CERTIFIED REFERENCE MATERIAL FOR DETERMINATION OF *p*-*n*-NONYLPHENOL AND *p*-*n*-HEPTYLPHENOL FROM THE NATIONAL METROLOGY INSTITUTE OF JAPAN

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Introduction

Certified reference materials (CRMs) are playing an increasingly important role in the national and international standardizing activities. CRMs of high-purity material are very useful for ensuring the reliability and traceability of the chemical measurements. The National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (NMIJ/AIST) has been developing for the preparation of primary standards, such as alkylphenols, phthalic acid esters and volatile organic compounds, based on Measurement Law of Japan[1,2]. High-purity *p*-*n*-Nonylphenol and *p*-*n*-Heptylphenol reference materials were certified as NMIJ CRM 4031-a and NMIJ CRM 4034-a in these activities, respectively.

In the certification of CRMs, the property values which are traceable to the International System of Units (SI) are preferably obtained using freezing point depression method, which are regarded as one of primary method of measurement having the highest metrological properties[3]. We would basically adopt the freezing point depression method by using a differential scanning calorimeter (DSC) for the certification of high-purity CRMs. This method is based on the principle in which freezing (or melting) point decreased in proportion to amount of impurities in compounds, van't Hoff equation approximately holds and allows the purity value to be calculated[3]. In the present paper, the certification and uncertainty estimation of NMIJ CRM 4031-a and 4034-a by using DSC are described.

Materials and Methods

Certification of NMIJ CRM 4031-a and 4034-a was conducted according to the ISO Guide 34 and 35[4,5]. Raw materials of *p*-*n*-Nonylphenol (NP, lot: FA001085) and *p*-*n*-Heptylphenol (HP, lot: 211G7503) were purchased from Lancaster Synthesis and Kanto Chemical, respectively. Infinity pure grade acetone and methanol for homogeneity and stability tests were purchased from Wako Pure Chemical Industries. Standard Reference Material 2225 (Mercury) and 2232 (Indium) used as calibration standards for DSC measurements were purchased from the National Institute of Standard and Technology (NIST SRM). Semi micro balances for homogeneity / stability and a Karl-Fisher titration (KF) used were AX 205 and AG 245 (Mettler Toledo), respectively. Another micro balance used for sample preparation of DSC was SC 2 (Sartorius). All balances were

calibrated against the standard weights certified by JCSS (Japan Calibration Service System)[6] to ensure the traceability of the mass values to the SI unit. DSC measurements were carried out using DSC 822e (Mettler Toledo) with a stepwise scan method at a heating rate of 0.01 °C/min. Samples of these CRMs (1.0 to 5.7 mg) were sealed into aluminum crucibles under dried-nitrogen atmosphere. Water content of these CRMs was evaluated by KF, AQ-7 (Hiranuma Sangyo). Gas chromatograph (GC) equipped with a flame ionization detector (FID) was a model Agilent 6890 (Agilent Technologies), and was used to evaluate homogeneity and stability, and to assess impurities of these CRMs. An Agilent 6890 Series GC interfaced with a Micromass GCT (GC-TOF/MS; Jasco International) was used to identify impurities of the CRMs. Mass spectrometer was operated in an electron impact with a scan mode.

Results and Discussion

Preparation of CRM

These CRMs were prepared and subdivided by a series of recrystallization, drying and distillation of the raw material NP and HP. CRM of NP is sealed in a nitrogen atmosphere in a 10-milliliter amber glass vial, and the vial is sealed in an aluminum-layered bag. This CRM is a white powder at ambient temperature. CRM of HP is sealed in an argon atmosphere in a 2-milliliter amber glass ampoule. This CRM is a white solid material at ambient temperature.

Homogeneity and stability tests

Homogeneity and stability of vials (or ampoules) subdivided were evaluated by the peak area percentages from GC-FID for organic contents and/or by water content from KF. Uncertainties associated with inhomogeneity and instability were estimated from analysis of variance of the analytical results.

In homogeneity, the between-vial variance of the CRMs were evaluated by analyzing ten vials selected out of total CRMs subdivided from the preparation lot to be assessed. The vials were subjected to replicate analyses (e.g. quadruplicate or quintuplicate) by GC-FID and/or KF. As these results, since there was a significant difference in homogeneity of KF results from HP, this between-vial inhomogeneity by KF was added to uncertainty of certified value from HP. In stability, the variance from monthly repeated measurements was also estimated as well as homogeneity tests using GC-FID. As these results, there was no significant difference in stability.

Certified value and uncertainty

Purity as certified value of CRMs was measured by DSC. The van’t Hoff plots were drawn from a stepwise DSC plot to determine melting point and melting point depression of alkylphenols (see Figure 1; only HP). Furthermore, impurity in the molar fraction was calculated by van't Hoff equation using molar enthalpy of fusion,

which also obtained by DSC, and gas constant[7]. Average of impurity was obtained by calculation, certified purities of NP (NMIJ CRM 4031-a) and HP (NMIJ CRM 4034-a) were determined with 0.9992 and 0.9954 in the molar fraction, respectively.

On the other hand, uncertainty of the CRMs was determined based on the results from the chemical analyses of high-purity materials. One of the sources of uncertainty came from purity determination by DSC. Uncertainty estimation of the purity determination was reported elsewhere[8]. We have considered parameters from van't Hoff equation such as the temperature, the enthalpy of fusion, uncertainty of atomic-weight value[9], uncertainty of gas constant[7] and the variation of the DSC measurements. Other sources related to the purity of the CRMs were such factors as the stability and between-vial homogeneity as mentioned above. Finally, uncertainties of the purity determination and homogeneity / stability were combined, and then uncertainty on certified value in the CRMs was calculated.

We have developed to disseminate high-purity of p-n-Nolylphenol and p-n-Heptylphenol as NMIJ CRMs, respectively (see Table 1).

Information value

To convert purity of the molar fraction by DSC into that of the mass fraction, average molecular weight of impurities of alkylphenols was calculated based on the results of identification and quantification of impurities. The impurity was identified by GC-TOF/MS, and was quantified by GC-FID using response factor of each impurity. Using quantification results of impurities including water content, the average molecular weight of impurities was calculated. And then, purities of NP and HP in the mass fraction were determined based on the average molecular weight of impurities, molecular weight of alkylphenols and the purity in the molar fraction. Uncertainty of information value was considered the mass and molecular weight of each impurity and alkylphenols[9]. The information value in the mass fraction is (0.9993 ± 0.0005) kg/kg for NP and (0.9992 ± 0.0006) kg/kg for HP. The number following the symbol ± is the expanded uncertainty.

Acknowledgements

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Figure 1: DSC plot of *p-n*-Heptylphenol

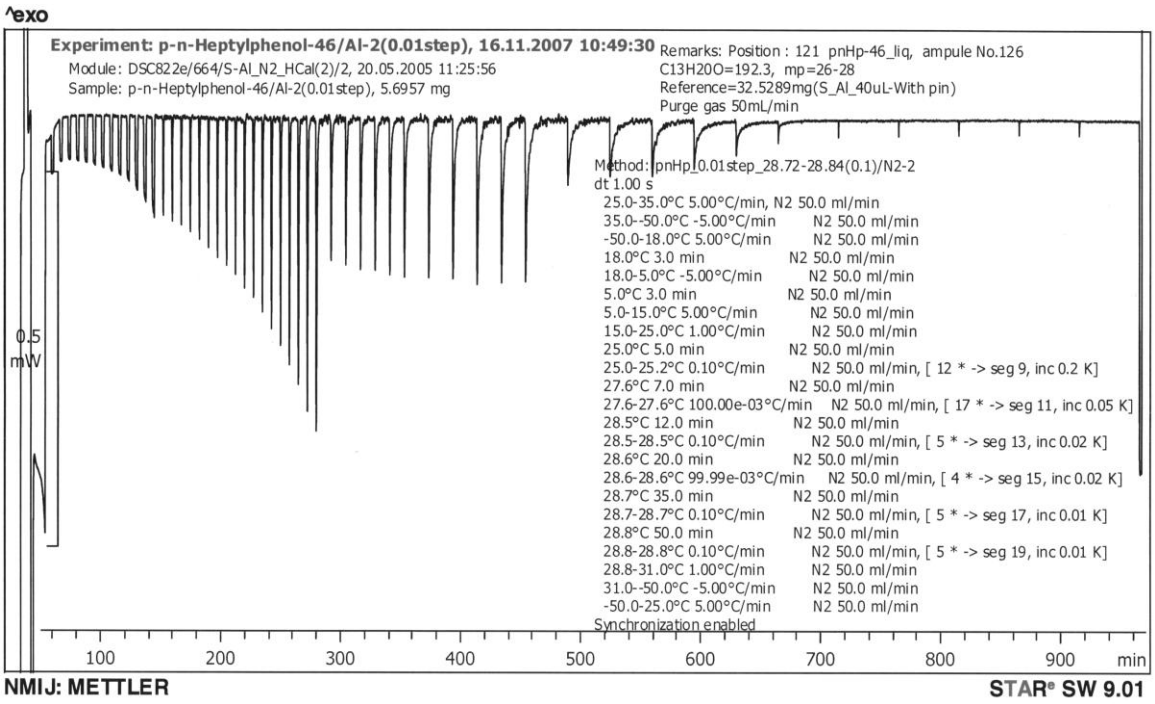

Table 1: Certified value and expanded uncertainty of CRMs

	NMIJ CRM	Certified value±Expanded uncertainty (mol/mol)
p-n- Nonylphenol	4031-a	0.9992 ± 0.0005
p-n- Heptylphenol	4034-a	0.9954 ± 0.0048