APMP mid-year symposium 2016 in Thailand,
8th Jun. 2016.

Providing CRMs, Calibration Services, and Skill-upgrading Programs

NMIJ Activities for Food and Water Safety

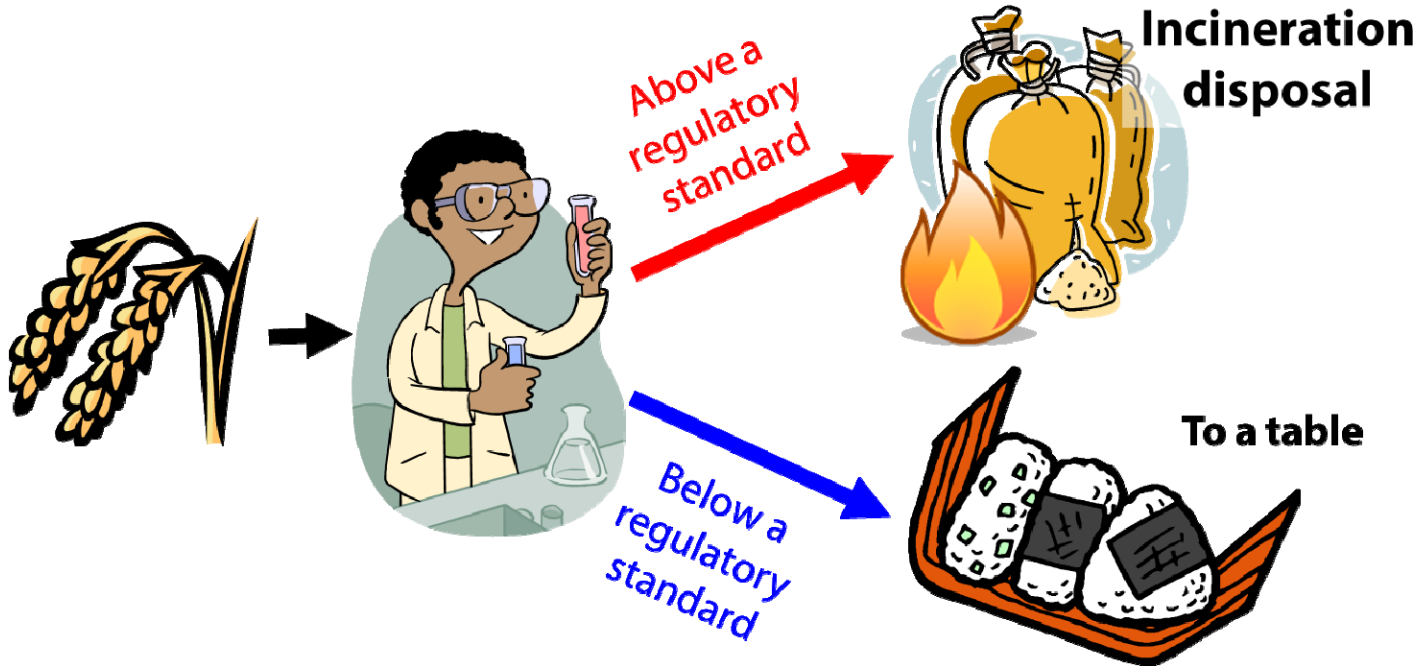
K. Inagaki and T. Fujimoto

National Metrology Institute of Japan（NMIJ）
National Institute of Advanced Industrial Science and Technology（AIST）

For Protecting Food and Water Safety: Ensuring Analytical reliability

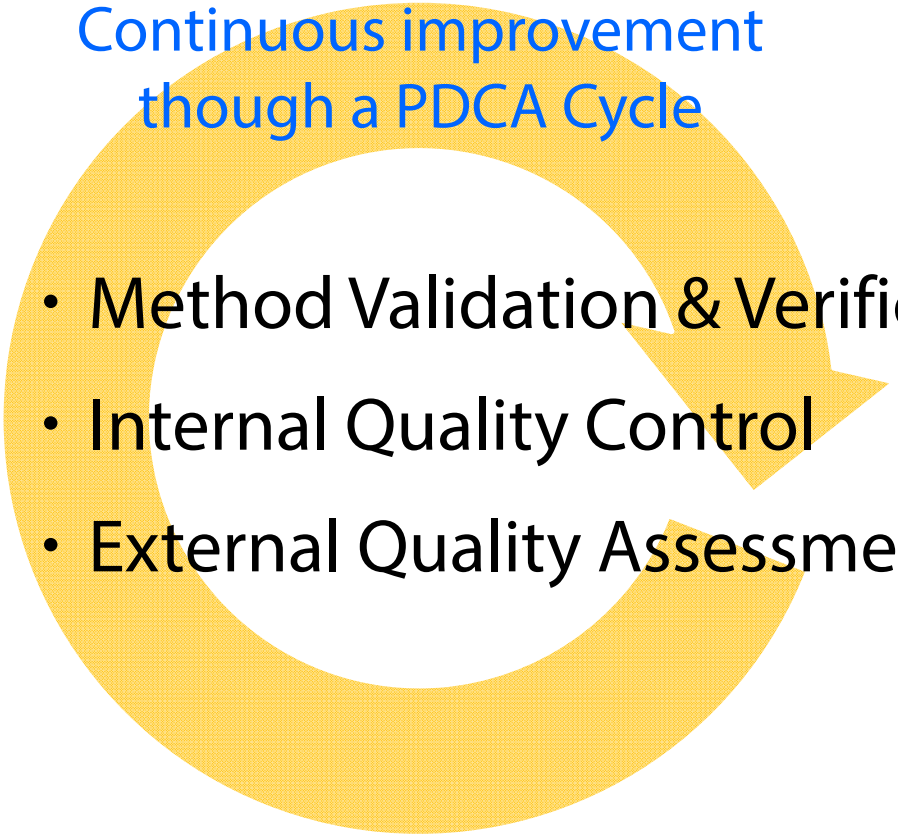
Various contaminants, undesirable residue, and toxic compounds are checked and monitored.

An analytical reliability in the testing and monitoring should be ensured.



How Do We get an Analytical Reliability ?

Continuous improvement
though a PDCA Cycle



- Method Validation & Verification
- Internal Quality Control
- External Quality Assessment

Assessing we need a corrective action is an easy,
but specifying and solving technical problems is not an easy.

NMIJ Provides

Services

Calibrations

Technical training
with Proficiency Testing

Technical Consulting

Knowledge

Analytical methods

Technical Know-how

Tools

Reference Materials

Analytical devices

For Ensuring Reliability
in Food and Water Analyses

Providing “Tools” and “Services”

From Development to Calibration : NMIJ activities for Reference materials

Reference Material (RM) for chemical analysis

“Measuring Scale” & “Self-checking Tool" in Chemical Analysis

High purity material type RM :

“Measuring scale” for calibrating a response in an instrumental analysis.

Matrix type RM:

“Self-checking tool” for validating, verifying, and quality controlling an analytical method and procedure.

Reference Material (RM) for chemical analysis

“Measuring Scale” & “Self-checking Tool" in Chemical Analysis

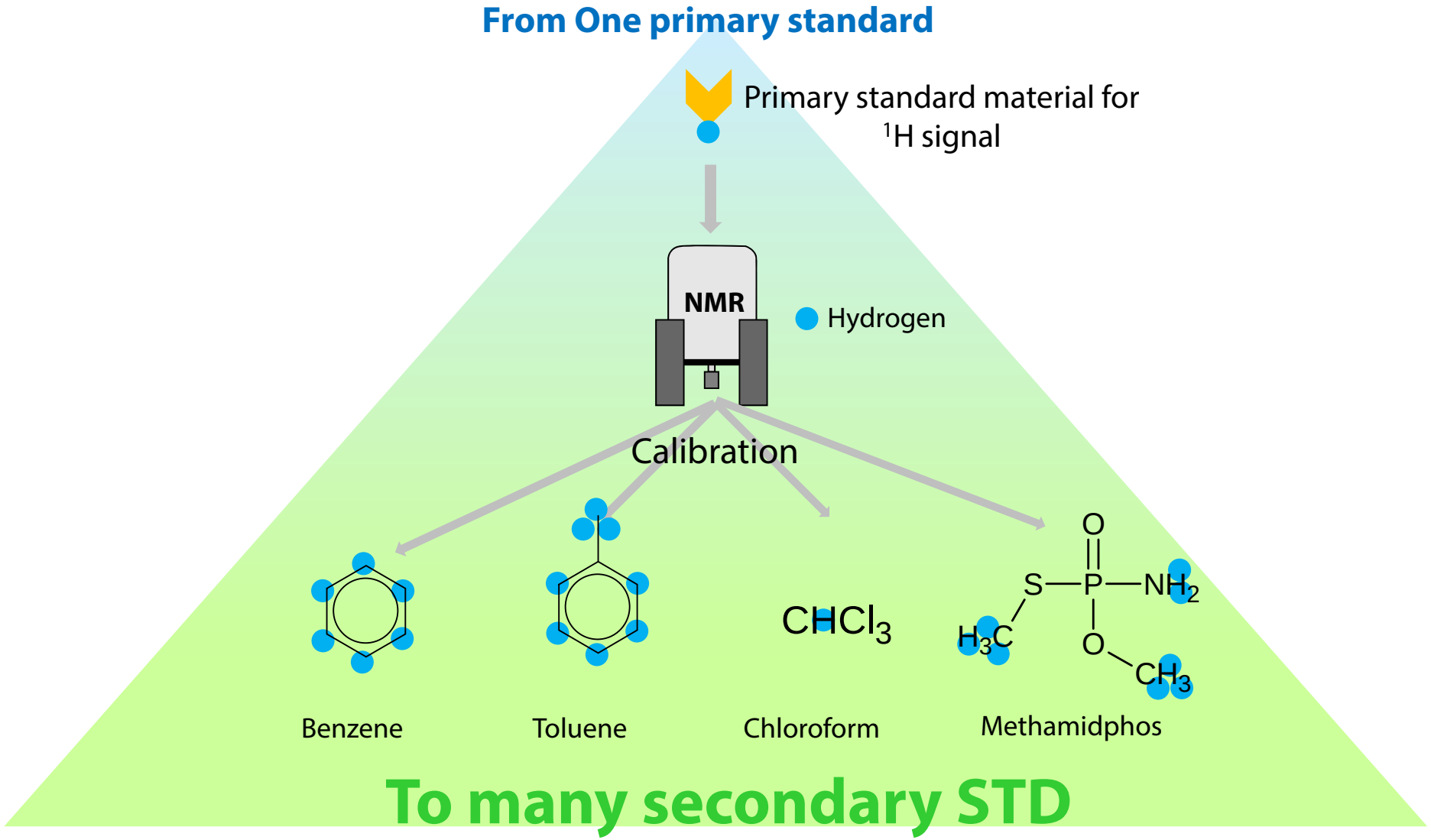
High purity material type RM :

“Measuring scale” for calibrating a response in an instrumental analysis.

Matrix type RM:

“Self-checking tool” for validating, verifying, and quality controlling an analytical method and procedure.

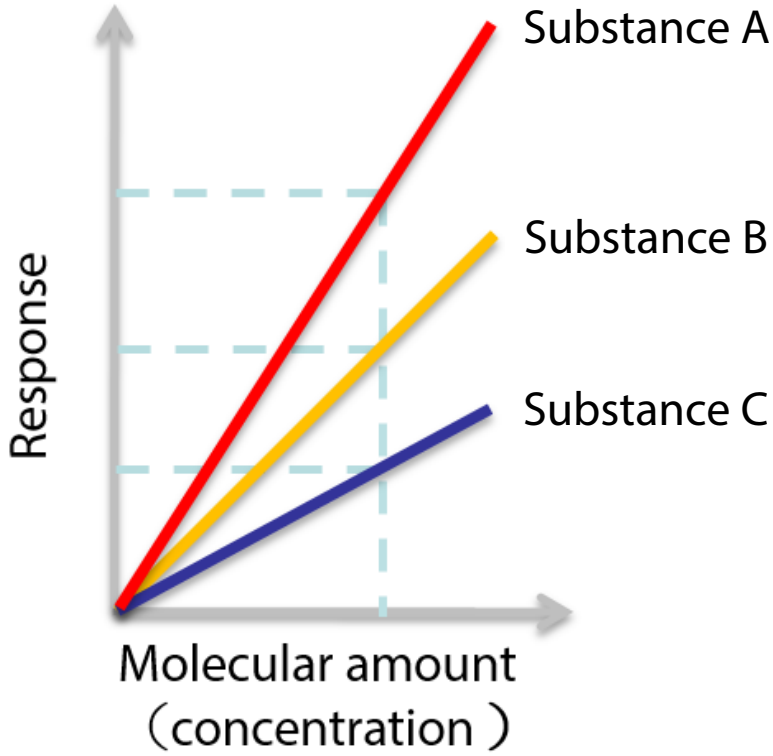
Quantitative NMR: game changer for calibration



Classic Style: One to One Calibration for Organic STD

Response in measurement depends on the structure of substance

→ Require individual STDs for all the substances we want to measure

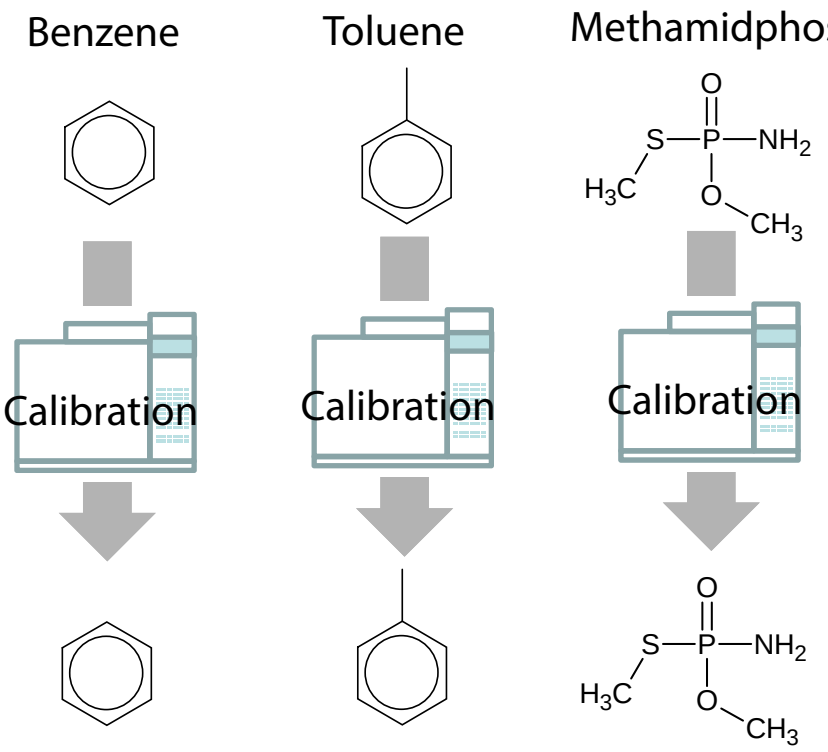


From a primary STD

To the same substance Secondary STD

Classic Style: One to One Calibration for Organic STD

How many RMs shall we disseminate, corresponding to regulations ?



Over **1000** compounds ?

Waterworks Law in JP

102 pesticides are listed

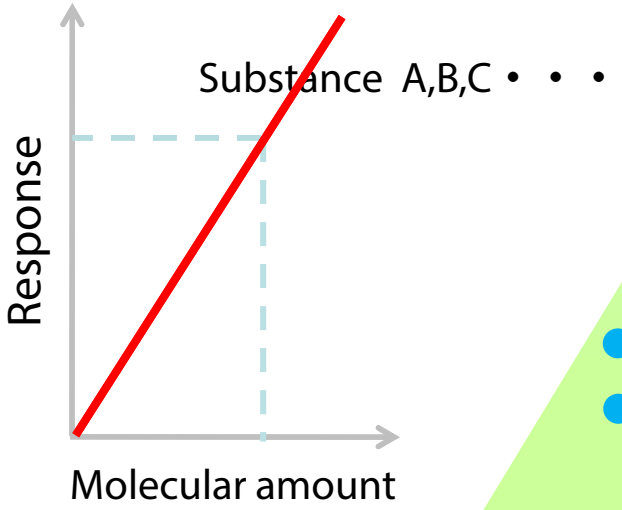
Regulation of Residual Pesticides in JP

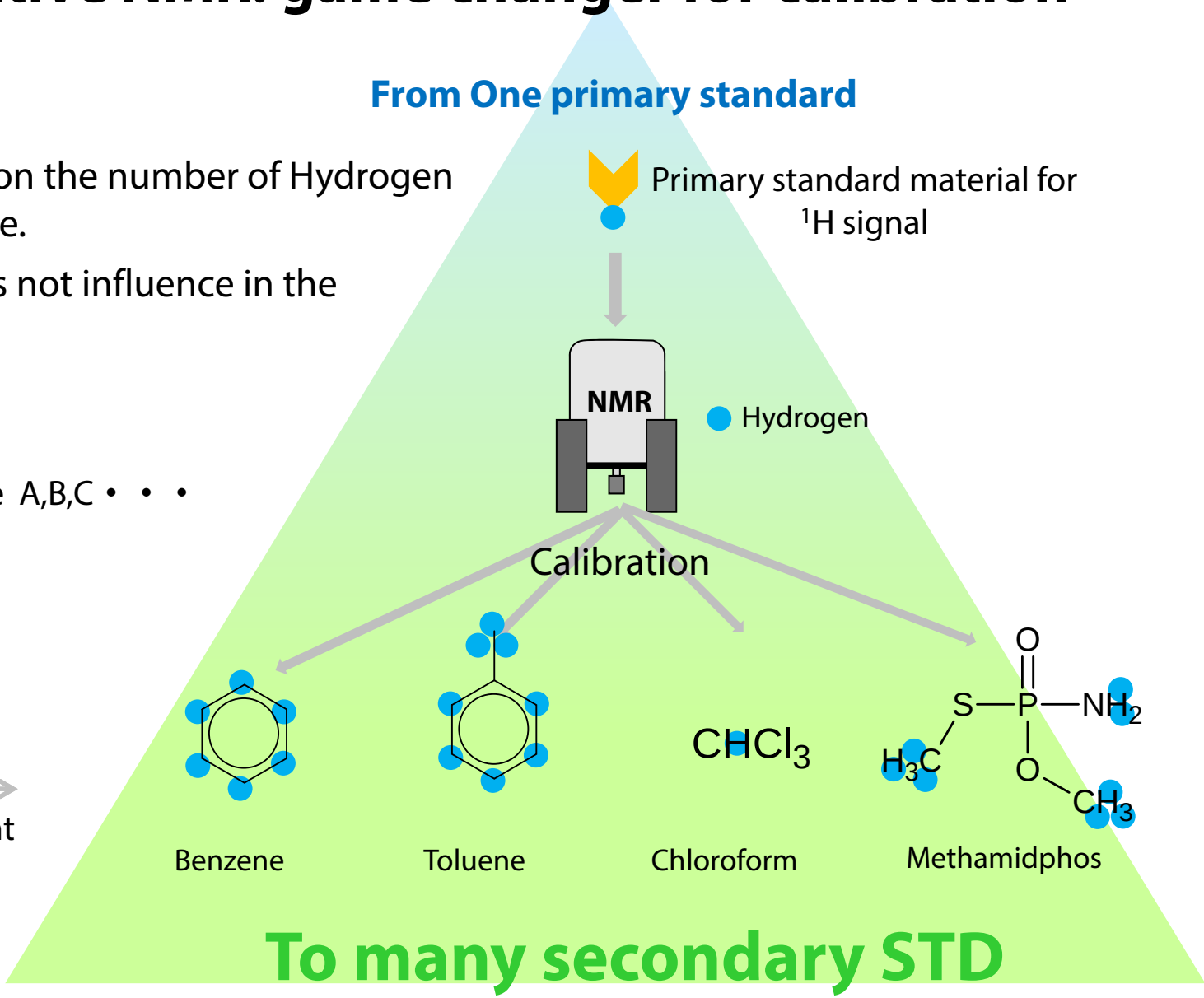
About **800** pesticides are listed

Quantitative NMR: game changer for calibration

Calibration bases on the number of Hydrogen atoms in substance.

The structure does not influence in the response in NMR.

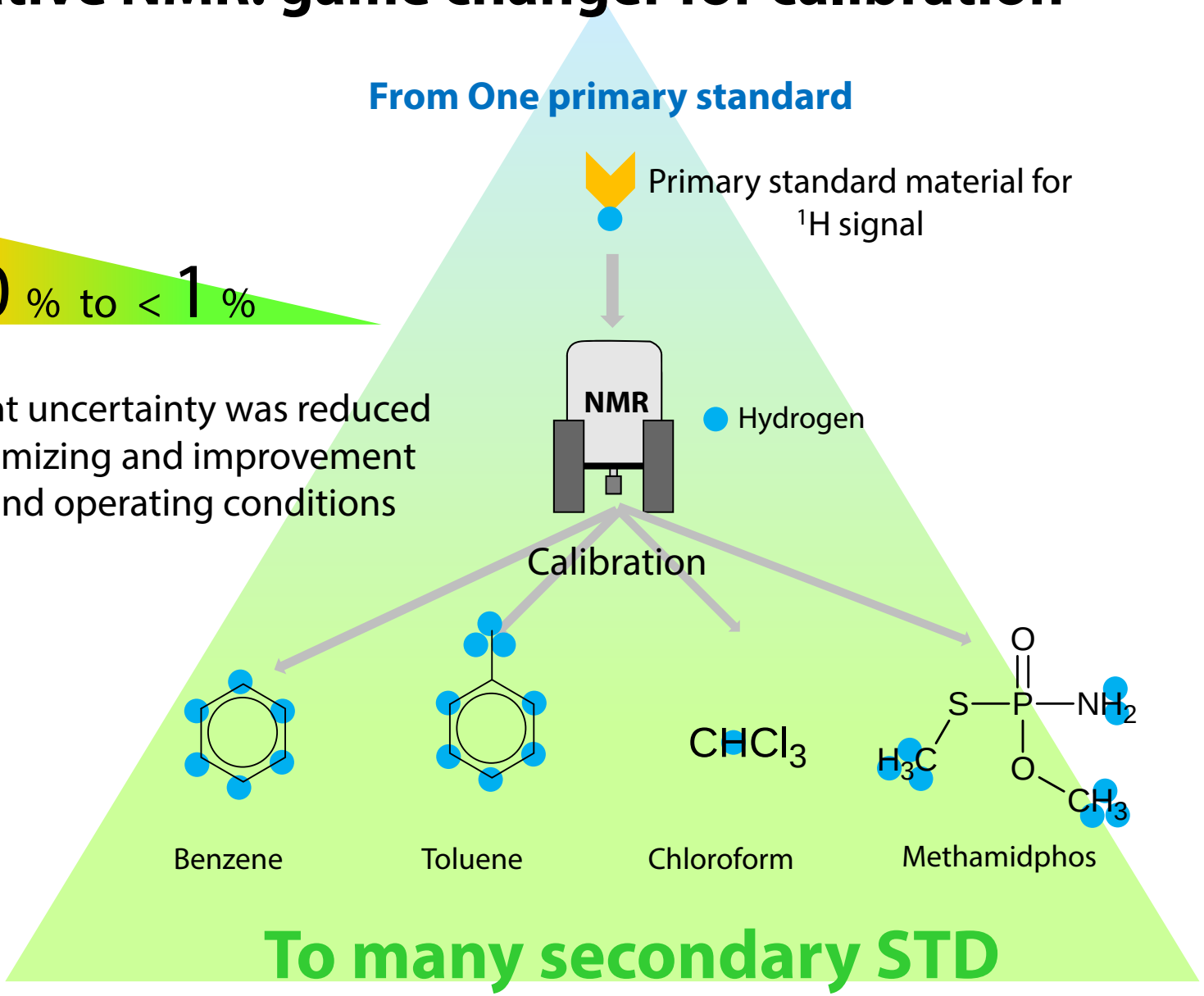




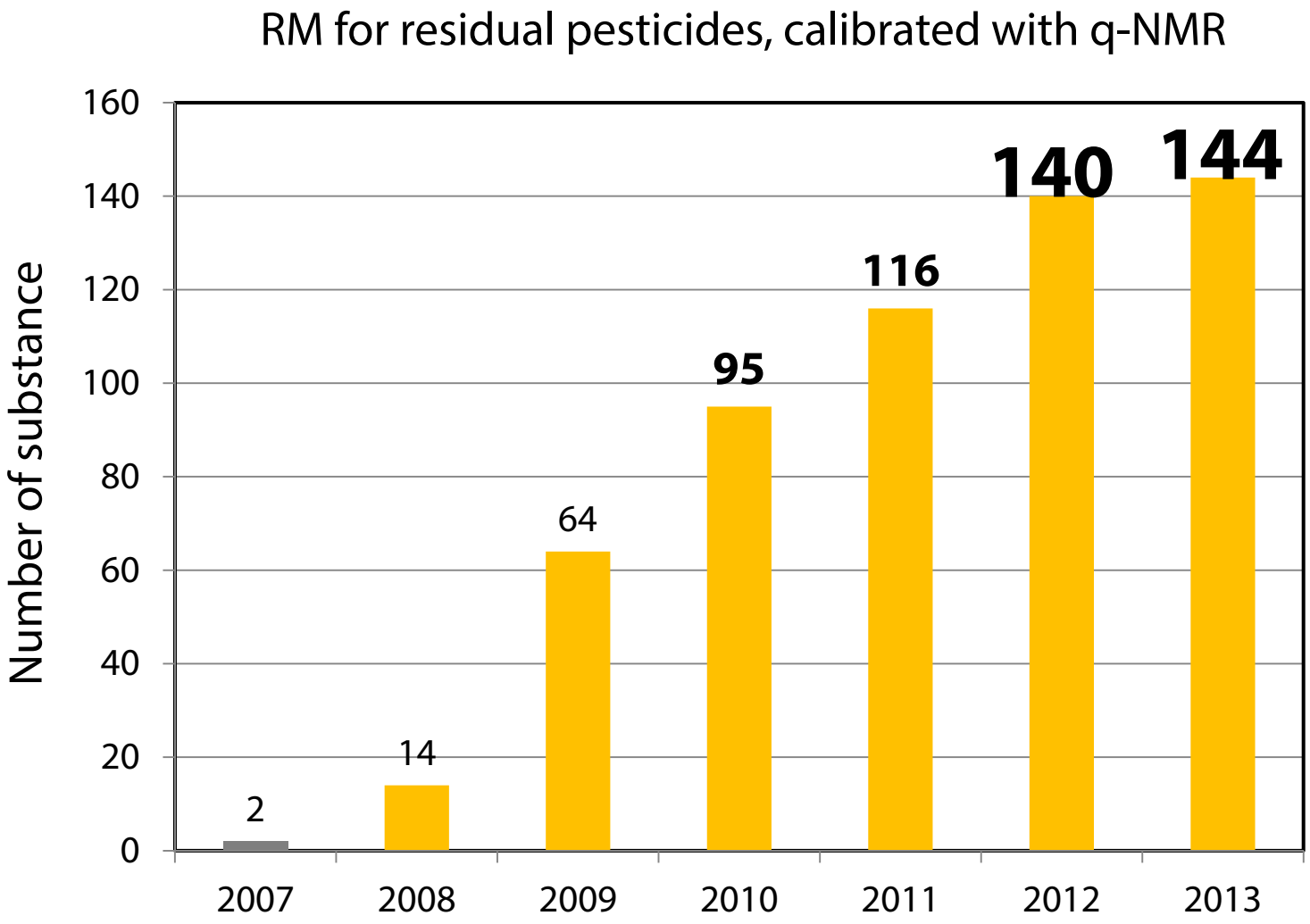
Quantitative NMR: game changer for calibration

From >10 % to <1 %

Measurement uncertainty was reduced through optimizing and improvement Instrument and operating conditions



Acceralating dissemination of Pesticide RM in Japan



Matrix type CRMs: Self-checking Tools for Chemical Analysis

Certified for the concentrations of Cd, As and other elements, corresponding to the CODEX regulatory standard.

Cd: 0.548 ± 0.020 mg/kg (*k*=2)

Total As: 0.109 ± 0.005 mg/kg (*k*=2)

Inorg.As: 0.098± 0.006 mg/kg (*k*=2)

Ex. NMIJ CRM 7501-a: White Rice Flour

How Do We Ensure the reliability of NMIJ CRMs ?

Cross-checking of analysis for certification

Quality of Our Certification: ex. Cd in white rice flour CRM

	NMIJ CRM7501-a*1	NMIJ CRM7502-a*1
MW digestion/ ID-ICP-MS	0.0516 ± 0.0020	0.551 ± 0.010
Dry-ash/ ID-ICP-MS	0.0514 ± 0.0011	0.552 ± 0.010
GFAAS	0.0524 ± 0.0016	0.545 ± 0.014
ICP-MS	0.0517 ± 0.0018	0.546 ± 0.006
Property Value	**0.0517 mg/kg**	**0.548 mg/kg**

Carefully evaluate analytical procedure, homogeneity, and stability.

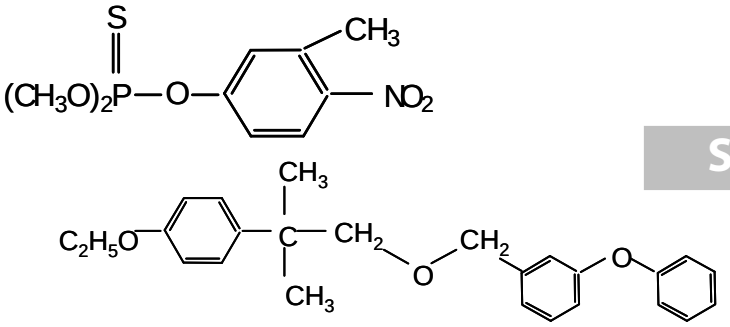
Matrix-type CRMs for Food and Water Analysis

7202-b	River Water (Elevated level, 19 elements)
7203-a	Tap Water (Elevated level, 19 elements)
7402-a	Cod fish Tissue (13 Elements, AsB, Methyl-Hg)
7403-a	Swordfish Tissue (14 Elements, AsB, Methyl-Hg)
7405-a	Seaweed (Hijiki) (18 Elements, Arsenate)
7406-a	Squid Tissue (10 elements)
7501-a	White Rice Flour: Cd Level I (11 Elements)
7502-a	White Rice Flour: Cd Level II (18 Elements)
7503-a	White Rice Flour (6 Elements, As(III), As(V), DMAA), *stock out, in prep.*
7505-a	Tea Leaf Powder (18 Elements)
7511-a	Soybean (8 Elements)
7512-a	Milk Powder (13 Elements)
7531-a	Brown Rice Flour (6 Elements)
7532-a	Brown Rice Flour (8 Elements, Inorg. As, DMAA)
7533-a	Brown Rice Flour (8 Elements, Inorg. As, DMAA)

Useful for Evaluating Extraction Efficiency:

Food CRM for Pesticide Residues Analysis

Candidate materials were prepared from grains, vegetables, and fruits sprayed pesticide during cultivations



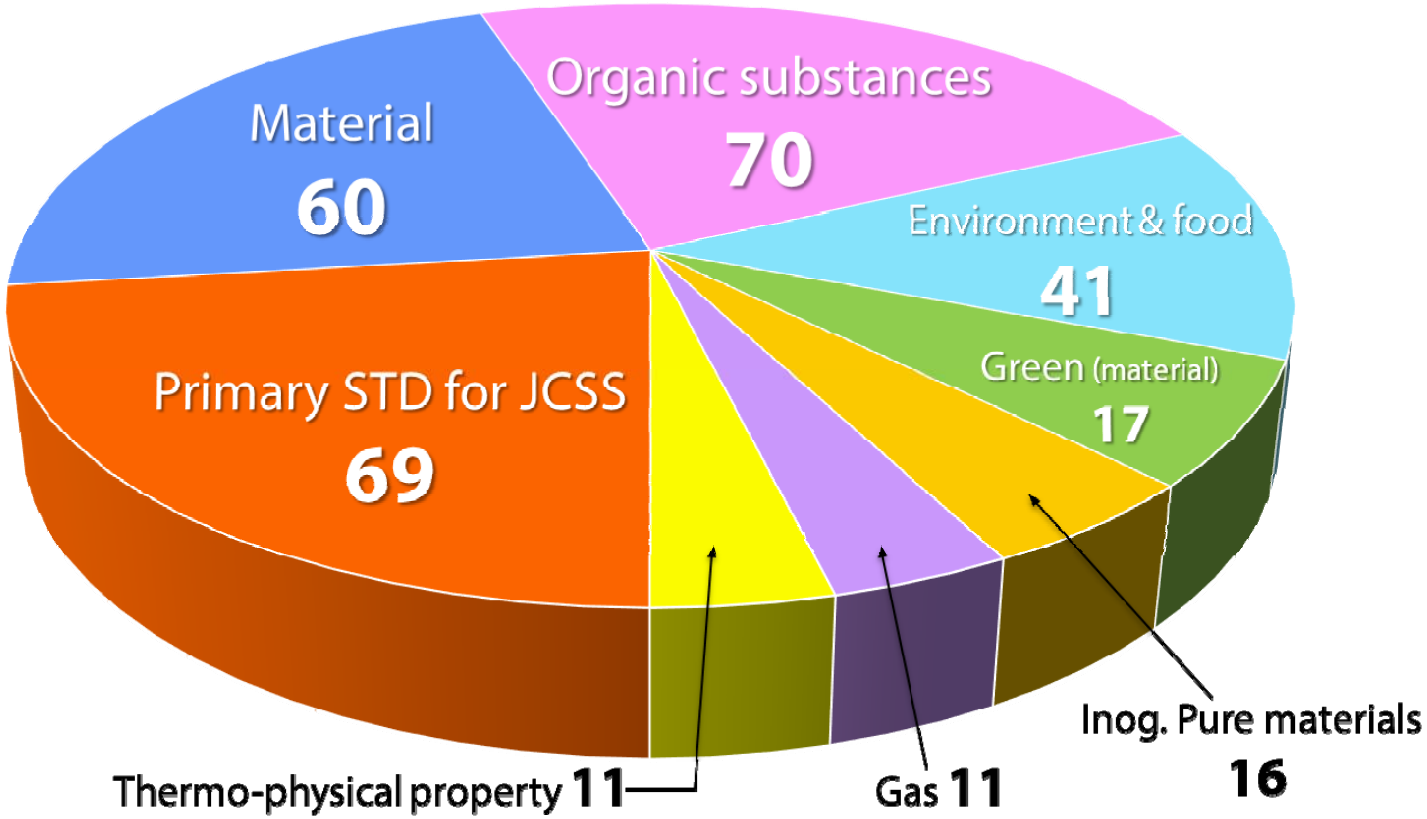
Spraying

Series of Food CRMs for Pesticides analysis

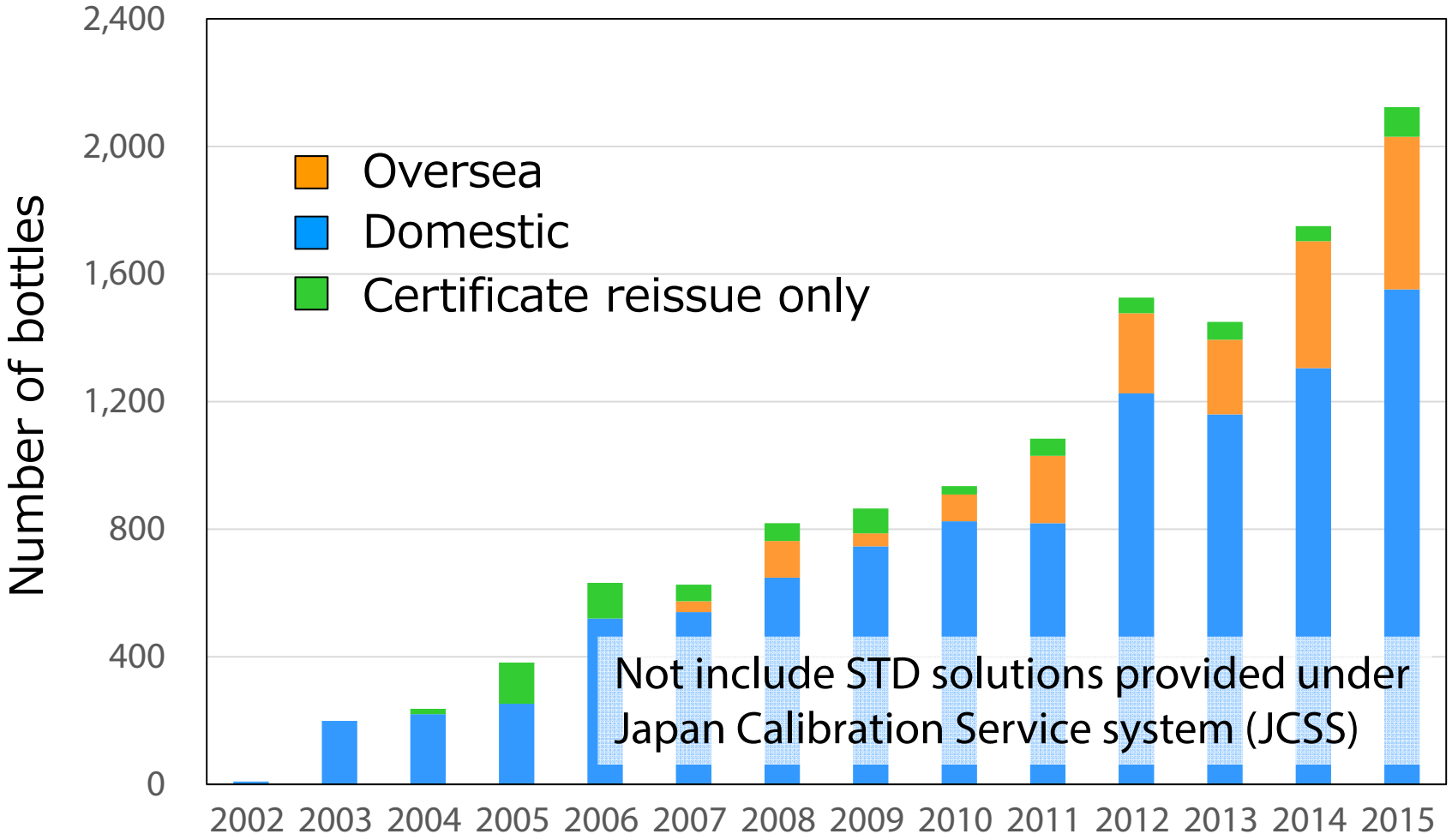
- NMIJ CRM 7504-a Unpolished Rice
- NMIJ CRM 7507-a Green Onion
- NMIJ CRM 7508-a Cabbage
- NMIJ CRM 7509-a Apple juice
- NMIJ CRM 7510-a Soy Bean

Providing NMIJ CRMs

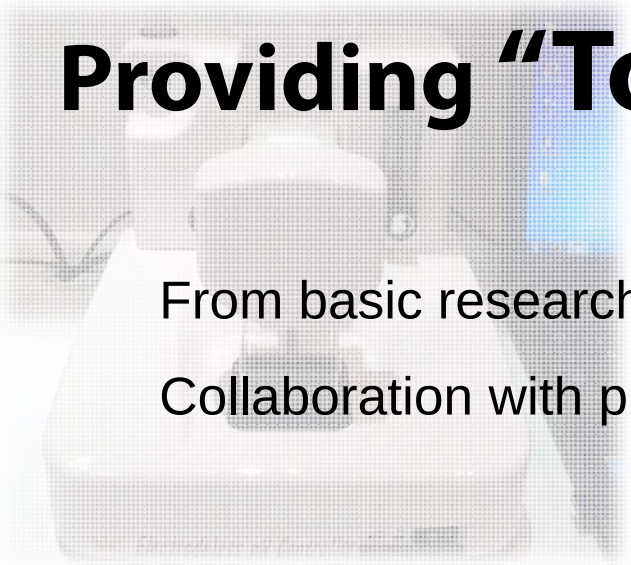
Total 297 CRMs



Distribution of NMIJ CRMs



Providing "Tools": Analytical devices



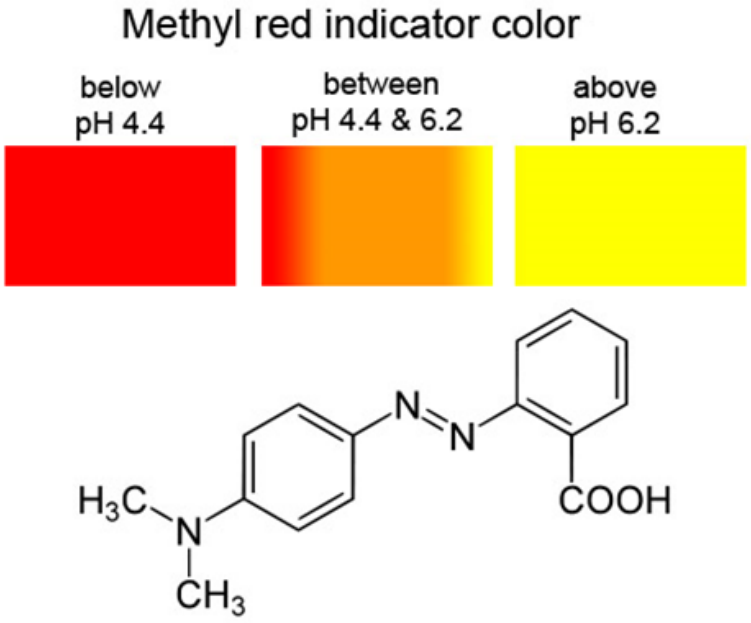
From basic research to product development

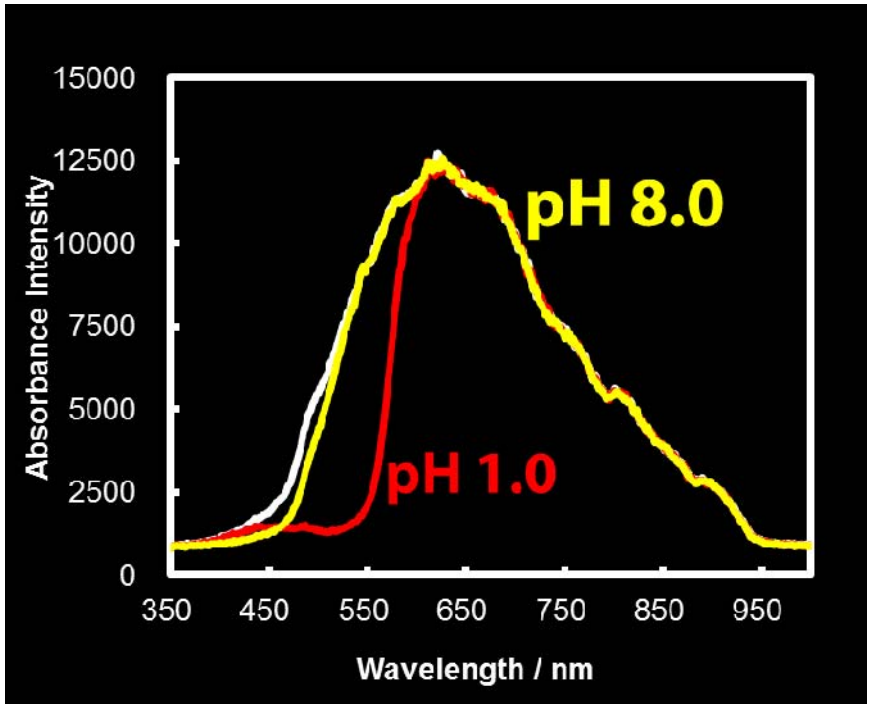
Collaboration with private companies

Realizing an Automatic pH Adjustment

Technical Points :

Electrode-less pH monitoring
Automatic addition of an ammonium solution using a sprayer (nebulizer)

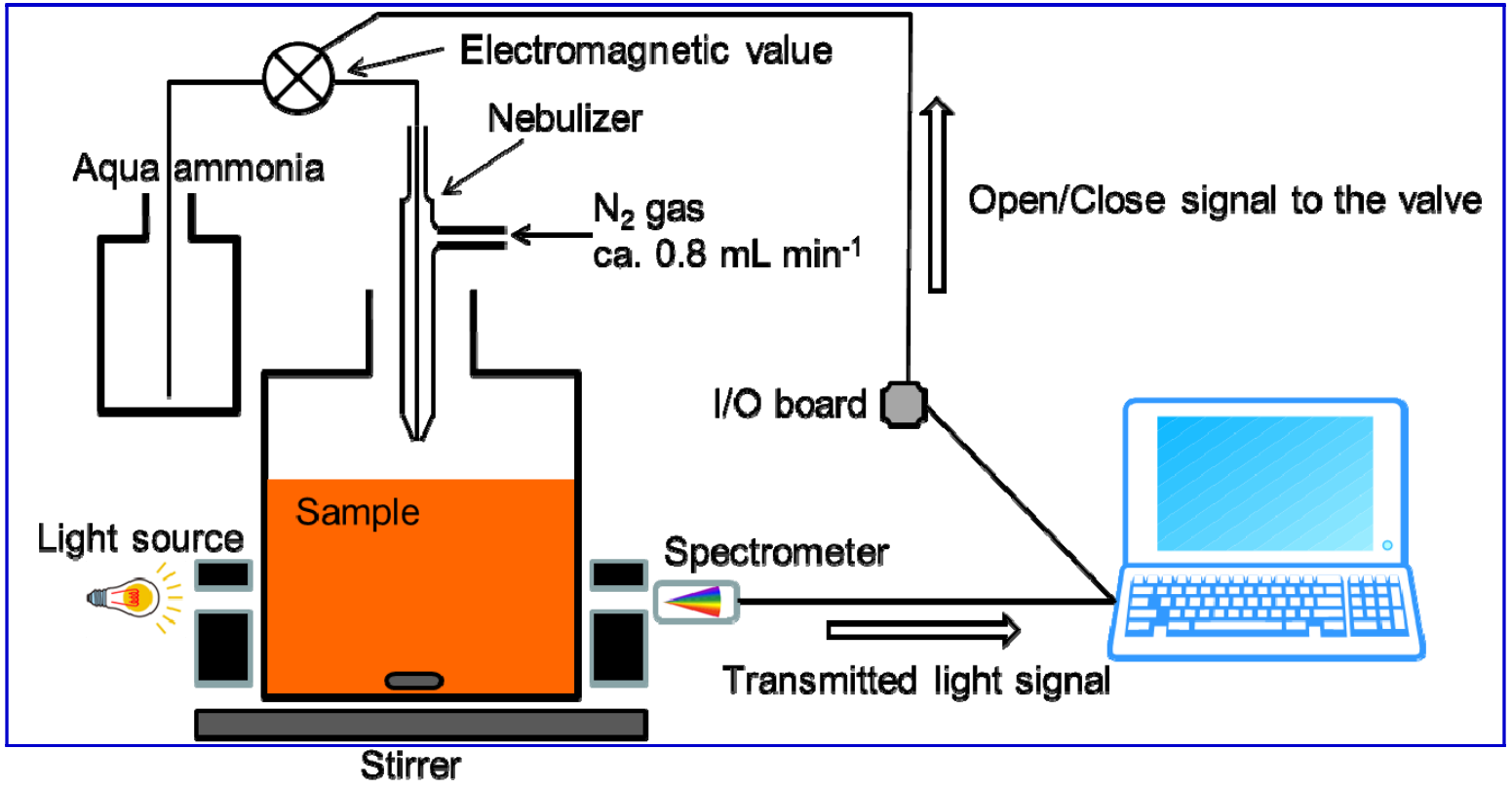




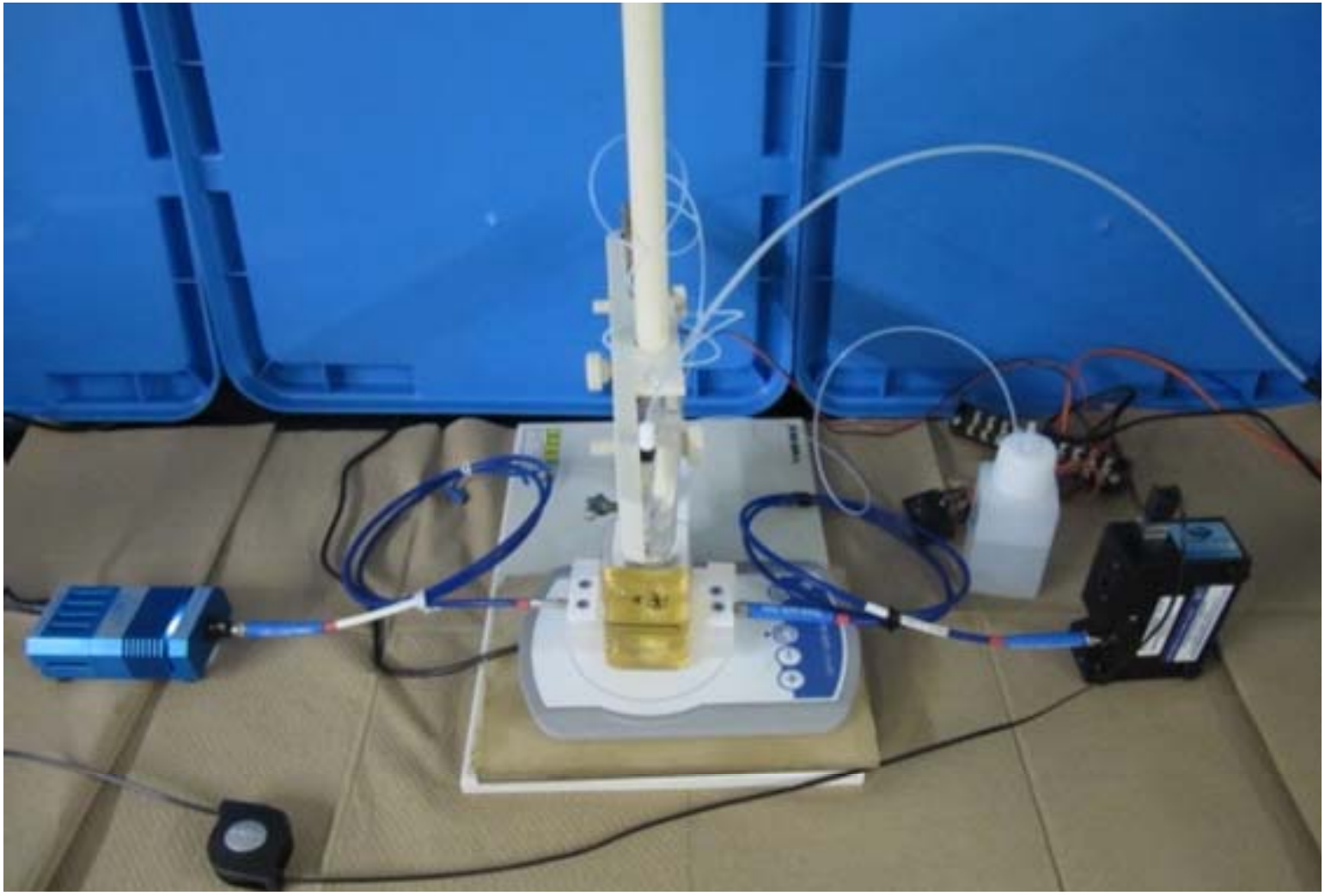
Realizing an Automatic pH Adjustment

Technical Points :

Electrode-less pH monitoring
Automatic addition of an ammonium solution using a sprayer (nebulizer)



Realizing an Automatic pH Adjustment

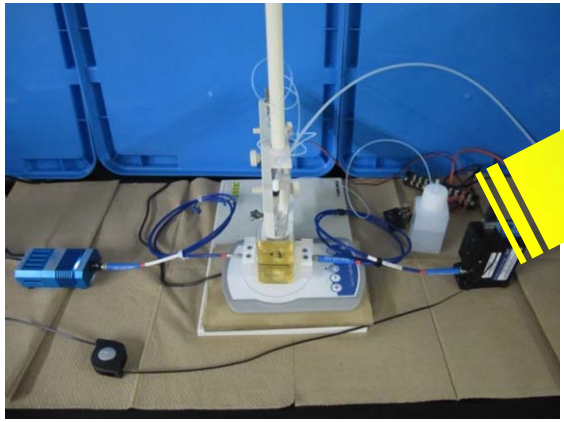


Realizing an Automatic pH Adjustment

Product development has been performed with a private company.

First product was launched in June 2016.

R&D now continue to improve a usability and to extend applications.

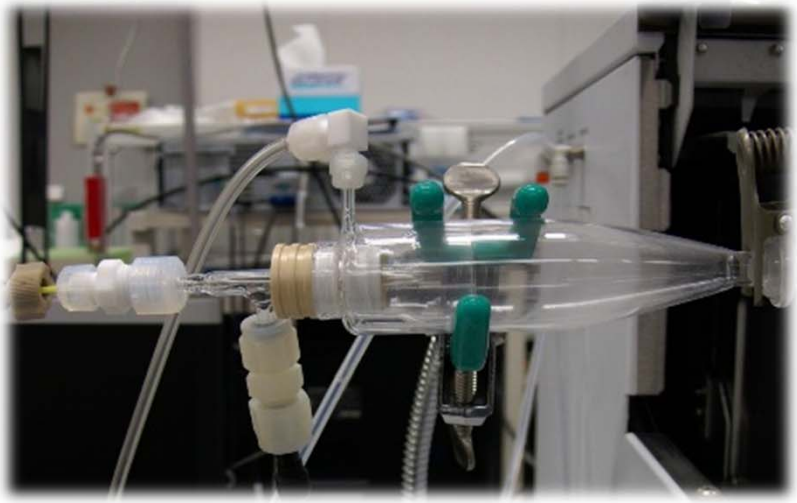


Providing "Tools": Analytical devices

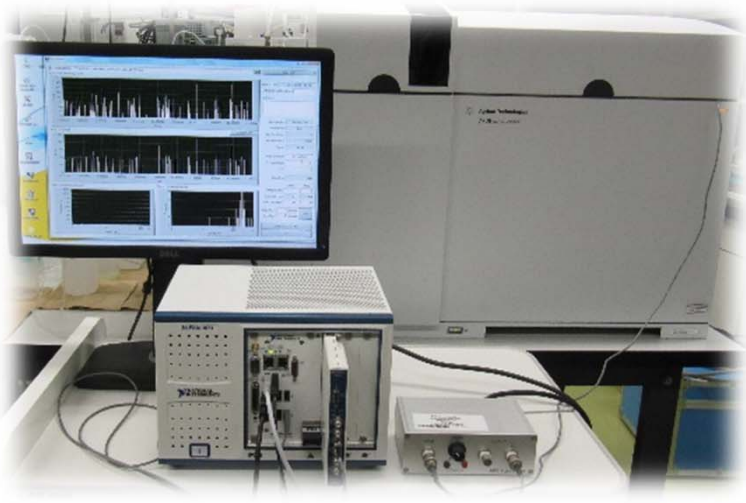
1 . Electrodeless pH controller for sample preparation

2. Sample introduction devices for plasma spectroscopy

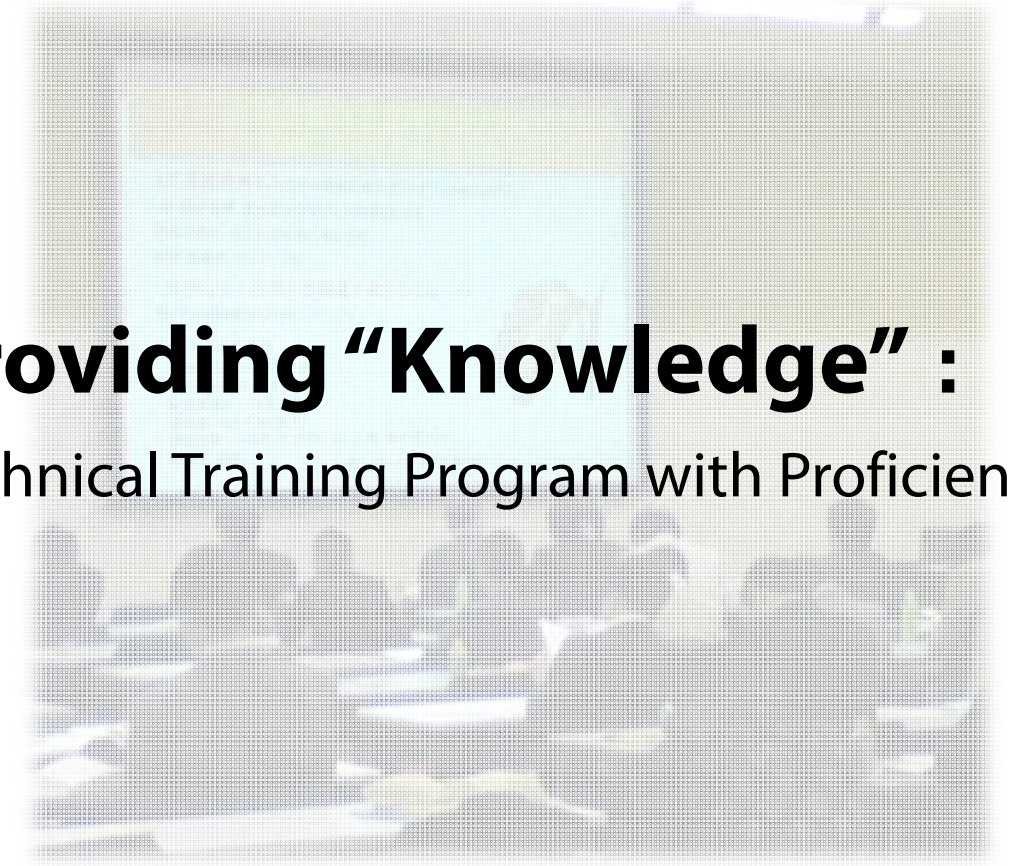
3. High-speed pulse-signal processing system for nanoparticle analysis



Sample introduction device for ICP-MS



Pulse-signal processor for ICP-MS

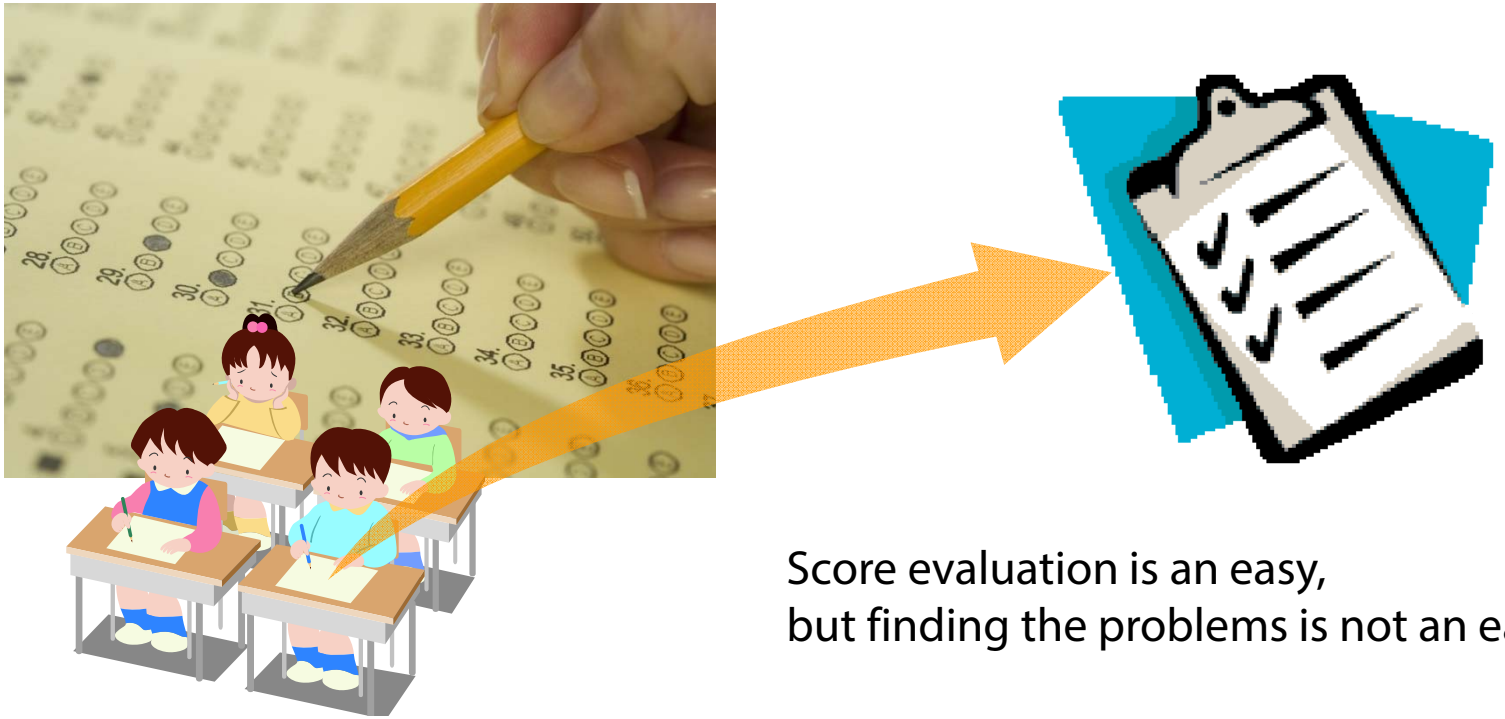


Providing “Knowledge” :

Technical Training Program with Proficiency Testing

Usual Proficiency Testing

- External quality assessment
  ← Capability assurance for laboratory accreditation
- Validation for new method to be used in SOP
- Staff training



Score evaluation is an easy,
but finding the problems is not an easy !

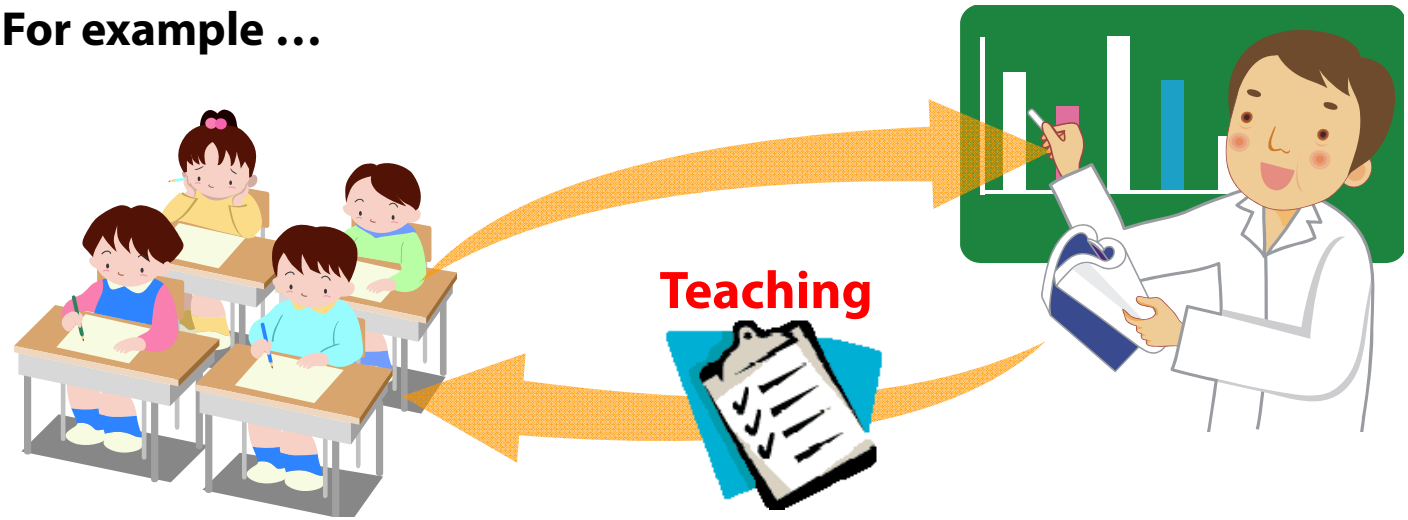
NMIJ Skill Upgrading Training Program

Including "Proficiency Testing" and "Technical Lecture"

Supporting for

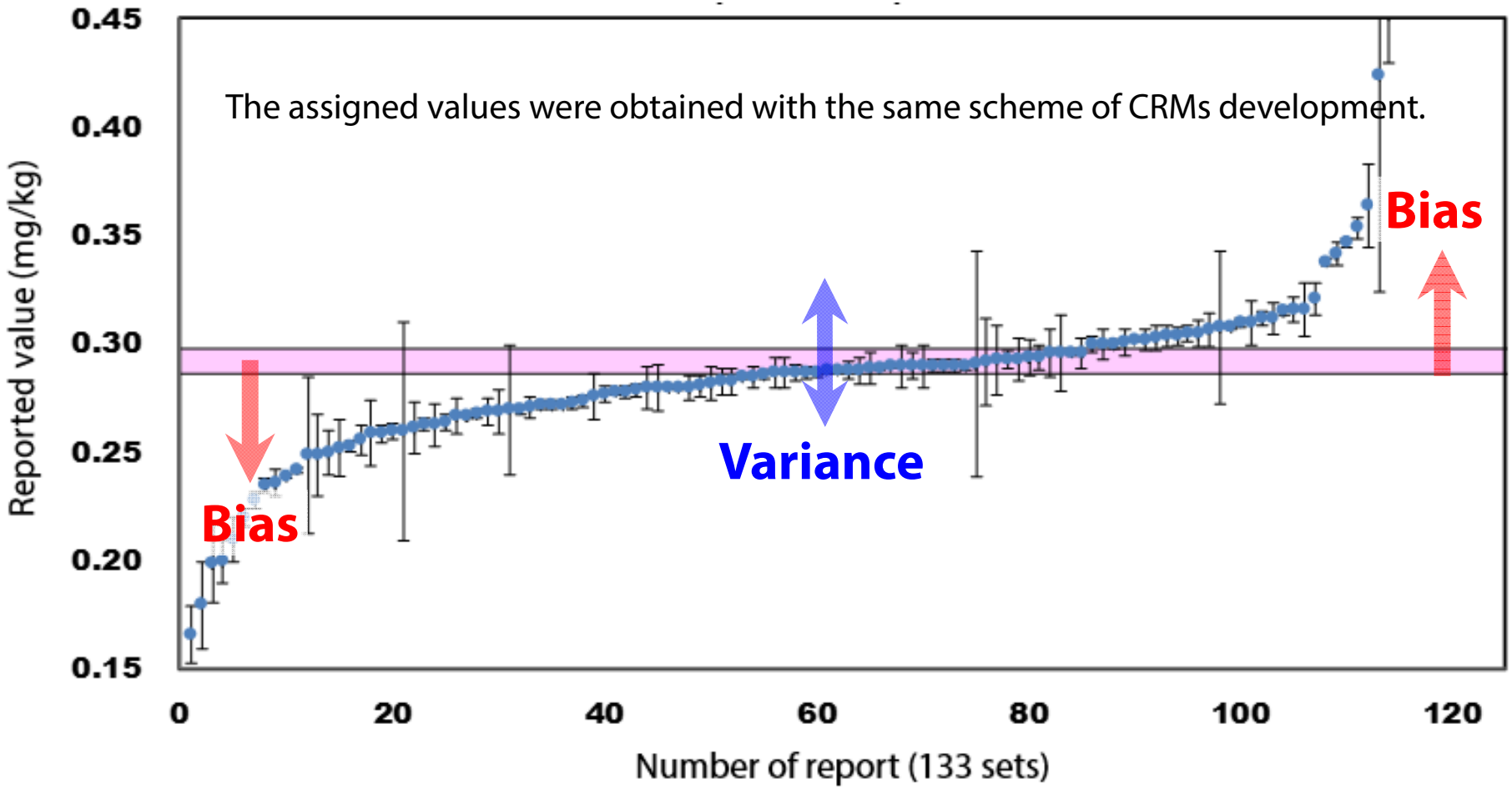
- Specifying technical problems
  through finding **"Bias"** and **"Variance"** sources

For example …



First step: Finding "Bias" and "Variance"

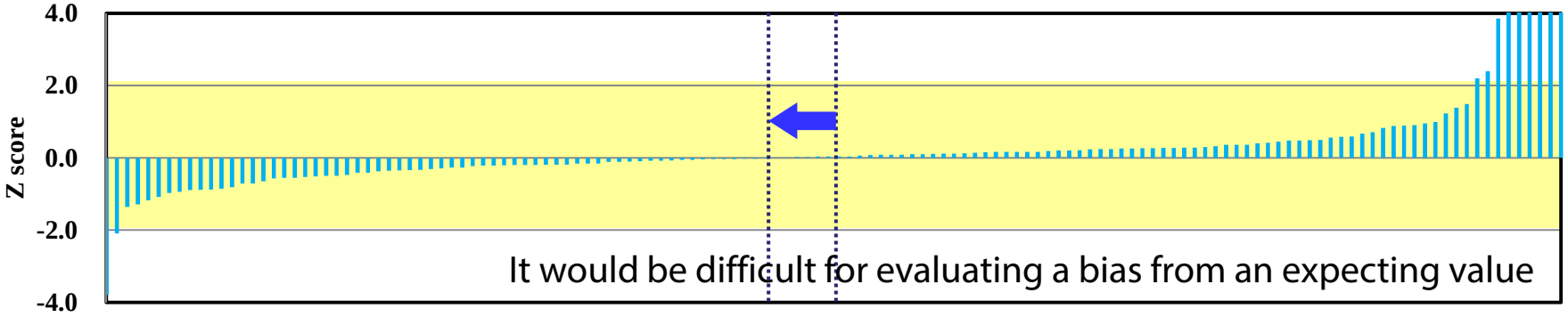
By comparing with an assigned value provided NMIJ/AIST



Ex. Scoring evaluation in PT: Cd in brown rice

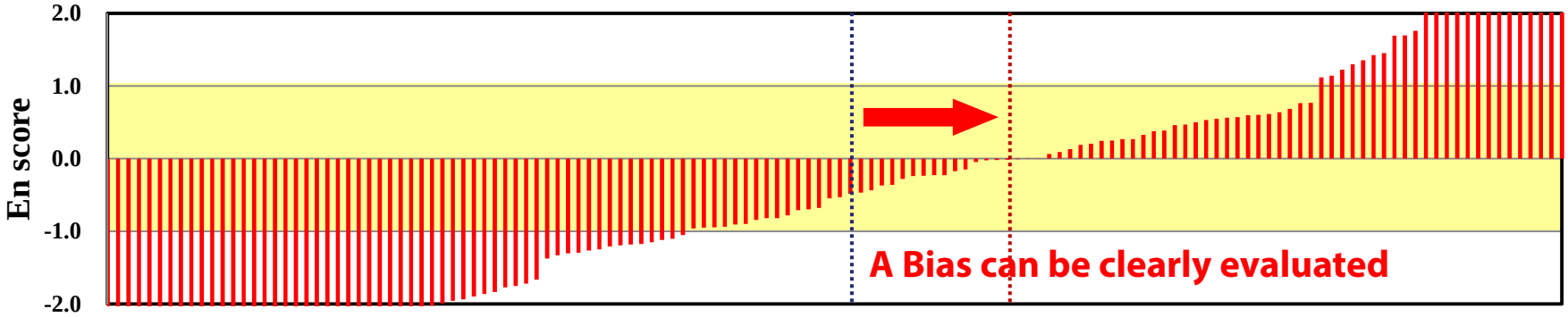
z score

Evaluating on the basis of a distribution of the reported values
It's a relative position in the distribution



E_n number

Evaluating on comparing with an assigned value (provide form NMIJ)
It's an independent of the distribution



Extraction "Bais" and "Variance" from the Results

	Sample preparation	Calibration curve	Problem in measurement
Mg	Ashing (contamination)	Front bias	FAAS
Ca	Ashing (contamination or loss)	Front bias	FAAS
Mn	Ashing & open digestion (contamination or loss)	Front bias	FAAS
Fe	Ashing & open digestion (contamination or loss)	Front bias	FAAS, ICP-OES
Cu	Ashing (loss)	Front bias	FAAS
Zn	Ashing (contamination)	Back & front bias	---
As	Ashing (loss)	---	Hydride generation
i-As	Extraction (loss)	---	---
Cd	Ashing & Extraction (loss)	Front bias	FAAS, ICP-OES

Recent Programs for Elemental Analysis

Program was started from 2009

- **Trace Elements in Brown Rice Flour** (Sep.-Nov. 2012)

  Participants: **155** in PT, **114** in lecture, **23** in individual consultation.

  Completely synchronized with PT in Mexico (15 labs.)

- **Trace Elements in Brown Rice Flour** (Sep.-Nov. 2013)

  Participants: **160** in PT, **120** in lecture, **32** in individual consultation.

- **Trace Elements in Squid** (Sep.-Nov. 2014)

  Participants: **116** in PT, **130** in lecture, **29** in individual consultation.

→ A part of this program transferred to a private company,
which is now providing a PT program accredited an accordance of ISO /IEC17043

Recent Programs for Pesticide Residue Analysis

The programs are suitable for evaluating extraction skills of pesticide residues

Samples are prepared from grains sprayed pesticide during cultivations

- **Pesticide Residues in Soybean Powder** (May-July 2012)

  Participants: **43** analysts

- **Pesticide Residues in Brown Rice Flour** (May-July 2013)

  Participants: **58** analysts

- **Pesticide Residues in Wheat Flour** (May-July 2014)

  Registrations: **72** analysts

NMIJ Provides

Services

Calibrations

Technical training
with Proficiency Testing

Consulting

Knowledge

Analytical methods

Technical Know-how

Tools

Reference Materials

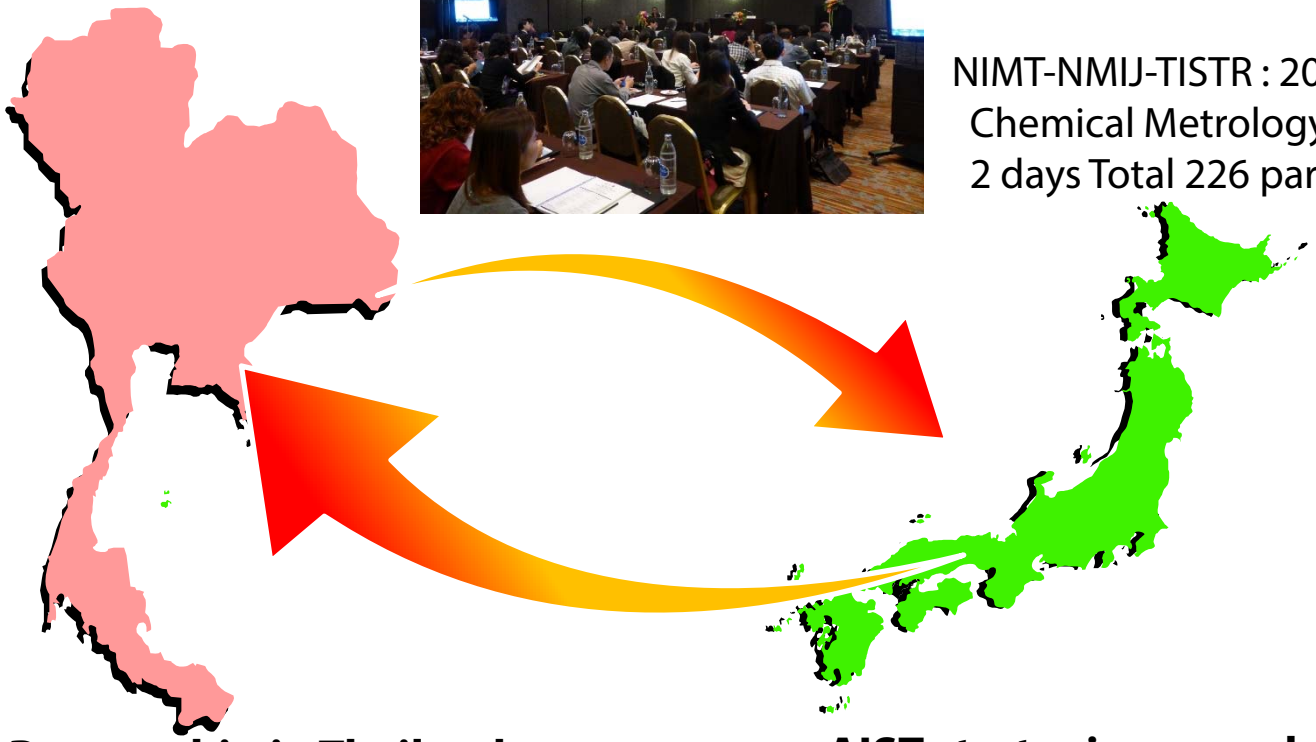
Analytical devices

For Ensuring Reliability
in Food and Water Analyses

Collaboration for PT program in Thailand

1st PT program: 2013-2014
trace elements in brown rice flour
42 labs. were participated

NIMT-NMIJ-TISTR : 2014
Chemical Metrology Seminar
2 days Total 226 participants



Partnership in Thailand

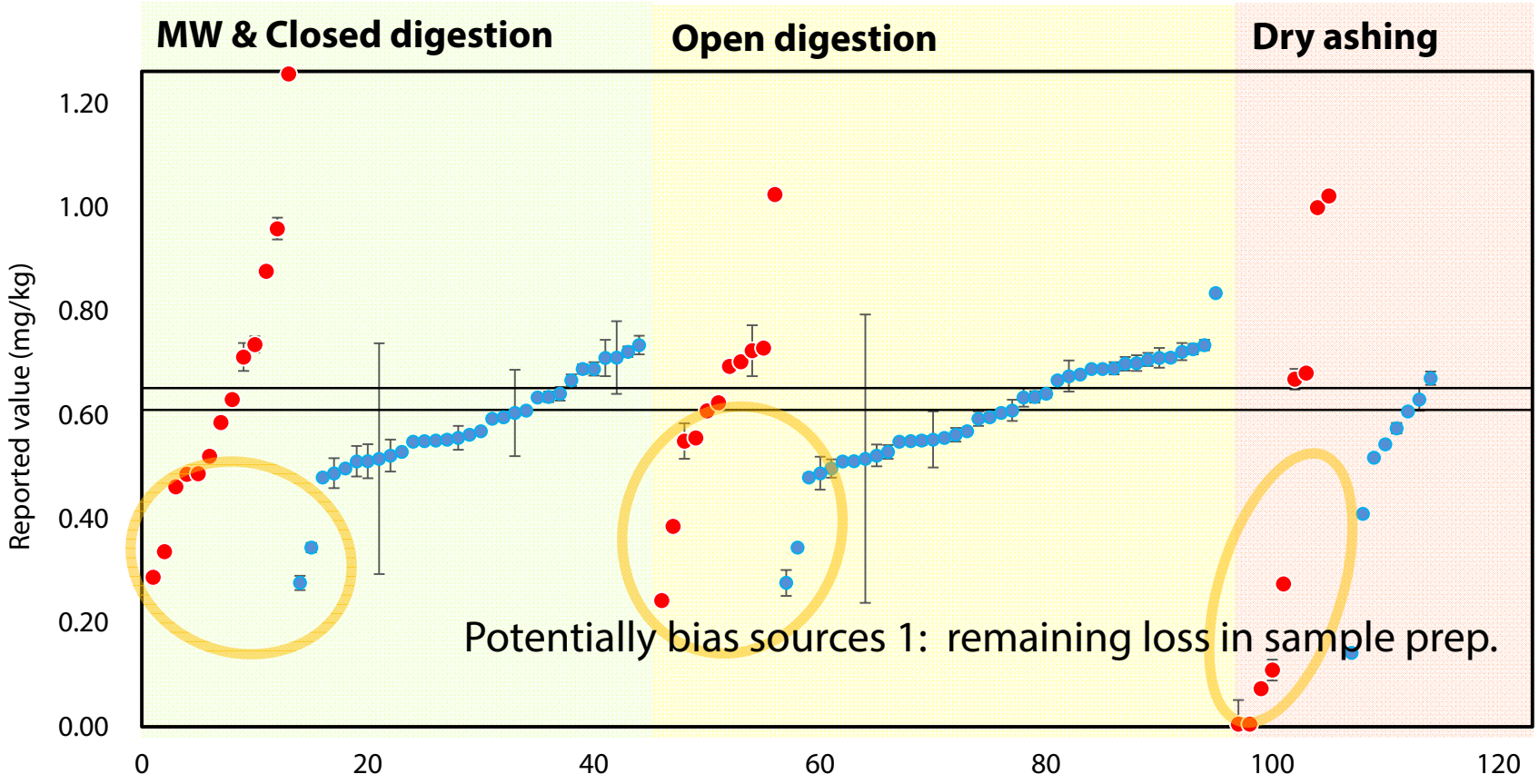
- TISTR (AIST-TISTR MoU)
- NIMT (NMIJ-NIMT MoU)

AIST strategic research program

2013-2014 Metrology-hub in ASEAN
2015-Metrology-arena in ASEAN

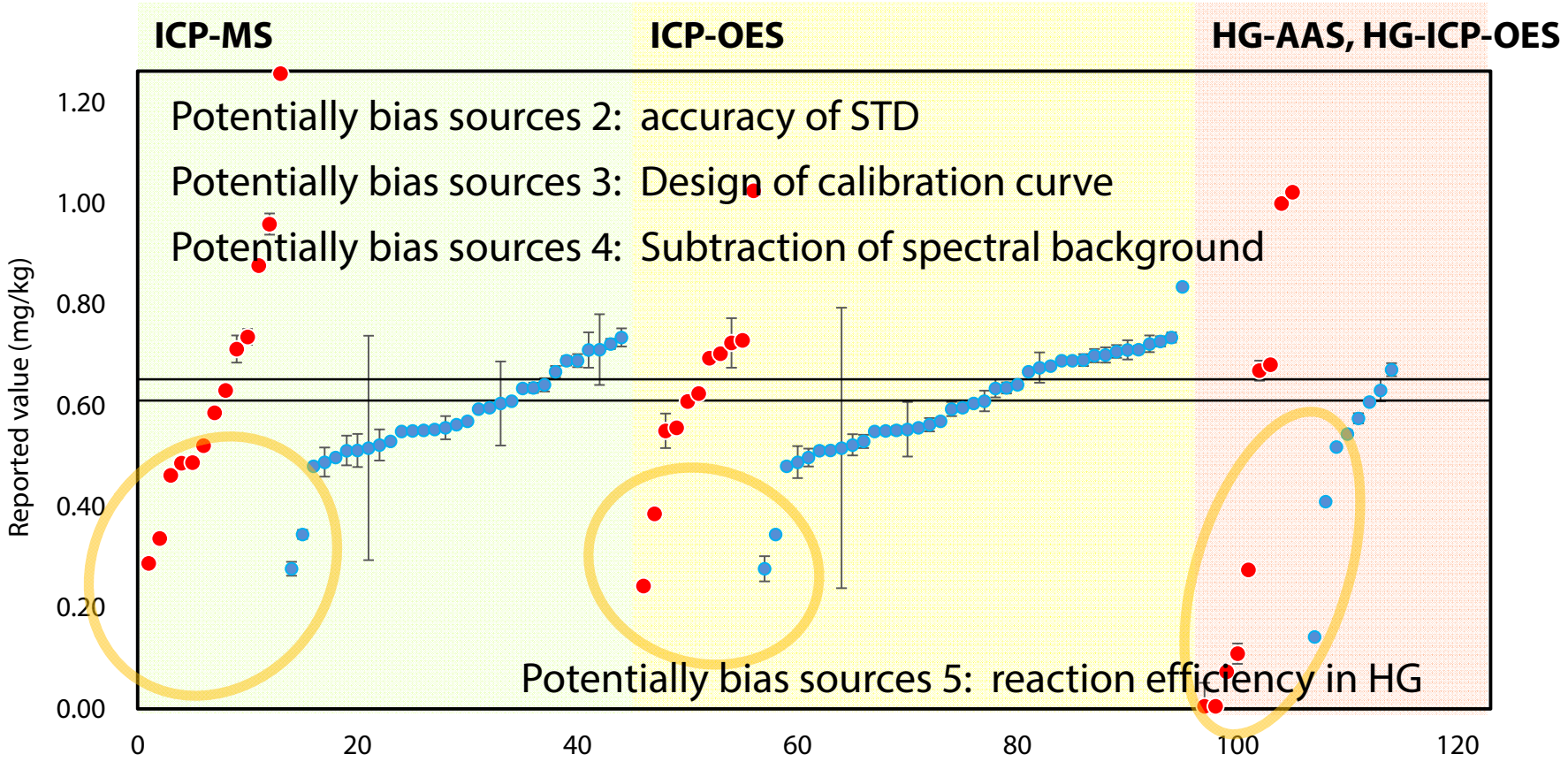
Dependence with Sample preparation: As results

Arsenic can hardly be contaminated during sample prep. and measurement,
except for cross-contamination during the preparation.



Dependence with Measurement Tech.: As results

Chemical forms of As and pH conditions strongly influence on the efficiency of HG.



Collaboration for PT program in Thailand

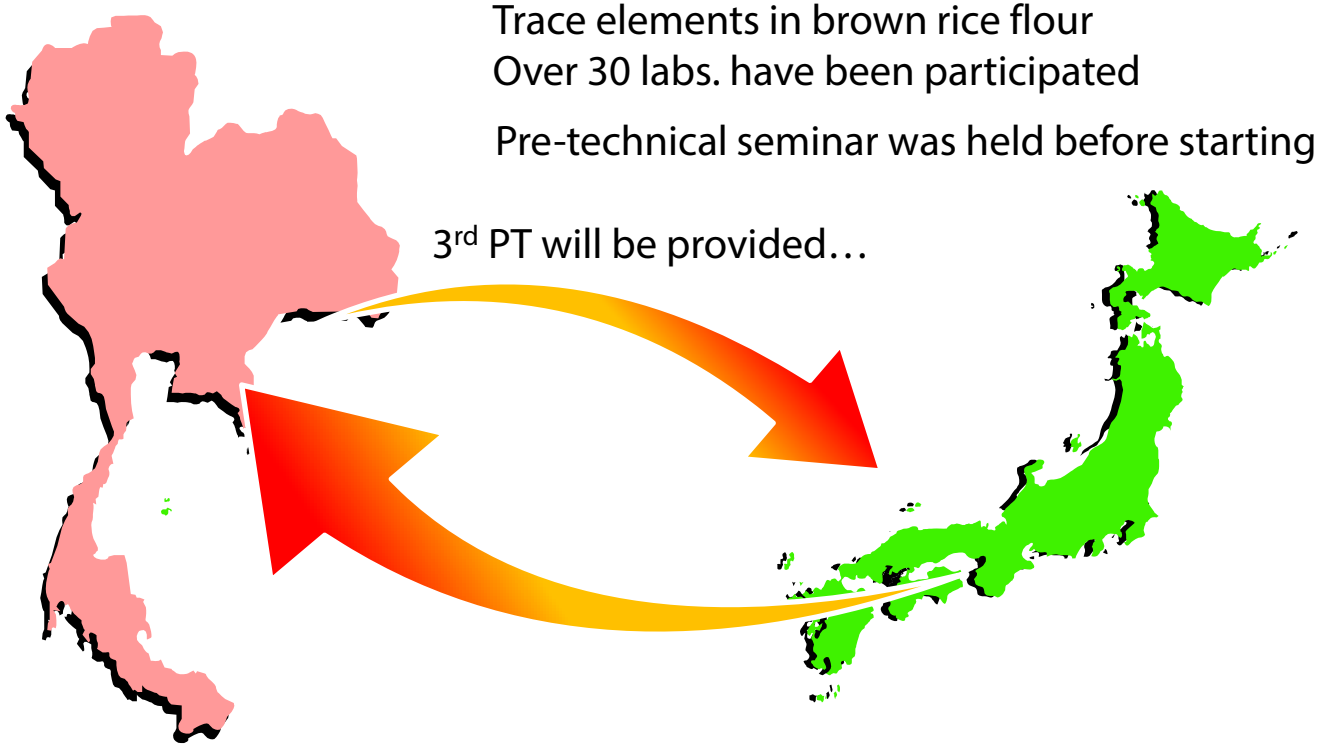
For Improving the analytical skills

2nd PT program was provided in 2015:

Trace elements in brown rice flour
Over 30 labs. have been participated

Pre-technical seminar was held before starting the PT

3rd PT will be provided…



Partnership in Thailand

- TISTR (AIST-TISTR MoU)
- NIMT (NMIJ-NIMT MoU)

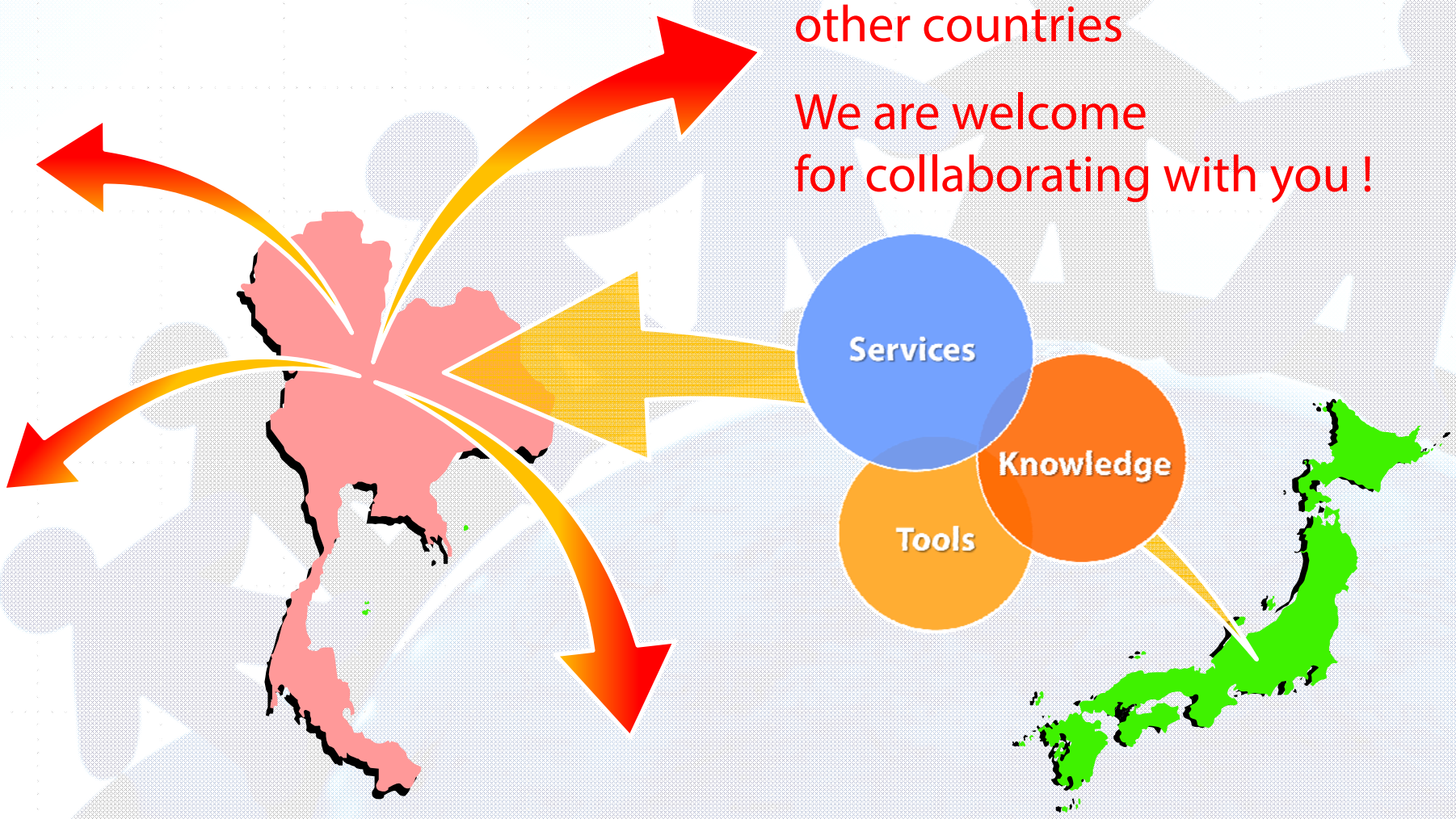
AIST strategic research program

2013-2014 Metrology-hub in ASEAN
2015-Metrology-arena in ASEAN

Future prospect for collaboration

Wide spreading to
other countries

We are welcome
for collaborating with you !



Thank you for your attention !