Adiabatic Calorimetry as Support to the Certification of High-Purity Liquid Reference Materials

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Abstract   The certification of high-purity liquid reference materials is supported by several analytical techniques (e.g., gas chromatography, liquid chromatography, Karl Fischer coulometry, inductively coupled plasma mass spectrometry, differential scanning calorimetry, adiabatic calorimetry). Most of them provide information on a limited set of specific impurities present in the sample (indirect methods). Adiabatic calorimetry [1] complementarily provides the overall molar fraction of impurities with sensitivity down to few $\mu mol \cdot mol^{-1}$ without giving any information about the nature of the impurities present in the sample (direct method). As the combination of adiabatic calorimetry with one (or more than one) indirect chemical techniques was regarded as an optimal methodology, NMi VSL developed an adiabatic calorimetry facility for the purity determination of high-purity liquid reference materials [2]. Within the framework of collaboration with NMIJ, a benzene-certified reference material (NMIJ CRM 4002) from NMIJ was analyzed by adiabatic calorimetry at NMi VSL. The results of this measurement are reported in this paper. Good agreement with the NMIJ-certified purity value (99.992 ± 0.003) $cmol \cdot mol^{-1}$ was found. The influence of different data analysis approaches (e.g., extrapolation functions, melting ranges) on the measurement results is reported. The uncertainty of the measured purity was estimated.

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1 Introduction

A knowledge of the purity of a material has become increasingly important in recent years. For example, the purity of the starting and process materials is critical for the quality of the end product for the pharmaceutical and semiconductor sectors. Furthermore, the search for more accurate measurements in physics and chemistry and the impact of international standardization and laboratory accreditation are leading to wider use of certified reference materials (CRM) [3] of high purity. Those materials are not only the purest available on the market, but they are also thoroughly characterized so that the purity is accurately known and stated in a certificate. In the case of liquids, there are several measuring techniques available to determine directly or indirectly the purity of the main component of the substance. On the one hand, analytical techniques such as gas chromatography–mass spectrometry, Fourier-transform infrared spectroscopy, and Karl Fischer titration/coulometry provide critical information on the presence and concentration of specific impurities or groups of impurities and thus contribute to the indirect methods of purity assessment. Thermal methods like differential scanning calorimetry or adiabatic calorimetry, on the other hand, can give an estimation of the overall impurity fraction. The latter technique has good sensitivity, down to a few $\mu mol \cdot mol^{-1}$.

During the past 3 years, the performance of our facility was tested first at the national level in collaboration with the Chemical Thermodynamic Group of Utrecht University and then at the international level with the National Metrology Institute of Japan (NMIJ).

At NMIJ, adiabatic calorimetry is currently used for the certification of high-purity organic liquid reference materials. In the framework of a collaborative activity on purity analysis, the Japanese benzene certified reference material, CRM 4002, was analyzed at NMi-VSL with an in-house fabricated adiabatic calorimeter [2]. The results of the purity determination and an overview of the effect of different data analysis approaches on the measurement result are presented in this paper.

2 Measurements

2.1 Specimens

Two ampoules of benzene-certified reference material (CRM 4002) were supplied by NMIJ. This high-purity material was certified by adiabatic calorimetric measurements in Japan. The stated purity concentration is (99.992 ± 0.003) cmol $\cdot$ mol^{-1}. Benzene is a volatile substance, and therefore special care is necessary to avoid evaporation and change in composition during sample handling.

2.2 Experimental

For the measurements, the NMi VSL adiabatic calorimeter unit B [2] was used. A detailed description of the configuration is given elsewhere [2], describing the setup, the data acquisition, and the analysis.

Table 1 Relevant input parameters of the automatic acquisition program selected for the measurements

Measurement date	Pulse time (s)	Recovery time (s)	Temperature steps outside plateau (K)	Number of pulses along plateau	Freezing rate $(K \cdot min^{-1})$
11/01/2006	800	3,000	3	10	2
13/01/2006	800	3,000	1	20	2
17/01/2006	800	6,000	2	20	2
25/01/2006	800	3,000	2	20	2
28/01/2006	800	3,000	2	20	2
04/08/2006	800	3,000	1	20	3
10/08/2006	800	3,000	1	20	2
15/08/2006	800	4,500	1	20	0.2
22/08/2006	800	4,500	1	20	2

The opening of the benzene ampoule and the preparation of the sample were done in a glove box filled with nitrogen. Approximately 5 mL of benzene was introduced into a 9 mL calorimetric vessel under slight vacuum (5 kPa). The vessel was then hermetically sealed by means of a screw cap and a gold septum. At different stages, the empty and filled vessels were repeatedly weighed with an analytical balance. The mass of the sample was (5.305 ± 0.005) g. The vessel was then mounted in the adiabatic calorimeter. The sample was initially cooled to a temperature about 20 K below its melting point. Then, the automatic acquisition program was initiated to apply heat pulses to the sample. The input parameters are:

- the expected melting temperature
- the expected enthalpy of fusion
- the expected melting plateau range
- the temperature step produced by each heat pulse outside the melting plateau
- the time of each heat pulse
- the equilibrium recovery time after each heat pulse
- the number of heat pulses along the melting plateau
- the sample time

To understand the effect of the parameters on the final results, many consecutive measurements with different input parameters were performed on the same sample.

In Table 1, some of the relevant parameters selected for each measurement are reported.

2.3 Uncertainty Evaluation

As described in the next section, Van't Hoff's equation is used to determine the purity of the material. This expression is in several ways a simplification. Van't Hoff's law is based on the integrated form of the Clausius–Clapeyron equation. For the integrated form of the Clausius–Clapeyron equation, the following assumptions have been made [4,5]:

1. the vapor obeys the ideal-gas law
2. the volume of the condensed phase (solid or liquid) is negligible in comparison with the volume of the same amount of vapor
3. the enthalpy of sublimation (vaporization) is independent of temperature

The impact of the first assumption can be assessed as follows. For benzene, the substance under study, the molar volume of the vapor phase at the triple point is $482.16\,\text{mL} \cdot \text{mol}^{-1}$ [6]. The value for the vapor-phase molar volume according to the ideal-gas law is $483.73\,\text{mL} \cdot \text{mol}^{-1}$ [6]; the relative error is therefore $(483.73 - 482.16)/482.16 = 3.26 \times 10^{-3}$. For the solid phase (sublimation), this error may be even smaller given that the molar volume of the solid is less than that of the liquid.

The second assumption can be readily assessed based on Goodwin's data for benzene [6]. The molar volume of the vapor is $482.16\,\text{L} \cdot \text{mol}^{-1}$, and that of the liquid is $0.0871\,\text{L} \cdot \text{mol}^{-1}$ at the triple-point temperature. Hence, $\Delta V = 482.07\,\text{L} \cdot \text{mol}^{-1}$.

The relative error of this approximation defined as $-V_{\text{liq}}/\Delta V = -1.8 \times 10^{-4}$ for benzene at the triple-point temperature and pressure.[1] The relative error in the enthalpy of fusion is the same. The assessment of the solid phase is somewhat more difficult, because little data about the molar volume of the solid phase are available. The molar volume of the solid phase is, however, generally smaller than that of the liquid phase, so the impact for the solid may be even smaller.

The impact of the third assumption depends to some extent on the purity of the sample. The melting range increases with the total amount-of-substance fraction of the impurities, so this assumption becomes more critical for samples of lower purity. In this study, benzene was used with a concentration of impurities such that the melting range is no more than $0.1\,\text{K}$. Based on the work of Goodwin [6], the difference in enthalpy of vaporization between the triple-point temperature and $0.1\,\text{K}$ above is $5.7\,\text{J} \cdot \text{mol}^{-1}$, or a relative difference of 1.64×10^{-4}.

In the following derivation of Van't Hoff's equation, Raoult's and Henry's laws [4,5] are used; their impact may be expected to be small because the concentration of impurities in the sample is low, so ideal behavior of the impurities in the solution and of the solute can be expected. Some mathematical simplifications are used, most notably the substitutions,

$$T_{\text{fus}} T = T_{\text{fus}}^2$$

and

$$\ln (1 - x) = x$$

The error arising from these simplifications depends on the purity of the sample. The magnitude of the latter simplification is negligible in view of the other contributions because of the high purity of the sample used. The magnitude of the replacement of $T_{\text{fus}} T$ by T_{fus}^2 gives a relative error of 7.18×10^{-4} for a temperature difference of $0.2\,\text{K}$.

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[1] These conditions are close to the conditions in the vessel during the freezing-point depression measurement.

3 Results

A total of nine adiabatic calorimetric measurements were carried out at NMi VSL to determine the purity of the benzene reference material (NMIJ CRM 4002). To obtain the purity of the benzene reference material, the Van't Hoff's law was applied:

$$T^{\text{eq}} = T_0^{\text{eq}} - \frac{R(T_0^{\text{eq}})^2 x}{\Delta H_{\text{fus}}} \left(\frac{1}{F}\right)$$

where F is the melted fraction of the frozen sample, T^{eq} is the equilibrium temperature at the melted fraction F, T_0^{eq} is the triple-point temperature of the pure substance, R is the universal gas constant, x is the impurity concentration (molar fraction), and ΔH_{fus} is the molar enthalpy of fusion.
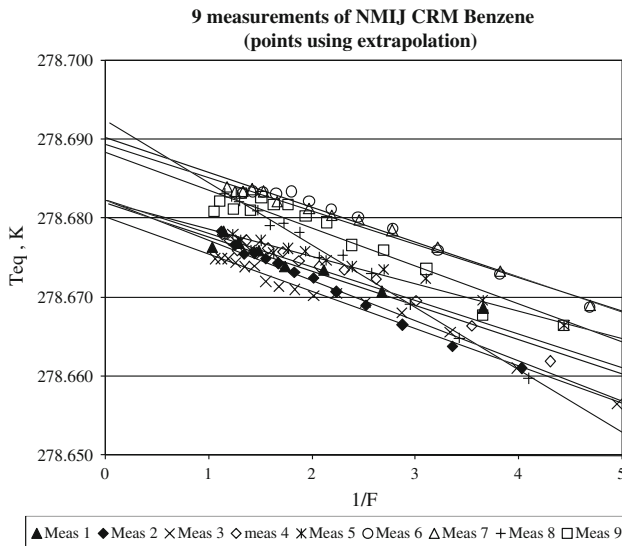
The equilibrium temperature and the inverse of the melted fraction are linearly correlated and the slope $A = \frac{R(T_0^{\text{eq}})^2 x}{\Delta H_{\text{fus}}}$ and the intercept T_0^{eq} are determined from regressing the results of T_{eq} versus $1/F$.

Once the overall impurity concentration x is known, the purity fraction p is simply given by

$$y = 1 - x$$

In Fig. 1, the regression lines of the nine measurements are indicated.

The measurement procedure consists of sending controlled heat pulses to the frozen sample, followed by stabilization periods during which the temperature is accurately

Fig. 1 Regression lines of equilibrium temperatures (T^{eq}) on the inverse of the melted fraction ($1/F$) of the nine benzene measurements

Table 2 Summary of T_o^{eq} values based on extrapolation or no extrapolation of the equilibrium temperature

Measurement No.	T_o^{eq} (K)	$T_o^{r\ eq}$ (K)
1	278.6806	278.6806
2	278.6846	278.6806
3	278.6806	278.6806
4	278.6836	278.6846
5	278.6950	278.6950
6	278.6907	278.6900
7	278.6900	278.6900
8	278.6930	278.6930
9	278.6890	278.6910
Standard deviation	0.0053	0.0057

T_o^{eq}: Melting temperature of the pure substance based on extrapolated equilibrium temperature values and a data set $1 < 1/F < 5$

$T_o^{r\ eq}$: Melting temperature of the pure substance based on not-extrapolated equilibrium temperature values and a data set $1 < 1/F < 5$

measured. To avoid long equilibration times after each heat pulse, the temperature of the sample in the adiabatic calorimeter vessel is measured during an interval between 3,000 s and 6,000 s. The equilibrium temperature T^{eq} after each pulse is obtained by extrapolation of the temperature data, fitting the last part of the decay curve with a second-order polynomial.

From the available data set, it appears that the use of an extrapolated equilibrium temperature, after short or long stabilization periods, has minimal effect on the calculation of the impurity concentration. Table 2 reports the intercept values of the linear regressions obtained by

(a) extrapolation of the equilibrium temperature (T_o^{eq}) and
(b) no extrapolation ($T_o^{r\ eq}$) (by simply using the last measurement data point).

The largest deviation of 4 mK was found in measurement 2; it corresponds to the lowest stabilization period (3,000 s) and it is within the standard deviation of the nine intercept values.

The same evaluation was performed on other materials of different purity, with similar stabilization periods, and a maximum deviation of 2 mK was found. From Table 2, it is apparent that fast or slow freezing of the sample has no significant effect on T_o^{eq} (see measurements 5 and 8).

The software controlling the data acquisition of the NMi VSL adiabatic calorimeter allows user selection of the number of heat pulses during the melting. Each pulse corresponds to a fraction of the melted sample and to a corresponding equilibrium temperature.

A study has been conducted on the influence of fitting a complete or a partial data set by the method of least squares. Figure 2 shows changes in the slope A and intercept T_o^{eq} by using different intervals of the inverse of the melted fraction $1/F$ in measurement 6. The range $1 < 1/F < 2$, corresponding to the part of the plateau where the sample passes from half-melted to completely melted, gives a poor representation of

Table 3 Summary of the purity results of benzene CRM

Measurement No.	Purity (% $mol \cdot mol^{-1}$)
1	99.9945
2	99.9905
3	99.9924
4	99.9926
5	99.9875
6	99.9927
7	99.9933
8	99.9871
9	99.9918
Average	99.9914
Standard deviation	0.0025

the impurity concentration. Both the slope and intercept deviate from the other curves, resulting in an underestimation of the impurity concentration. The explanation of this behavior might be that close to the complete melting, when only a small part of the solid remains, the sample temperature needs a longer time to reach equilibrium. In fact, the thermal impedance between the solid-liquid interface (which is what we want to measure) and the thermometer (which is what we really measure) is the largest, and the Van't Hoff law fails. In this case, the extrapolated equilibrium temperature used in the plot is not a realistic representation. On the other hand, the partial data set $1 < 1/F < 5$ and the complete set (up to $1/F = 15$) show similar behavior. The deviation between the calculated purity concentrations using a partial or a complete data set is within $0.0005 \% mol \cdot mol^{-1}$ for all measurements. Based on our previous experience, the interval $1 < 1/F < 5$ was used for the final calculation of the purity concentration of the sample. This range is not uncommon for purity determination (see, e.g., [1]).

Table 3 shows the results of the purity concentration y of the nine measurements of the benzene CRM (NMIJ CRM 4002). The average purity concentration is 99.991 $cmol \cdot mol^{-1}$ with a standard deviation of $0.003 \, cmol \cdot mol^{-1}$. This result is in good agreement with the certified value reported by NMIJ, $(99.992 \pm 0.003) \, cmol \cdot mol^{-1}$.
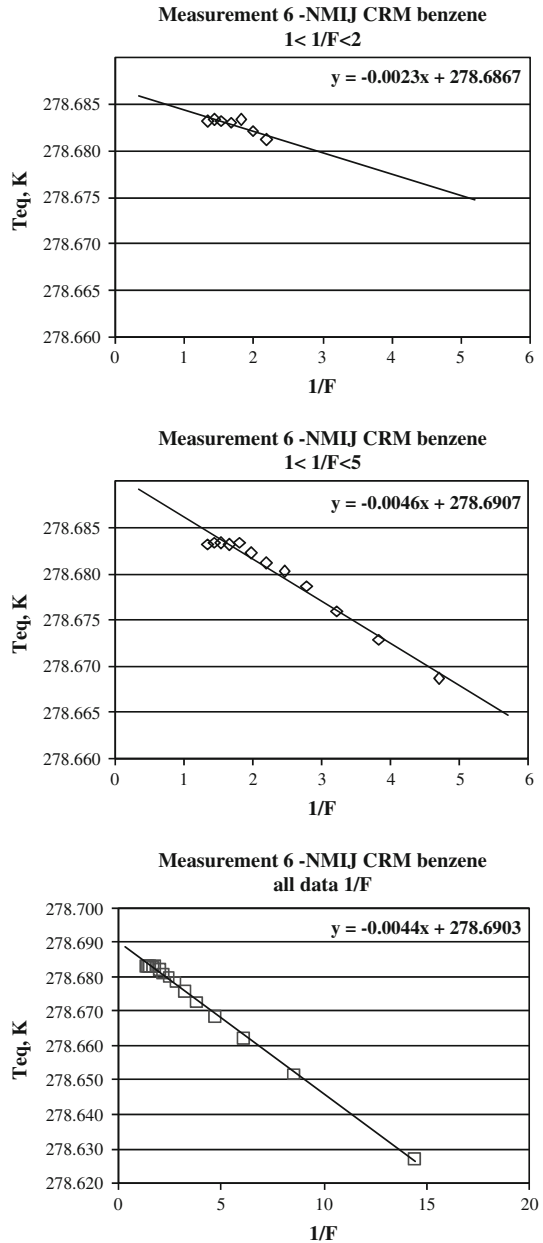
An initial calculation of the uncertainty of the measurement results has been carried out. The mathematical model adopted for the calculation of the uncertainty sources is

$$y = 1 - x = 1 - \frac{\Delta H_f A}{R(T_0^{eq})^2} = 1 - \frac{\frac{Q_{fus}}{n} A}{R(T_0^{eq})^2}$$

where Q_{fus} is the total heat of fusion and n is the number of moles of the sample, determined as the ratio of the sample mass to the molar mass of benzene.

Table 4 gives the uncertainty budget for a single measurement of benzene. The worst-case contributions to the uncertainty of the nine measurements have been taken into account. The uncertainty estimate is then $0.002 \% mol \cdot mol^{-1}$. The major contributions to the uncertainty, $u_i(y)$, arise from the determination of the slope (A) and the total heat of fusion (Q_{fus}). For the slope A, a study is still ongoing to evaluate the best approach to estimate this uncertainty source. The uncertainty of the total heat of

Fig. 2 Plot of the observed
equilibrium temperature (T^{eq})
and the corresponding inverse of
the melted fraction, $1/F$, and the
effect on the calculation of the fit
by using the least squares
method

Measurement 6 -NMIJ CRM benzene
1< 1/F<2

$y = -0.0023x + 278.6867$

Measurement 6 -NMIJ CRM benzene
1< 1/F<5

$y = -0.0046x + 278.6907$

Measurement 6 -NMIJ CRM benzene
all data 1/F

$y = -0.0044x + 278.6903$

fusion includes the approximation made in the measurement of the heat leak, which is
the main cause of the deviation of the observed value for the molar enthalpy of fusion
from the literature value.

Based on the average of nine observations, the calculated T_{o}^{eq} is (278.687 ± 0.008) K
and this value is consistent (within the uncertainty) with the literature value for the

Table 4 Uncertainty budget for a single purity measurement of benzene by adiabatic calorimetry

Source	x_i	$U(x_i)$	Sensitivity coefficient	$u_i(y)$
R	$8.314472 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$0.000015 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	1.03×10^{-05}	1.55×10^{-10}
n	$0.06792 \, \text{mol}$	$0.00006 \, \text{mol}$	1.27×10^{-03}	8.13×10^{-08}
$Q_{(\text{fus})}$	$699.31 \, \text{J}$	$26.76 \, \text{J}$	1.23×10^{-07}	3.30×10^{-06}
T_{eq}	$278.687 \, \text{K}$	$0.008 \, \text{K}$	6.17×10^{-07}	4.94×10^{-09}
A	$0.00588 \, \text{K}$	$0.00065 \, \text{K}$	1.46×10^{-02}	9.25×10^{-06}

triple-point temperature of benzene (278.680 K) taken from the NIST database. The standard uncertainty of T_{o}^{eq} is obtained by combining the type A uncertainties (5 mK), the type B uncertainties (5 mK, mainly from the calibration of the thermometer), and the uncertainty of the intercept in the extrapolation of the curve T^{eq} versus $1/F$.

The repeatability of the nine measurements is calculated as the mean standard deviation, and it is $0.0008 \, \text{cmol} \cdot \text{mol}^{-1}$. The uncertainties are then combined and a coverage factor $k = 2$ is used to calculate the expanded uncertainty. The final result of the benzene purity measurement is $(99.9914 \pm 0.0026) \, \text{cmol} \cdot \text{mol}^{-1}$.

4 Conclusions

The purity measurement of the benzene CRM indicates good agreement between the Dutch and Japanese adiabatic calorimetric facilities. Adiabatic calorimetry has been demonstrated to be a helpful tool in certifying the purity of liquid materials.

The data analysis approach (particularly the selection of the data range for the determination of A and T_{o}^{eq}) has been shown to significantly influence the purity result.

Future investigations will be extended to non-ideal systems, for which the impurities do not remain confined within the liquid phase during the melting, and, therefore, the Van't Hoff law cannot be applied.

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