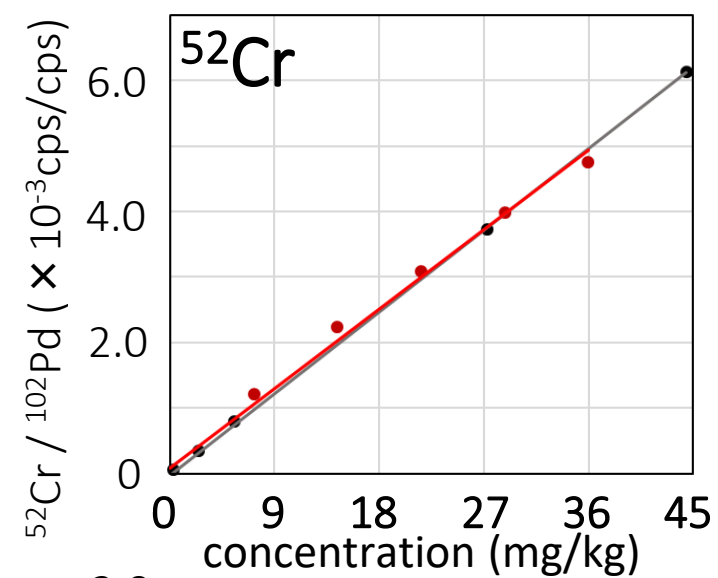
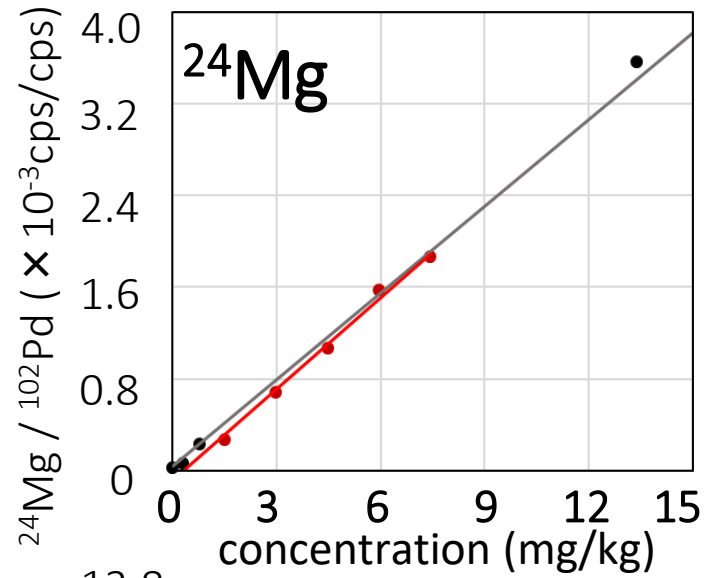


X RM

Y Blank

If the two calibration curves are comparable, only the RM of dissimilar metals can be used to determine trace elements in alloys.

3-3 Comparative verification of measurement results with Pd alloy ^{15/18}



- using alloy RMs
- using RMs of dissimilar metals

The two calibration curves overlap each other.
⇒ Almost the same measurements are likely to be obtained.

Verification by comparing measured values from two calibration curves^{16/18}

| | ICP-OES | Alloy RMs | combining RMs of dissimilar metals |
|----|---------|-----------|------------------------------------|
| B | 1 | 2 | 1 |
| Mg | 2 | 2 | 2 |
| Al | 25 | 34 | 28 |
| Si | 68 | 40 | 59 |
| Ca | 1 | 2 | 1 |
| Cr | 10 | 7 | 8 |
| Mn | 1 | 2 | 2 |
| Fe | 49 | 47 | 48 |
| Co | 1 | 1 | 1 |
| Ni | 27 | 24 | 24 |

| | ICP-OES | Alloy RMs | combining RMs of dissimilar metals |
|----|---------|-----------|------------------------------------|
| Zn | 9 | 10 | 10 |
| Ga | 1 | 0 | 1 |
| Mo | 2 | 0 | 0 |
| Rh | 58 | 56 | 57 |
| Ag | 488 | 440 | 485 |
| Cd | 11 | 10 | 9 |
| Sb | 1 | 1 | 1 |
| Pt | 473 | 386 | 533 |
| Au | 180 | 170 | 209 |
| Pb | 5 | 6 | 6 |

(mg/kg)

Results with alloy RMs \cong Results with combining RMs of dissimilar metals

Realization of trace element analysis in solid alloys using combining RMs of dissimilar metals.

8. Summary

- ▶ We have verified the analysis method of Pd and Pd alloy, by LA-ICP-MS with high-speed multiple spot laser ablation function.
- ▶ We have demonstrated that multiple calibration curves can be created by only two RMs with different concentrations.
- ▶ We have proposed two methods for the analysis of alloy, and confirmed that both results were consistent with values from ICP-OES.
- ▶ We have demonstrated that LA-ICP-MS can be applicable for the new analysis method of precious metals.



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Please do not hesitate to send any inquiries to
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