Development of a New Certified Reference Material, NMIJ CRM 4229-a, for Determination of Trace Water Content in Liquids

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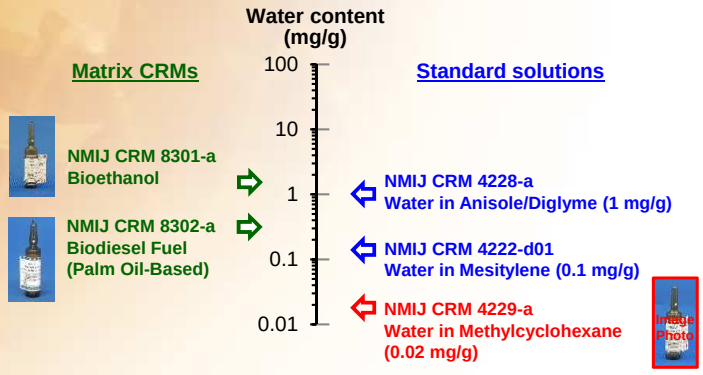
1. Introduction

The accurate determination of water content is essential for the quality control of pharmaceuticals, petroleum products, chemical reagents, food products, advanced materials *etc*. In recent years, in the fields of fine chemicals and electric and electronic materials, particularly for synthetic organic materials and battery materials, the water content as impurities should be maintained at levels much lower than ever before. To ensure reliable measurements, certified reference materials (CRMs) for determination of water contents, which are traceable to the International System of Units (SI), are required. National Metrology Institute of Japan (NMIJ) has issued a CRM, Water in Methylcyclohexane (0.02 mg/g) for use in quality control of trace water analyses in liquids.

2. CRMs for water content supplied from NMIJ



The CRMs for water content are virtually impossible to use after dilution since they are affected by water contained in the diluent and water absorption and/or desorption during preparation. Therefore, these CRMs at each required concentration level must be supplied.

3. Preparation of the candidate material

2 L of methylcyclohexane was transferred into 2-L glass bottle and stand under ambient air.

↓

To avoid water absorption, a silica gel tube was attached to the bottle.

↓

8 mL of the solution was dispend in a 10-mL amber glass ampoule under argon gas.

↓

Total of 210 ampoules were prepared.

NMIJ CRM 4229-a
Candidate material

4. Sample handling

Shake the ampule gently and stand for a few minutes.

↓

Open the ampule and attach the rubber cap immediately.

↓

Attach a silica gel tube into the cap.

↓

Rinse a gas-tight syringe with ca. 1 mL of the CRM adequately.

↓

Take ca. 6.5 mL of the CRM carefully to avoid the formation of air bubbles.

↓

Weigh the syringe using a balance.

↓

Inject ca. 1.5 mL of the aliquot into the electrolytic cell.

↓

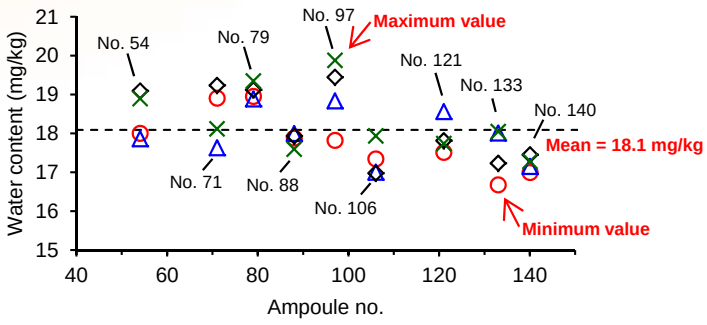
Weigh the syringe again using a balance.

Repeat the procedures and analyze 4 times.

Conditions of coulometric Karl Fischer (KF) titration

Apparatus	AQ-2200 (Hiranuma Sangyo)
Generator electrolyte	Aqualyte GRO-A (Kanto Chemical)
Counter electrolyte	Aqualyte CN (Kanto Chemical)
Sample amount	1.5 mL (1.1 g)
Interval time for the detection end point	20 s
Automatic BG correction	On
Current	Slow
Minimum count	1 μg (20 mA × 0.5 s)

5. Evaluation of homogeneity



*○: 1st, △: 2nd, ◇: 3rd, ×: 4th analysis

✓ Ampoule no. 54 to no. 140 were used as the final candidate material.

→ ANOVA was used to analyze the concentration differences among the bottles. The between-bottle variance was significant ($p < 0.05$). However, s_{bb} was much smaller than the uncertainty due to other factors.

→ The candidate was deemed sufficiently homogeneous for its intended use.

✓ The assessment by the uniform distribution assume between the maximum and minimum values as well as that by ANOVA was carried out.

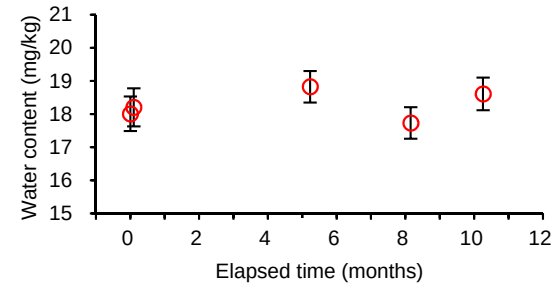
Assessment by ANOVA	
s_{bb}	3.55 %
u_{bb}	0.785 %
Assessment by the uniform distribution assumed between the maximum and minimum values	
|Maximum value – minimum value|/√3	5.11 %
|Certified value – value farthest from the certified value|/√3	**5.71 %**

Uncertainty due to homogeneity

u_{hom} = 5.71 % (relative value)

6. Evaluation of stability

Long-term stability



*Bars show the standard deviations.

✓ Uncertainty due to long-term stability was evaluated according to ISO Guide 35.

→ The slope of the regression line shows no significant difference.

✓ The standard uncertainty due to long-term stability is $t \times s(b_1)$, where t and $s(b_1)$ represent the term of validity and the standard deviation of the slope, respectively. The expiry date of this candidate material has been set as about 3 years from the beginning of the long-term stability test.

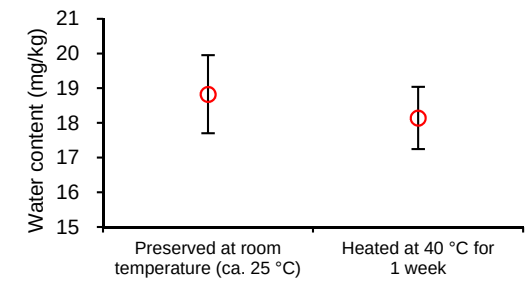
Uncertainty due to long-term stability

u_{lts} = 10.3 % (relative value)

Short-term stability

✓ The ampoules were heated at 40 ℃ for 1 week, which was 10 ℃ higher than the upper limit of the storage temperature, and then, the change in the water content of the ampoules was evaluated.

→ Since no significant differences were observed, the candidate material would be stable during transportation.



*Bars show the standard deviations.

Uncertainty due to short-term stability

u_{sts} = 0 % (relative value)

7. Characterization

✓ The certified value of this CRM was determined by the coulometric KF titrator of which the electric charge was verified by JCSS-calibrated standard resistor, voltmeter and frequency counter.

✓ The standard uncertainty of the certified value (u_{CRM}) was evaluated by combining u_{anal}, u_{hom}, u_{lts}, and u_{sts}.

Comparison of the amounts of water obtained by the JCSS-calibrated coulometric titrator and coulometric KF titrator

	Amount of the water obtained by the JCSS-calibrated coulometric titrator	Amount of water indicated by the coulometric KF tirrator	Deviations of the measured value between both titrators
Run 1	22.1 μg	22.6 μg	+2.09 %
Run 2	22.8 μg	23.8 μg	**+4.44 %**
Run 3	23.0 μg	22.8 μg	-0.81 %
Run 4	23.9 μg	24.3 μg	+1.77 %
Run 5	22.0 μg	21.7 μg	-1.22 %
Run 6	29.0 μg	30.3 μg	+4.32 %
Run 7	25.8 μg	26.2 μg	+1.48 %
Run 8	17.2 μg	16.6 μg	-3.52 %
Mean ± SD			**(+1.07 ± 0.98) %**

Maximum value

✓ As maximum value of the absolute value of the deviation was +4.44 %, |+4.44|/√3 = **2.56 % (relative value)** was used as the standard uncertainty due to the electric charge applied in coulometric KF titration.

Uncertainty budget for the analytical method

Parameter	Estimate /x_i	Standard uncertainty /$u(x_i)$	Sensitivity coefficient /c_i	Contribution /$\|c_i\|u(x_i)$
W_{sample}	20.83 μg	0.619 μg*	0.872 g^{-1}	0.539 μg/g
W_{blank}	0.067 μg	0.0236 μg	-0.872 g^{-1}	0.021 μg/g
M_{sample}	1.1475 g	0.00057 g	-15.8 μg/g^2	0.0090 μg/g
C**	18.1 μg/g			0.540 μg/g
				0.0298 (relative value)

***Uncertainty due to repeatability of coulometric KF titration and electric charge applied were combined.**

***$C = (W_{sample} - W_{blank})/M_{sample}$**

Uncertainty due to analytical method

u_{anal} = 2.98 % (relative value)

Uncertainty budget for the certified value

Uncertainty source	Symbol	Unit	Value	Uncertainty
Certified value	C_{CRM}	mg/kg	18.1	
Analytical method	u_{anal}	(relative value)		0.0298
Homogeneity	u_{hom}	(relative value)		0.0571
Long-term stability	u_{lts}	(relative value)		0.103
Short-term stability	u_{sts}	(relative value)		0
Combined standard uncertainty	u_{CRM}	(relative value)		0.121
	u_{CRM}	mg/kg		2.20

Certified value and expanded uncertainty ($k = 2$)

Water	**(18 ± 5) mg/kg**

8. Conclusions

✓ We developed a NMIJ CRM 4229-a (Water in Methylcyclohexane (0.02 mg/g)) for the quantification of trace water content in liquids. The water content of the CRM was determined by coulometric KF titration as the primary method of measurements.

✓ The traceability of the electric charge applied on the titration was ensured to realize metrological traceability of the certified value to the SI.

✓ The uncertainties due to the analytical method, homogeneity, and long-term and short-term stabilities of the CRM were evaluated, and the uncertainty of the certified value was estimated by combining them.

✓ This CRM is particularly suitable for quality assurance and method validation for the measurement of trace water content in liquids.

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