

DSC temperature calibration over the range -125 °C to 50 °C

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Abstract

The lack of Nationally Certified Reference Materials for the calibration of DSC equipment in the sub-ambient range has been addressed by the introduction of a Certified Reference Material of purified cyclohexane by the National Metrology Institute of Japan. This sample, in conjunction with the CRM material phenyl salicylate and the ITS-90 fixed point material mercury, has enabled a DSC-thermomicroscopy system to be accurately calibrated over the temperature range -90 °C to 50 °C. The DSC has then been used to measure values for the solid-solid transitions in the potential Certified Reference Materials ammonium sulphate, adamantane and ammonium dihydrogen phosphate, which have the advantage of being thermally stable and easy to handle, and for the melting point of diphenyl ether. In addition, the effect of temperature cycling on these materials has been investigated.

Keywords:

Sub-ambient DSC, Calibration, Ammonium sulphate, Adamantane, Ammonium dihydrogen phosphate.

1. Introduction

For accurate temperature calibration of DSC equipment, it is desirable to use a high purity sample material whose melting temperature is a fixed point on the International Temperature Scale of 1990 (ITS-90) [1]. Alternatively, a Certified Reference Material (CRM) may be used where the transition temperatures have been determined by adiabatic calorimetry using a platinum resistance thermometer calibrated to ITS-90 by a National Measurement Institute. Although the temperature range from 42 °C to 660 °C is well catered for by a set of CRMs from LGC Limited (formerly the UK Laboratory of the Government Chemist), there is a scarcity of standards in the sub-ambient range.

Originally the International Confederation for Thermal Analysis (ICTA, now ICTAC with the inclusion of Calorimetry) offered a set of low temperature standards covering the range from -87 °C to 58 °C [2]. These however were not suitable for accurate temperature calibration due to the large errors for the specified temperatures. These errors arose from the round-robin programmes used to determine the values for the materials where rigorous calibration procedures could not be carried out by a number of the participating laboratories [3].

Camenea *et al.* as part of the Recommendation of the working group “Calibration of Scanning Calorimeters” of the Gesellschaft für Thermische Analyse e.V. (GEFTA), Germany, recommended using cyclopentane as a temperature calibration substance in addition to the ITS-90 fixed point samples of water and gallium [4]. The ICTAC Group “Thermochemistry” has listed a range of organic low temperature reference materials covering the range from above ambient temperature down to -160 °C suitable for both temperature and enthalpy calibration [5]. The paper lists suitable commercial sources of the samples and the thermodynamic values listed have been chosen from literature values determined by adiabatic calorimetry.

This approach has been criticised by Archer [6], who pointed out that the recommended samples available commercially had a much lower purity than the highly purified samples used in the adiabatic calorimetry studies and this would be likely to introduce significant errors. Archer measured the fusion temperature of a 99.5% purity sample of cyclopentane by DSC and obtained a difference of 1.2 K from the adiabatic calorimetry results. This difference was confirmed by Jakobi *et al.* [7] who used adiabatic calorimetry to measure a 99.9% purity commercial sample of cyclopentane. They obtained a value of -95.56 °C compared with the previously measured value of -93.43 °C by Aston *et al.* on the highly purified sample using adiabatic calorimetry [8].

The lack of certified low temperature reference materials has recently been addressed by the National Metrology Institute of Japan (NMIJ) who have introduced a sample of highly purified cyclohexane for the calibration of DSC equipment. The transition temperatures at -86.97 °C and 6.71 °C and the corresponding enthalpy values for this CRM were determined by adiabatic calorimetry [9].

A number of workers are reluctant to use the fixed point materials gallium and mercury due to the possibility of damage to the DSC equipment and some laboratories find it difficult to handle volatile organic liquids. This has resulted in a search for materials which have a low vapour pressure and exhibit low temperature solid-solid transitions. In a study of possible low temperature calibration materials, Haakvort found that adamantane was a good candidate for DSC calibration [10] and that it was also suitable for calibration in the cooling mode since it showed only a small amount of supercooling. The transition temperature and enthalpy of a commercial 99.0+% purity adamantane has been recently measured by DSC, using mercury as the calibrant [11] and samples of adamantane, for the calibration of DSC equipment, are now available from at least two thermal analysis equipment manufacturers [12, 13].

Ammonium sulphate and ammonium dihydrogen phosphate have also been investigated as possible low temperature calibrants since they show well-defined s-s transitions in the region of -50 °C [14] and -125 °C [15], respectively. These stable non-volatile materials have the

advantage of being commercially available in high purity and do not suffer from the handling problems associated with volatile organic liquids. Further, Price has suggested that a two-point calibration could be obtained by using a mixture of these materials [16].

The aim of the present paper was to calibrate a simultaneous DSC-thermomicrometry system in the temperature range $-90\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$ using only CRMs and an ITS-90 fixed point material. The calibrated instrument was then used to determine values for the solid-solid transitions in the potential CRMs ammonium sulphate, adamantane and ammonium dihydrogen phosphate. Their behaviour on cooling and the effect of cycling on the transition temperatures has also been investigated. Finally, measurements have been made on diphenyl ether (mpt $\sim 27\text{ }^{\circ}\text{C}$), which has been suggested as a possible alternative to gallium as a DSC standard since it has low volatility and is easily handled [17]. This material was also included in the original ICTA set of low temperature standards [2].

In this preliminary study, we have carried out measurements at a low fixed heating rate, chosen in order to reduce the possible variation of the heating rate dependency of the transition temperature for the different materials. It is intended to follow this initial study by more detailed experiments under thermodynamic equilibrium conditions, using a conventional high sensitivity DSC.

2. Experimental

2.1. Instrumentation

Transition temperature measurements were made using a simultaneous DSC-thermomicrometry system which incorporates a chromel heat flux DSC plate into a hot-stage operating over the range -150 to $450\text{ }^{\circ}\text{C}$ (Optical DSC450, Linkam Scientific) which has been described recently [18]. Sub-ambient temperatures were achieved by pumping liquid nitrogen through the system using the LNP controller (Linkam Scientific) at a setting of 100% for all experiments. The DSC was operated under a flowing atmosphere of nitrogen (50 ml min^{-1}) throughout this study.

The extrapolated onset temperature measurements were made on the DSC peaks using the LINK software (Linkam Scientific, v1.2.5.13) which enabled the temperature to be measured to $0.1\text{ }^{\circ}\text{C}$. All data sets were then exported as text files and processed using Excel (Microsoft, Office 365 ed.).

2.2. Materials

Samples were prepared and sealed into aluminium crucibles (Tzero, TA Instruments) and empty crucibles of the same specifications were used as a reference. Crucibles were pre-treated

by heating at 500 °C for 2 hours to provide a protective oxide film, which is essential in the case of mercury. Table 1 shows the temperature calibration standards used in this programme and Table 2 the potential standard materials under investigation. The latter samples were the highest purity materials available commercially and the listed purities are those given by the manufacturers. The samples were used without any further purification.

In all cases, a sample mass of 5.0 mg (± 0.1 mg) was used and for solid samples, the materials were lightly compressed into the crucible using a brass tamping tool and the liquid samples were transferred using a micropipette.

Table 1. Low Temperature DSC CRMs used in present study.

Sample	Purity	Transition	Temperature / °C	Source
Phenyl salicylate	99.994%	s-l	41.79 \pm 0.03	LGC CRM 2613
Cyclohexane	>99.99%	s-l	6.71 \pm 0.06	NMIJ CM 5401a
"		s-s	-86.97 \pm 0.04	"
Mercury	99.999 %	s-l	-38.8344	Acros Organics

Note: The uncertainties quoted are the half widths of the expanded uncertainty interval which give a level of confidence of approximately 95%. These were calculated using coverage factors of 2.776 for phenyl salicylate and 2 for cyclohexane.

Table 2. Potential CRMs for low temperature DSC calibration.

Sample	Purity	Source
Diphenyl ether	≥ 99.9 %	Sigma-Aldrich ReagentPlus™
Ammonium sulphate	99.999 %*	Alfa Aesar Puratronic™
Adamantane	>99 %	Acros Organics
Ammonium dihydrogen phosphate	99.999 %*	Acros Organics

*Trace metals basis

2.3. Procedure

Throughout this study, the software temperature calibration feature of the instrument was turned off. However, the single point enthalpy calibration (indium, ΔH_{fus} 28.45 J g⁻¹) remained active throughout.

Initial cycling experiments on the potential calibration materials were performed at a heating rate of 10 K min^{-1} . Each material was heated and cooled through the transition 5 times to test its reproducibility on cycling. Following these experiments, triplicate measurements were made at 2.5 K min^{-1} using a new sample for each experiment. This relatively slow heating rate was chosen to reduce the possible variation of the heating rate dependency of the transition temperature for the different materials.

The uncertainties associated with the present measurements are single standard deviations and include the uncertainties in the values for the calibration standards.

3. Results & Discussion

3.1. Calibration

Typical curves for the preliminary experiments on the calibration standards at a heating rate of 10 K min^{-1} are grouped together in Fig. 1. The results of the triplicate calibration experiments at 2.5 K min^{-1} are summarised in Table 3 and show excellent reproducibility. The measured temperature corrections are plotted as a function of sample temperature in Fig. 2. The results gave a quadratic fit and indicate that the calibration correction changes by less than 0.1 K over a sample temperature range of $\sim 130 \text{ }^\circ\text{C}$.

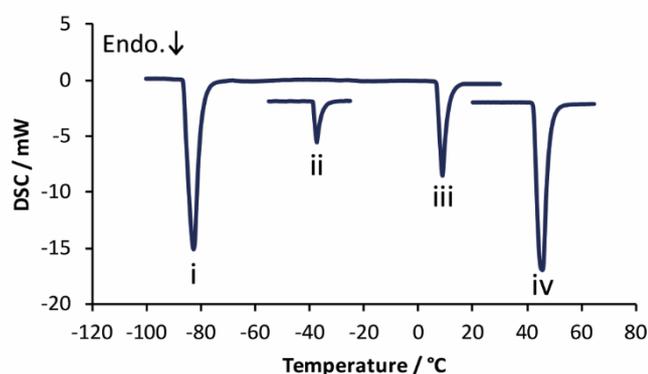


Fig. 1. A combined DSC profile of the CRMs. The transitions are: i) cyclohexane (s-s), ii) mercury (s-l), iii) cyclohexane (s-l) and iv) phenyl salicylate (s-l). The transitions of mercury and phenyl salicylate have been offset by 2 mW for clarity. (Sample mass, 5 mg; heating rate, 10 K min^{-1} ; atmosphere, nitrogen)

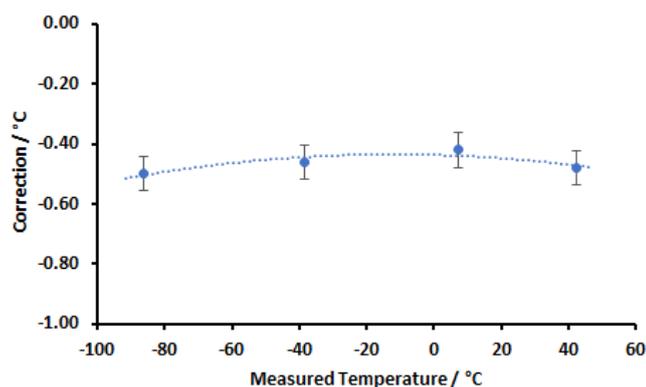


Fig. 2. DSC calibration plot (Sample mass, 5 mg; heating rate, 2.5 K min⁻¹; atmosphere, nitrogen)

Table 3. Measured extrapolated onset temperature values for mercury and the CRMs phenyl salicylate and cyclohexane. (Sample mass, 5 mg; heating rate, 2.5 K min⁻¹; atmosphere, nitrogen)

Material (Transition)	Temperatures / °C				Certified Value	Correction
	Sample 1	Sample 2	Sample 3	Mean		
Phenyl salicylate (s-l)	42.3	42.3	42.2	42.27 ± 0.06	41.79	-0.48
Cyclohexane (s-l)	7.2	7.1	7.1	7.13 ± 0.06	6.71	-0.42
Mercury (s-l)	-38.3	-38.4	-38.4	-38.37 ± 0.06	-38.83	-0.46
Cyclohexane (s-s)	-86.5	-86.5	-86.4	-86.47 ± 0.06	-86.97	-0.50

3.2. Materials under Investigation

The results of the preliminary cycling experiments on the 4 potential CRMs at 10 K min⁻¹ are shown in Figs. 3 to 6 and the measured extrapolated onset temperatures are summarised in Table 4. In all cases excellent reproducibility is given with no significant change on cycling the samples although, in the case of the diphenyl ether, it was necessary to cool the sample some 50 °C below the melting point to cause the sample to recrystallise.

It can be seen in Figs. 3, 4 and 6 that, although the results are very reproducible, there is some distortion of the DSC peaks for diphenyl ether and the two ammonium salts. This will be investigated further when the studies under equilibrium conditions are carried out.

Table 4. Influence of cycling on the transition temperature of diphenyl ether, ammonium sulphate, adamantane and ammonium dihydrogen phosphate. (Sample mass, 5 mg; heating/cooling rate, 10 K min⁻¹; atmosphere, nitrogen)

Material	Temperature / °C					Mean
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	
Diphenyl ether	26.9	26.9	27.0	26.9	27.0	27.0 ± 0.1
Ammonium Sulphate	-49.7	-49.8	-49.9	-49.9	-49.9	-49.8 ± 0.1
Adamantane	-65.4	-65.5	-65.5	-65.4	-65.4	-65.4 ± 0.1
Ammonium dihydrogen phosphate	-124.7	-124.8	-124.8	-124.8	-124.6	-124.7 ± 0.1

The results of the extrapolated onset temperature measurements made at 2.5 K min⁻¹ are summarised in Table 5 and have been corrected using the equation generated from the calibration plot. The results will be discussed individually in terms of the literature values shown in Table 6. The literature values have been converted to ITS-90 values where necessary using the correction tables provided by Goldberg & Weir [19] and Weir and Goldberg [20].

Table 5. Measured transition temperatures of potential calibration standards. (Sample mass, 5 mg; heating rate, 2.5 K min⁻¹; atmosphere, nitrogen)

Material	Temperature / °C				
	Sample 1	Sample 2	Sample 3	Mean	Corrected
Diphenyl ether	27.4	27.4	27.4	27.40 ± 0.00	27.0 ± 0.1
Ammonium sulphate	-48.8	-48.8	-48.9	-48.83 ± 0.06	-49.3 ± 0.1
Adamantane	-64.3	-64.3	-64.4	-64.33 ± 0.06	-64.8 ± 0.1
Ammonium dihydrogen phosphate	-123.9	-123.8	-123.8	-123.83 ± 0.06	-124.4 ± 0.1

Table 6. Literature and present study values of diphenyl ether, ammonium sulphate, adamantane and ammonium dihydrogen phosphate [temperatures are expressed in terms of ITS-90 (see text)]

Material	First Author	Year	Technique	Purity / %	Temperature / °C	Ref
Diphenyl ether	Furukawa	1951	Adiabatic Calorimetry	99.9987	26.87 ± 0.01	21
"	Donnelly	1990	DSC	99.58	26.62	22
"	Present work		DSC	99.9	27.0 ± 0.1	
Ammonium Sulphate	Shomate	1945	Adiabatic Calorimetry	99.96	-49.7	23
"	Charsley	1993	DSC	99.999	-49.6 ± 0.2	14
"	Price	1995	DSC	98+	-48.8 ± 0.1	16
"	Present work		DSC	99.999	-49.3 ± 0.1	
Adamantane	Chang	1960	Adiabatic Calorimetry	Purified	-64.49 ± 0.04	24
"	Van Ekeren	2006	Adiabatic Calorimetry	99.0+	-65.2 ± 0.2	26
"	Bazyleva	2011	Adiabatic Calorimetry	99.80	-64.43 ± 0.05	25
"	Blaine	2016	DSC	99.0+	-65.54 ± 0.2	11
"	Present Work		DSC	99.0+	-64.8 ± 0.1	
Ammonium dihydrogen phosphate	Stephenson	1944	Adiabatic Calorimetry	Purified	-125.2 ± 1.0	27
"	Loiacono	1970	DTA	Purified	-124.6 ± 0.5	28
"	Gough	1979	Dielectric x	Reagent Grade	-124.2 ± 0.2	29
"	"	"	Dielectric z	"	-123.9 ± 0.2	"
"	"	"	EPR	"	-123.6 ± 0.2	"
"	"	"	NMR	"	-124.3 ± 0.2	"
"	"	"	DSC	"	-123	"
"	Odlyha	1989	DSC	-	-127.0 ± 0.4*	15
"	Price	1995	DSC	98+	-121.4 ± 0.1	16
"	Present Work		DSC	99.999	-124.4 ± 0.1	

*Mean and standard deviation of initial set of values obtained at 10 K min⁻¹ on sample masses from 2-10 mg

3.2.1. Diphenyl ether

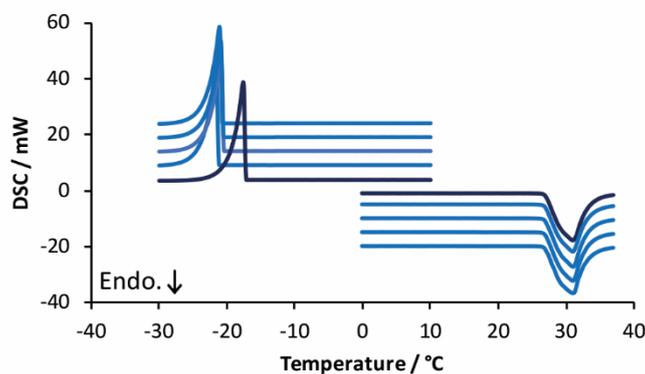


Fig. 3. DSC profile of diphenyl ether undergoing five identical thermal cycles. The dark blue line shows the first cycle and for clarity each subsequent cycle has been offset by 5 mW. (Sample mass, 5 mg; heating/cooling rate, 10 K min⁻¹; atmosphere, nitrogen)

Our measured temperature of 27.0 ± 0.1 °C is in good agreement with the value of 26.86 ± 0.01 °C, measured on a purified sample by Furakawa *et al.* using adiabatic calorimetry [21]. The sample has the advantage of low volatility and can be used more than once, provided the DSC apparatus is equipped with suitable cooling facilities. However, its proximity in temperature to the LGC CRM phenyl salicylate would make its development as a standard less useful than the other potential standards.

3.2.2. Ammonium sulphate

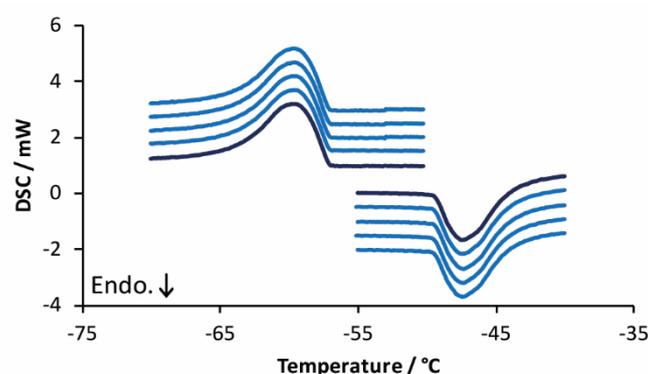


Fig. 4. DSC profile of ammonium sulphate undergoing five identical thermal cycles. The dark blue line shows the first cycle and for clarity each subsequent cycle has been offset by 0.5 mW. (Sample mass, 5 mg; heating/cooling rate, 10 K min⁻¹; atmosphere, nitrogen)

The reproducibility of the measurements to date obtained for ammonium sulphate is indicated by the fact that the literature values fall within a span of 1 °C. Our value of -49.3 °C is some 0.4 K higher than the values obtained by adiabatic calorimetry [23] and in the ICTAC round robin programme [14].

3.2.3. Adamantane

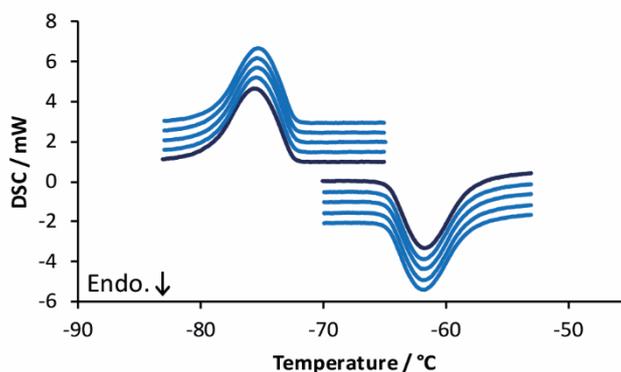


Fig. 5. DSC profile of adamantane undergoing five identical thermal cycles. The dark blue line shows the first cycle and for clarity each subsequent cycle has been offset by 0.5 mW. (Sample mass, 5 mg; heating/cooling rate, 10 K min⁻¹; atmosphere, nitrogen)

Although the measurements of Chang & Westrum [24] and Byazleva *et al.* [25] on purified samples of adamantane by adiabatic calorimetry were made some 70 years apart, the results are in close agreement. However, the value obtained by Van Ekeren *et al.* [26] on a commercial 99+% sample, using the same technique, was ~ 0.6 K higher. Van Ekeren attributed this to the difference in sample purity between the materials and suggested it would be preferable to use their value when working with a similar commercial material. In the present work, our result on a similar purity material to Van Ekeren is within 0.4 K of their adiabatic calorimetry measurements.

3.2.4. Ammonium dihydrogen phosphate

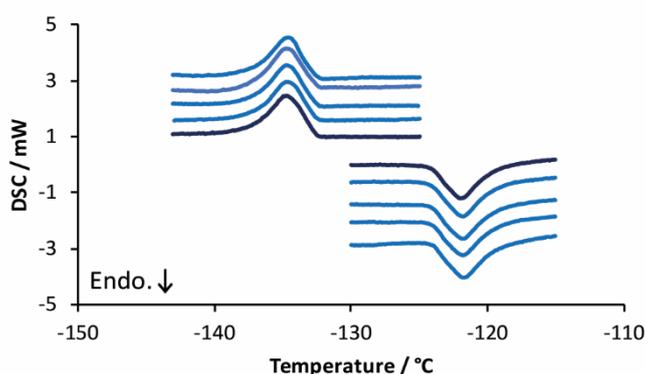


Fig. 6. DSC profile of ammonium dihydrogen phosphate undergoing five identical thermal cycles. The dark blue line shows the first cycle and for clarity each subsequent cycle has been offset by 0.5 mW. (Sample mass, 5 mg; heating/cooling rate, 10 K min⁻¹; atmosphere, nitrogen)

Our measured value of -124.4 °C is close to the values obtained by Gough [29] *et al.* using dielectric, NMR and ESR techniques which gave values ranging from -123.7 to -124.4 °C and

to the earlier value of -124.7 ± 0.5 °C measured by Loiacono using DTA [28]. The cycling studies at 10 K min^{-1} confirmed the observation of Gough *et al.* that the material could be heated through the transition without any significant change in the transition temperature.

4. Conclusions

All the four potential CRMs studied showed excellent reproducibility and could be reheated several times without changing the transition temperature. However, the diphenyl ether exhibited marked supercooling and required cooling below 0 °C before recrystallisation took place. The results confirm the possibility of using diphenyl ether as a substitute for gallium, where users are concerned about the possibility of damage to the equipment from the latter sample. Our studies on adamantane confirm its suitability as a low temperature standard. However, the difference in the values obtained by adiabatic calorimetry on the purified and commercial materials highlights the difficulty in assigning a literature value to the commercial sample being used. Thus, the values for the samples of adamantane of similar purity offered by two manufacturers, as part of their DSC calibration sets, differ by ~ 1 K.

The studies on the two ammonium salts (ammonium sulphate and ammonium dihydrogen phosphate) confirm the potential of these materials as DSC standards which are readily available in high purity, can be handled without any special precautions and heated a number of times without change. As indicated in the introduction, we will be following these initial studies by DSC measurements of the transition temperatures of the potential calibration standards under thermodynamic equilibrium conditions, using a conventional high sensitivity DSC. These measurements will also enable the anomalous peak shapes observed for diphenyl ether and the two ammonium salts to be investigated in more detail.

The methods that will be used are the GEFTA extrapolation to zero heating rate technique [30] and the stepwise heating technique [31]. In the latter technique, the equilibrium temperature is obtained from the final step of a heating programme where the temperature is raised in small increments, e.g. 0.05 °C, with isothermal intervals between the steps, until melting is complete.

Acknowledgements

The authors would like to thank Linkam Scientific for the provision of the Optical DSC450 and the University of Huddersfield for funding.

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