

Conventional and new traceability schemes of organic standards for safe water supply in Japan

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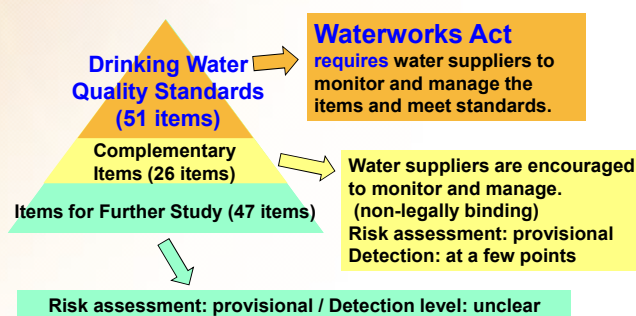
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Introduction

In these days, importance of metrologically traceable reference materials for ensuring reliability of chemical analyses has been recognized.

National Metrology Institute of Japan, National Institute of Advanced Industry, Science and Technology (NMIJ/AIST) has been supplying many types of reference materials. In 2015, the demand of traceable certified reference materials (CRMs) for drinking water analyses rose by an amendment of a notification under the Waterworks Act of Japan. In this presentation, NMIJ's activities such as supplying organic CRMs and providing calibration services for purity assessment of organic compounds are outlined. Especially, efforts to improve efficiency of reference material supply by applying new techniques such as quantitative NMR (qNMR) are described.

Drinking water quality control by Waterworks Act of Japan



Modified from http://www.mhlw.go.jp/english/policy/health/water_supply/4.html

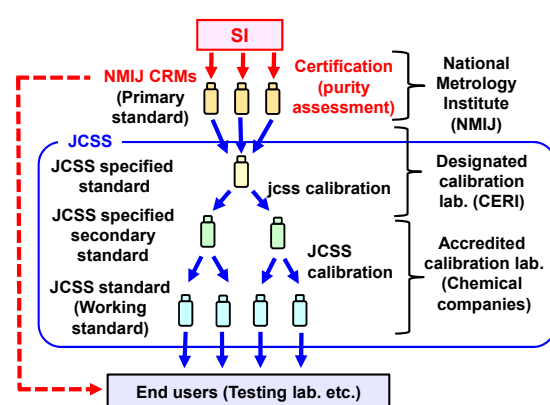
A new notification (Notification of the Ministry of Health, Labour and Welfare No.56, March 2015) allows use of standard solutions which are traceable to national standards based on the Measurement Law of Japan.

Drinking water quality standards (Organics)

Solvents	Disinfection byproducts
Carbon tetrachloride	Chloroform ^a
1,4-Dioxane	Bromodichloromethane ^b
Dichloromethane	Dibromochloromethane ^c
Tetrachloroethylene	Bromoform ^d
Trichloroethylene	Total Trihalomethanes (a-d)
<i>cis-trans</i> -Dichloroethylene	Chloroacetic acid
Benzene	Dichloroacetic acid
Detergents	Trichloroacetic acid
Anionic surfactants	Formaldehyde
Nonionic surfactants	Others
Musty odor	Phenols
Geosmin	Total Organic Carbon
2-Methylisoborneol	

CRM supply and Japan Calibration Service System (JCSS)

Supply of chemical standards by JCSS scheme



JCSS consists of the national standards provision system and the calibration laboratory accreditation system. [CERI, Chemicals Evaluation and Research Institute]

<https://www.nite.go.jp/en/iajapan/jcss/index.html>

Examples of high purity organic NMIJ CRMs

Item	Characterization	Certified value $\pm U$
1,4-Dioxane	Adiabatic calorimetry ^a (& MBA) ^c	(0.9993 \pm 0.0002) mol/mol
Bromodichloro-methane	Differential scanning calorimetry ^b (& MBA) ^c	(0.9993 \pm 0.0012) mol/mol
Trichloroacetic acid	Differential scanning calorimetry ^b & Titrimetry	(0.999 \pm 0.002) kg/kg
17 β -Estradiol ^d	MBA & qNMR	(0.984 \pm 0.003) kg/kg

^a Freezing point depression method (FPD) / Fractional melting method. ^b FPD / Stepwise scan method. ^c For verification. (MBA, Mass balance approach) ^d Item for Further Study.

Examples of JCSS organic standard solutions

Item	Concentration	Specification
23 VOCs	1000 mg/L	$\pm 1.0\%$ to $\pm 4.4\%$ ^b
25 VOCs	1000 mg/L	$\pm 1.0\%$ to $\pm 4.4\%$ ^b
6 Alkylphenols ^a	100 mg/L	$\pm 0.5\%$ to $\pm 1.0\%$ ^c
8 Phthalate esters ^a	100 mg/L	$\pm 0.5\%$ to $\pm 1.5\%$ ^c

^a Some of them are the Items for Further Study; CERI directly supplies them as the JCSS standards. ^b Range. ^c Expanded uncertainty.

Calibration service (purity assessment)

To realize rapid calibration services for purity assessment,

- Quantitative NMR is mainly applied.
- Continuous scan method by differential scanning calorimetry is applied instead of time consuming other FPD methods.
- Area percentage method with GC or HPLC is used instead of the strict mass balance approach.

NMIJ provides the services and issues calibration certificates for domestic reference material producers.

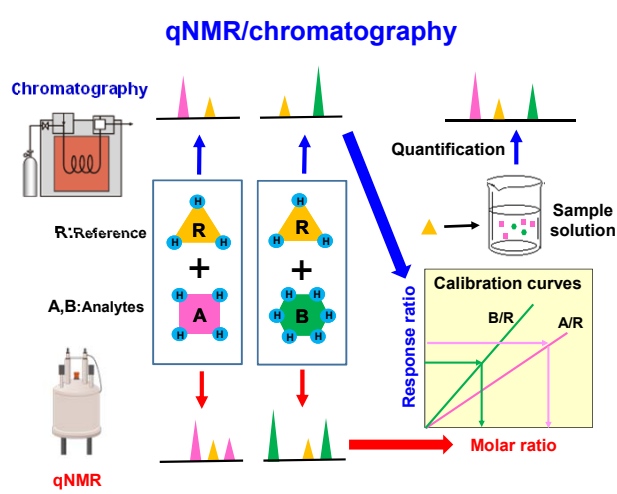
NMIJ's calibration services of purity assessment (2018)

Method for characterization	Item
qNMR & FPD	29 pesticides
qNMR with verification by GC	70 pesticides and naphthalene
qNMR with verification by HPLC	46 pesticides and 2 vitamins
FPD with verification by GC	4 pesticides and 8 hydrocarbons etc.
qNMR & titrimetry	23 amino acids

Some of the pesticides are the Complementary Items.

Ihara T et al., 2009 *Synthesiology* 2 13-24.

Direct characterization of standard solutions for more efficient standard supply



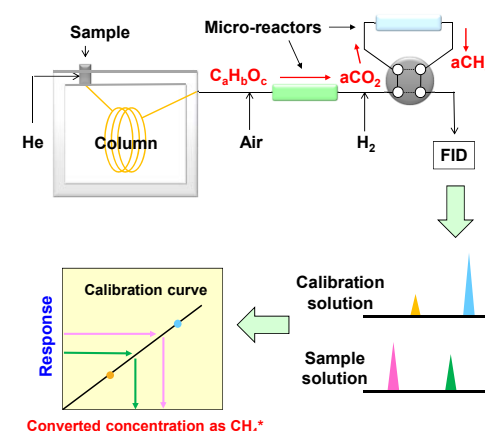
Kitamaki Y. et al., 2017 *Anal. Chem.*, 89 6963-6968.
Kuroe M et al., 2018 *Bunsekikagaku* 67 541-549.

JCSS organic standard solutions for drinking water analysis

JCSS standard solution	Item	CMC for JCSS specified standard		Characterization
		Concentration	U	
Phenols (1000 mg/L each)	Phenol	(1100 to 1400) mg/kg	0.6 %	qNMR/GC
	2-Chlorophenol	(1100 to 1400) mg/kg	0.6 %	
	4-Chlorophenol	(1100 to 1400) mg/kg	0.6 %	
	2,4-Dichlorophenol	(1100 to 1400) mg/kg	0.6 %	
	2,6-Dichlorophenol	(1100 to 1400) mg/kg	0.6 %	
Haloacetic Acids (1000 mg/L each)	2,4,6-Trichlorophenol	(1100 to 1400) mg/kg	0.7 %	qNMR/LC
	Chloroacetic acid	(1200 to 1500) mg/kg	0.5 %	
	Dichloroacetic acid	(1200 to 1500) mg/kg	0.3 %	
	Trichloroacetic acid	(1200 to 1500) mg/kg	0.4 %	
Musty odor substances (100 mg/L each)	Bromoacetic acid	(1200 to 1500) mg/kg	0.4 %	Post-column reaction GC
	2-Methylisoborneol	(90 to 110) mg/L	1.3 %	
Nonionic surfactant (100 mg/L)	Geosmin	(90 to 110) mg/L	1.3 %	qNMR/LC (Planned)
	Heptaoxyethylene dodecyl ether	(110 to 140) mg/kg	1.4 %	

NMIJ provides calibration services for CERI to characterize the JCSS specified standard solutions.

Post-column reaction GC-FID

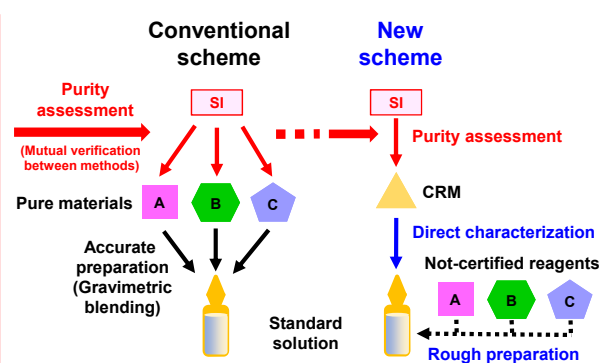


Converted concentration as CH_4^*
* (Amount-of-substance concentration) \times (number of carbon atoms in the molecule)

Kitamaki Y et al., 2018
Accred. Qual. Assur. 23 297-302.

Conventional and new traceability schemes

- Mass balance approach**
 - For most of organic compounds
 - Impurity information for other methods
 - ⊗ "Dark" impurities
- Freezing point depression**
 - Primary method
 - For highly pure materials (>98 %)
 - ⊗ Solid solution, degradation etc.
- qNMR**
 - Direct method
 - For most of organic compounds
 - ⊗ Low resolution
- Titrimetry**
 - Primary method
 - Direct method
 - For acids and bases
 - ⊗ Limited targets



Numata M. et al., 2019 *Metrologia*, <https://doi.org/10.1088/1681-7575/ab04c6>

Conclusions

NMIJ supplies organic reference materials to end users directly or via the JCSS traceability scheme. In the latter case, high purity CRMs are supplied as primary standards for calibration of standard solutions. To realize more efficient organic standard supply, NMIJ has also provided calibration services of purity assessment for reference material producers by adopting the qNMR and other techniques. Furthermore, NMIJ has investigated methods for the direct characterization of target compounds in standard solutions. As a result, NMIJ has started calibration services for the designated calibration laboratory, CERI to directly characterize the JCSS specified standard solutions by qNMR/chromatography and post-column reaction GC.

Acknowledgements

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