Establishment and Application of Rapid Supply Method for SI-traceable Organic Standard Materials Using Standard Materials Calibration System

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In order to ensure international consistency of analytical values, it is necessary to assure metrological traceability to international system of units (SI), whereas most of organic standard materials are not assured SI-traceability. New system, Standard Materials Calibration System, was developed in collaboration with HORIBA STEC Co., Ltd. and National Institute of Advanced Industrial Science and Technology (AIST). In this report, we studied new determination method which was easy and quick to assure SI-traceability to various analytes using this system.

Introduction

Many analytical instruments are used for determining the quantity of organic compounds, and the method based on gas chromatograph (GC) is one of them. The GC has a function that can separate chemical mixture and determine quantify of each chemical substance in one analysis. On the other hand, however, since each chemical substance has each own property, the sensitivity of GC detector is different and depends on each chemical substance. Therefore, in order to ensure the reliability of the result of quantitative determination, the sensitivity of GC detector needs to be calibrated for respective chemical standard materials.

Universality is required for the calibration of analytical equipment, that is, the calibration result must be the same regardless of where in the world, by whom, and when the calibration is performed. This requirement can be met by calibrating devices using a standard material whose traceability to International Unit System (SI) ("SI Traceability") is secured. Actually, SI Traceability is regarded as an international standard (General requirements for the competence of testing and calibration laboratories: ISO/IEC 17025[1, 2]). In addition, the Japanese Industrial Standards (JIS) stipulate the provisions of analytical methods and devices wherein analytical equipment must be calibrated using a standard material whose SI Traceability is secured, and it is preferable that the obtained analytical values have SI Traceability when using them for measurement certificates.[3]

However, because there are a huge number of chemical substances, it is not practical to prepare SI-Traceable standard materials for every single chemical substance to meet the wide variety of analytical requirements. It is because the number of types of chemical substance is not only enormous but there are also many technical issues in the production of standard materials.[4, 5] The details of such issues are described in the literature, and one of the reasons is that it requires techniques, labor, and costs and some chemical substances are hard to obtain.

Solutions for technical issues

A research study aimed at solving such issues was conducted by the National Institute of Advanced Industrial Science and Technology (hereinafter referred to as "AIST"), and the method for assuring SI-Traceability directly for each chemical substance to be measured without requiring standard materials was realized for the first time in the world for wide variety of organic mixed liquids and gases to be measured.[4-8] This time, we developed a standard materials calibration system (Model: TE-1000) to realize the above method in collaboration with AIST. Please refer to the existing report[9] for the details of this device.

Measurement method

The measurement is performed according to the procedures shown in Figure 1.

The details of the procedures are explained below in the order described in Figure 1:
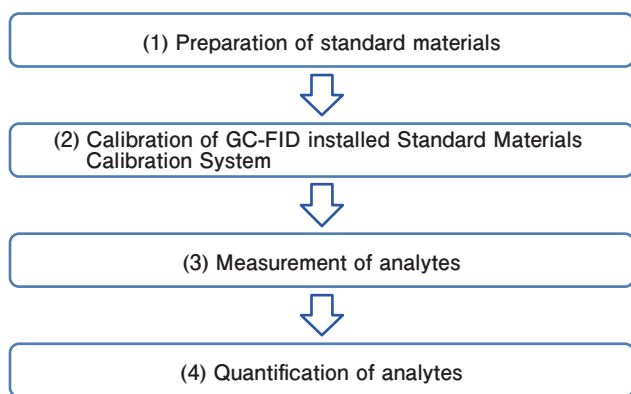(1) Preparation of a mixed standard material for calibra-

Figure 1   Analysis procedure using Standard Materials Calibration System

tion based on the gravimetric method

In order to prepare a mixed standard material for calibration, the SI Traceability of mass and purity must be assured. In many cases, the purity of reagents that are commercially available is expressed in percentages. However, the purity of almost all of them is expressed based on the peak area percentage method but not in SI units. Therefore, how to prepare a mixed standard material for calibration based on the gravimetric method using a high-purity substance whose SI Traceability is assured is explained in **Figure 2**.

In **Figure 2**, standard materials A, B, and C are dissolved into a solvent. As this example shows, the concentration of the standard material A (mol/kg) is calculated using the calculating formula described in **Figure 2**, and three values that are the mass (kg), the
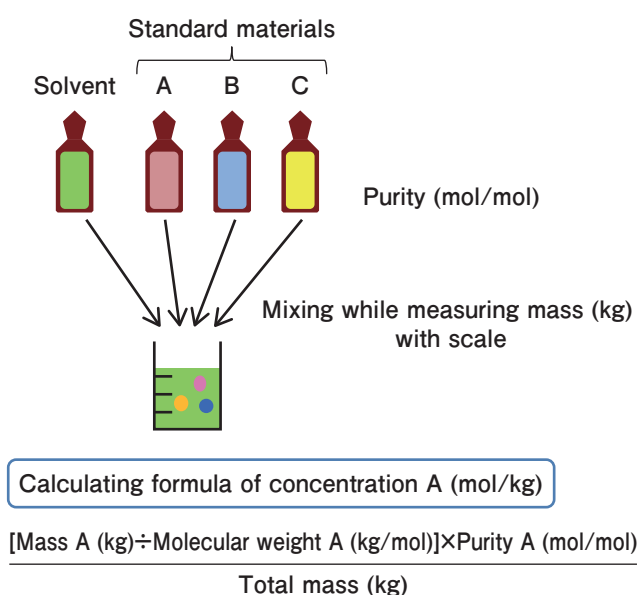
molar mass (kg/mol), and the purity (kg/kg) of the material A are required.

The SI Traceability of the purity of standard materials must be assured using certified reference materials distributed by the AIST (NMIJ CRM). The SI Traceability of the mass must be assured by the electronic balance calibrated by the certified standard weight based on Japan Calibration Service System (JCSS). In this way, after assuring the SI Traceability of the mass and purity, the mixed standard materials for calibration must be prepared by the gravimetric method.

(2)   Calibration of GC-FID with standard materials calibration system[1]
Perform an analysis with a GC-FID installed standard materials calibration system using the mixed standard material for calibration. Create a calibration curve with the CH_4 (methane)-converted concentration on the horizontal axis and the area value of GC on the vertical axis.

(3)   Analyze the analyte using the GC-FID installed standard material calibration system

(4)   Calculate the CH_4-converted concentrations from the area values of each analyte using the calibration curve described in (2). Figure out the concentration by dividing the CH_4-converted concentration by the carbon number of each analyte.

[1]: FID (Flame Ionization Detector): hydrogen flame ionization detector

Standard materials and analytes

This time, decane (C10), dodecane (C12), pentadecane (C14), and hexadecane (C16) were used as standard materials. Under the research consignment contract with the National Metrology Institute of Japan of the AIST, the SI-Traceable purity evaluation (mass fraction) was conducted on these materials based on the cryoscopic method to obtain the purity (mass fraction) and uncertainty values as shown in **Table 1**.

As the analytes, γ-terpinene, geraniol, methyl decanoate, and β- caryophyllene, which are used for flavoring agents and foods, were used. The standard materials shown in **Table 1** and the analyte were dissolved into the same hexane solvent. **Table 2** shows the concentrations and uncertainties of the standard materials after mixing.

Calculating formula of concentration A (mol/kg)

$$\frac{[\text{Mass A (kg)} \div \text{Molecular weight A (kg/mol)}] \times \text{Purity A (mol/mol)}}{\text{Total mass (kg)}}$$

Figure 2   Preparation procedure of mixed standard material for calibration

Table 1   Results of purity evaluation (mass fraction) at AIST

Substance	Symbol	Purity		Molar mass[12]	
		Mean	Standard uncertainty (k=1)	Mean	Standard uncertainty (k=1)
		kg/kg	kg/kg	g/mol	g/mol
Decane	C10	0.998	0.002	142.282	0.005
Dodecane	C12	0.996	0.003	170.335	0.006
Tetradecane	C14	0.995	0.005	198.388	0.007
Hexadecane	C16	0.997	0.003	226.441	0.008

Table 2   Concentration and uncertainty value of mixed standard material

Substance	Symbol	Concentration	
		Mean	Standard uncertainty (k=1)
		kg/kg	kg/kg
Decane	C10	92.596	0.189
Dodecane	C12	11.906	0.038
Tetradecane	C14	38.387	0.175
Hexadecane	C16	68.023	0.173

Devices

As a gas chromatograph, a 6890 model gas chromatograph with FID, which is equipped with a cool on column inlet and an auto injector (manufactured by Agilent), was used. As a capillary column, DB-5 (with a length of 30 m, an internal diameter of 0.53 mm, and a film thickness of 1.0 µm, manufactured by Agilent) was used. And a TE-1000 model standard material calibration system (manufactured by HORIBA STEC, Co., Ltd.) was installed between the capillary column and the detector. The hydrogen gas generator OPGU-7200 model (manufactured by HORIBA STEC, Co., Ltd.) was used as the hydrogen supplied to the FID and TE-1000.

Measurement conditions

Helium, used as a carrier gas, was supplied to the capillary column at a constant pressure of 70 kPa at the inlet. The heat-up condition of the cool on column was 40°C of initial temperature (0.5 min) → 10°C/min → 285°C (30 min), and the heat-up condition of the oven was 35°C of initial temperature (0.5 min) → 10°C/min → 280°C (30 min). The FID temperature was 300°C, the amounts of hydrogen, high-purity air, and makeup gas (nitrogen) were 30 mL/min, 400 mL/min, and 25 mL/min, respectively. The high-purity air was supplied at 2 mL/min as a gas for oxidation reaction in the TE-1000, and the hydrogen was supplied at 6 mL/min as a gas for the reduction reaction. The amount of sample filled was 0.1 µL, and measurement was performed six times repeatedly on the same sample.
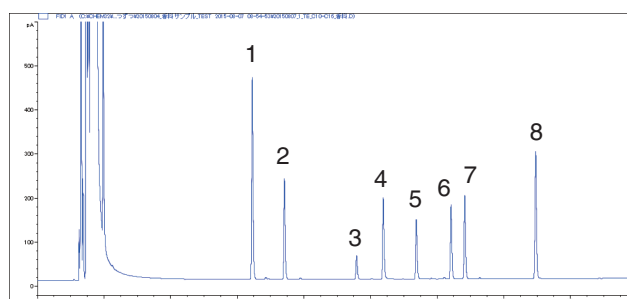
Experiment

Figure 3 shows the chromatogram of the mixed liquid composed of the standard materials and the analytes.

The standard materials were confirmed to be completely separated from the analytes. The calibration curve shown in Figure 4 was obtained by using the peak areas of the standard materials C10, C12, C14, and C16 and the concentrations shown in Table 2.

The calibration curve was created based on the least square method[11] of Deming according to the provisions stipulated in ISO 6143[10]. As a result of figuring out the Goodness-of-fit parameter to test the linearity of the calibration curve, it was less than two. From this result, the linearity of the calibration curve shown in Figure 4 was confirmed.

The concentrations of analytes were calibrated using the calibration curve shown in Figure 4. The methane-converted concentrations were calculated from the chromatogram areas of analytes shown in Figure 3 and the calibration curve shown in Figure 4. Table 3 shows the quantitative results.

1: Decane (C10), 2: γ-Terpinene, 3: Dodecane,
4: Geraniol, 5: Methyl Decanoate, 6: Tetra decane,
7: β-Caryophyllene, 8: Hexadecane (C16)

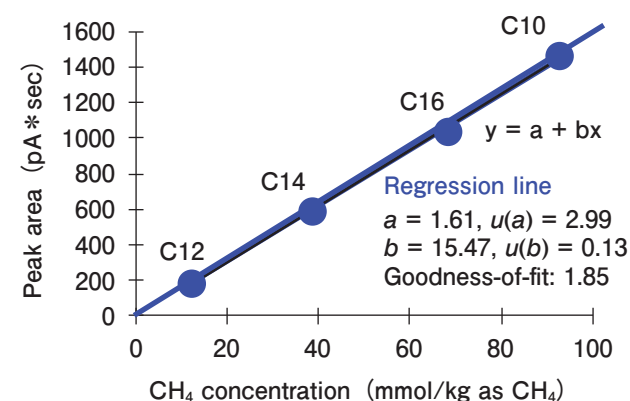Figure 3   Chromatogram of standard materials and analytes

y = a + bx

Regression line
a = 1.61, u(a) = 2.99
b = 15.47, u(b) = 0.13
Goodness-of-fit: 1.85

Figure 4   Calibration curve of standard material

Table 3   Quantitative result of analytes

Analyte	Concentration	
	Mean	Standard uncertainty ($k=1$)
	mmol/kg as CH_4	mmol/kg as CH_4
γ -Terpinene	47.3	0.7
Geraniol	41.3	0.7
Methyl Decanoate	30.6	0.5
β -Caryophyllene	43.0	0.7

In this way, the concentration and uncertainty values were obtained after mixing materials, without conducting the evaluation of the purity of the components of each analyte. In other words, using this method enables to determine the concentration and uncertainty values from the materials that are different from analytes, without using standard materials for each analyte.

Since the SI Traceability of the concentrations and uncertainties of γ-terpinene, geraniol, methyl decanoate, and β-caryophyllene were assured, the user of this system expands the component group with SI Traceable mixture quickly using this mixed standard solution.

Conclusion

In this application using mixed solution with standard materials and analytes in the same solvent, the concentration and uncertainty values could be assigned to analytes by using a standard materials calibration system. To determine concentration values accurately by the conventional method such as GC-FID only, it was required to prepare the same standard materials as analytes. On the other hand, however, the method using the standard materials calibration system showed that the concentration and uncertainty values could be determined from the materials that were different from analytes. It was proved that the use of this system enabled to supply SI-Traceable organic mixed standard materials quickly. This is the first system in the world that allows users to ensure and expand the traceability by themselves. As a result of testing the calibration curve, its linearity was found to be excellent. Therefore, it is also expected that the concentration and uncertainty values can be determined from one standard liquid in actual measurements.

In the future, we are planning to expand this method further not only to organic mixed liquids but also to organic mixed gases.

We expect that SI-Traceable organic standard materials are expanded and used for quantitative analyses through the use of this system, and the reliability of analysis values is assured.

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