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DEVELOPMENT AND ACCREDITATION TO ISO/IEC 17025 CALIBRATION STATUS OF A MELTING POINT MEASUREMENT FACILITY FOR THE UK

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A melting point measurement facility for the UK has been developed and accredited to ISO/IEC 17025 Calibration status for the determination of the liquefaction temperature of pure substances from 35 to 250°C.

The facility is based upon a commercial instrument, i.e. an oil bath fitted with an aluminium block (Isotech, model 798 EHT), a precision multimeter (Isotech TTI-7), a thermocouple directly inserted in the sample under investigation and a platinum resistance thermometer (PRT) tracking the block temperature. The homogeneity of temperature bath/block was investigated and the PRT used for the traceability of the measurements was calibrated by NPL and traceable to ITS-90. The process was validated using four current LGC Certified Reference Materials (CRMs):

- Phenyl salicylate; material number: LGC2411, batch number: 001; liquefaction point: 41.85±0.05°C
- 4-Nitrotoluene; material number: LGC2401, batch number: 007; liquefaction point: 51.71±0.21°C
- Benzoic acid; material number: LGC2405, batch number: 005; liquefaction point: 122.37±0.21°C
- Carbazole; material number: LGC2409, batch number: 007; liquefaction point: 245.58±0.07°C
- Different approaches were used to identify reproducible features of the melting point (time–temperature) curves of these four CRMs. Excellent correlation was observed between the certified values for the liquefaction point of the four CRMs and the temperature at the end of their respective melting point curve plateau, determined using a temperature differential approach. An uncertainty budget was derived and the expanded uncertainty at the 95% confidence interval (k=2) was found to be:
- Phenyl salicylate: ±0.20°C ; 4-Nitrotoluene: ±0.17°C; Benzoic acid: ±0.24°C; Carbazole: ±0.27°C

Keywords: *certified reference materials, ISO 17025, liquefaction point, melting point*

Introduction

Producing pure substances is a very important process, especially in the pharmaceutical industry. Recrystallisation is commonly used and the melting point of the substance is measured and compared against its literature value using a melting point instrument. The determination of the melting point is quick and cost effective as a first step in structure confirmation and purity check. However, the melting point instrument [1] needs to be calibrated regularly but it is rarely appropriate to remove the temperature sensor for calibration. In situ calibration is normally performed using traceable certified melting point RMs. LGC produces a wide range of organic melting point CRMs from 41 to 285°C as shown in Table 1.

There are many different methods of measuring melting points [2] e.g. capillary melting point method, Kofler method and differential scanning calorimetry [3]. The strategy adopted by LGC for the certification of our materials was based upon a time–temperature curve method where the sample is heated at a constant rate (0.2°C) which is used traditionally by end users. Historically the melting points of these materials have been characterised by national measurement institutes (NMIs) such as the Laboratoire National de Métrologie et d'Essais [4] (LNE, France) using a visual method, by the National Research Centre for Certified Reference Materials [5, 6] (NRC-CRM, China) using

Table 1 Melting point standards produced by LGC

Material	Melting point/°C	Catalogue No.
Phenyl salicylate	41	LGC 2411
4-Nitrotoluene	52	LGC 2401
Naphthalene	81	LGC 2402
Benzyl	95	LGC 2403
Acetanilide	115	LGC 2404
Benzoic acid	123	LGC 2405
Diphenylacetic acid	147	LGC 2406
Anisic acid	184	LGC 2407
2-Chloroanthraquinone	210	LGC 2408
Carbazole	246	LGC 2409
Anthraquinone	285	LGC 2410

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an instrumental method with data treatment based upon bespoke software and the Instituto de Metrologia [7] (Italy). Access to these external facilities is becoming increasingly difficult and a UK facility is needed to provide the capability to replace some of the materials listed in Table 1, where stocks are low.

Three types of melting point have been determined historically [8]:

- Onset point: The onset point is generally considered the start of the melt; liquid clearly appears for the first time as a separate phase in coexistence with crystals.
- Meniscus or mid-point: The meniscus point corresponds to the stage during the melt when the meniscus liquid becomes visible; there is a solid phase at the bottom and a clear liquid phase on the top with a well-defined and visible meniscus.
- Liquefaction point: the liquefaction point corresponds to the stage during the melt at which the substance becomes completely liquid – no more solid is left (i.e. the last crystals have melted).

A survey of the requirements of users revealed that for practical purposes only liquefaction melting temperature was required.

The objectives of the project were:

- To develop a melting point calibration facility at LGC, traceable to the International Temperature Scale (ITS-90) [9] via the National Physical Laboratory (NPL).
- To carry out melting point determinations, based on objective measurements rather than visual observations (identify reproducible features of the melting point curves and correlate them with traditional melting points).
- To validate the method using phenyl salicylate (LGC2411), 4-nitrotoluene (LGC2401), benzoic acid (LGC2405) and carbazole (LGC2409).
- To develop a full uncertainty budget in collaboration with NPL.
- To obtain ISO/IEC 17025 accreditation for the determination of melting point of pure substances from 35 to 250°C.

Experimental

Melting point certified reference material

Phenyl salicylate; material number: LGC2411, batch number: 001; purified by fractional recrystallisation, purity 99.57 mol% (DSC); liquefaction point: 41.85±0.05°C

4-Nitrotoluene; material number: LGC2401, batch number: 007; purified by fractional recrystallisation, purity 99.94 mol% (DSC); liquefaction point: 51.71±0.21°C

Benzoic acid; material number: LGC2405, batch number: 005; purified by fractional recrystallisation, purity 99.99 mol% (DSC); liquefaction point: 122.37±0.21°C

Carbazole, material number: LGC2409, batch number: 007; purified by sublimation, purity 99.87 mol% (DSC); liquefaction point: 245.58±0.07°C

Instrumentation

An oil bath (model 798 EHT, Isothermal Technology Limited (Isotech), Pine Grove, Southport, UK) fitted with an aluminium block was used for this work as shown in Fig. 1. The oil bath was filled with 5 L of oil (Dow Corning, 210H/100cS fluid, Lot 124528, Batch 0001901414). Temperatures were measured by a platinum resistance thermometer (100Ω PRT, Isotech) and a thermocouple (Type N, ceramic coated, Isotech) connected to a precision multimeter (Isotech TTI-7). Two PRTs were calibrated by NPL in terms of ITS-90 and using the International Electrotechnical Commission standard for PRTs (IEC 751) [10] for the range 0 to 250°C, R(0°C) and coefficients a and b were determined and input into the TTI-7 meter (each in a dedicated channel). The measurements required only one PRT and one thermocouple. However, prior to each run the temperature determined by the PRT used for in situ thermocouple calibration was checked with the second calibrated PRT.

The temperature of the oil bath was raised by 0.2°C min^{-1} using the manufacturer's data logging software (Cal Note Pad). The temperature of the sample in the block follows that of the oil bath with a time lag. A sample of the material under investigation was initially dried in a desiccator over phosphorus pentoxide over a 24 h period. About 1.5 g of sample was packed in a clean dry glass tube. A thermocouple was inserted into the sample tube ensuring that it was in good contact with the sample. The sample tube was designed in-house and is shown schematically in Fig. 2. The main feature of the tube is the dimples which allow the thermocouple to be placed exactly in the centre of the tube and consequently in the centre of the material under examination. Care needs to be taken to ensure the thermocouple does not touch the surface of the glass at the bottom of tube. About 3 mm clearance is allowed between the tip of thermocouple and the bottom of the tube. The tube was placed in an aluminium sample block in the Isotech 798EHT oil bath containing silicone oil. The oil bath temperature was held approximately 7°C below the sample melting point. The sample temperature, block temperature, and oil bath temperatures were monitored on the TTI-7 precision multimeter.

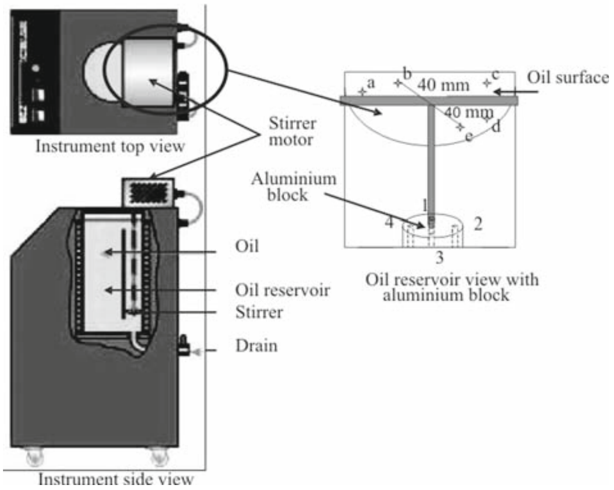

Fig. 1 Schematic of the oil bath and the block

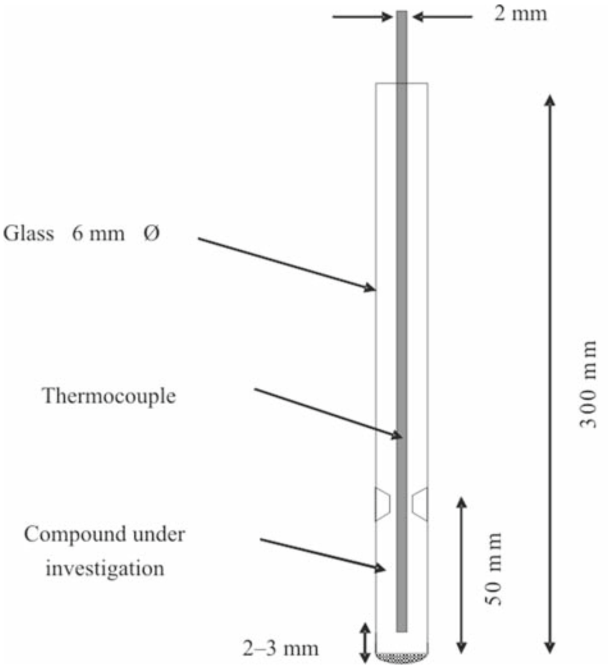

Fig. 2 Diagram of the glass tube containing the sample and the thermocouple

Temperature bath uniformity study

There appears to be some confusion among manufacturers about the best way to represent the uniformity of their liquid baths (and furnace blocks). In response to the need to provide relevant data for United Kingdom Accreditation Services (UKAS), procedures developed over the years at NPL were used to test the homogeneity of our bath. The aim was to profile the bath volume and the block. However, the temperature uniformity of the block is the most important of these because the measurements will be performed in it. NPL make measurements of three parameters, normally using two standard PRTs (SPRTs), which are known to have good short-term stability (e.g. Tinsley SAs). A good resistance bridge capable of measuring the ratios of two thermometers and the ratio of a thermometer against a standard resistor is used (e.g. ASL F17). The uniformity of the bath and the block were studied temporally and spatially.

The spatial temperature uniformity was first investigated and is a measure of the temperature differences throughout the bath volume under test. The uniformity of the bath and the block were studied using the measurement of the ratio of two SPRTs recorded using a F700 resistance bridge (ASL; S/N 1256 005 361). One thermometer was fixed and the other was moved to various positions in the bath (Fig. 1). It is NPL practice to hold one thermometer at about 30 cm immersion in the middle of the baths cross-section – dependent on what thermometer holder is normally used. The other thermometer was then held for about 3–6 min at 2–4 positions around the 'central' thermometer, first at the same immersion depth and then lower, e.g. 40 cm immersion and higher, e.g. 10 or 15 cm immersion. (At less than 10 cm immersion there is concern that the long stem thermometers used may show immersion effects. It is NPL's experience that temperature gradients become more severe in the top 10 cm immersion distance.

The temporal stability in the oil bath/block was also investigated and is the amount by which the temperature of a probe changes over a set period of time, i.e. the range of temperature values (max–min) that are measured during that period and in that location. For comparison calibrations, the period could be 6 min which would give enough time for five tests and two standard thermometers to be cycled through in both directions at half minute intervals. Longer or shorter periods may be appropriate for different purposes. The temporal stability in different parts of the bath was also checked. Measurements were carried out at the start and at the end of each measurement for the spatial stability (approximately 5 min) for convenience.

Data treatment

The data processing seeks to:

- Robustly (numerically/analytically) identify reproducible melting features, ideally with physical significance.
- Map onto the traditional melting points, comparing with certified melting point values of four CRMs (phenyl salicylate, 4-nitrotoluene, benzoic acid and carbazole).

Validation

A validation study was undertaken to assess and quantify the following:

- The homogeneity of temperature bath/block.
- A comparison/calibration of temperature sensors traceable to ITS-90.
- Robust (numerically/analytically) identification of reproducible melting features.
- Mapping onto the traditional melting points. Comparison with certified melting point values of four CRMs (phenyl salicylate, 4-nitrotoluene, benzoic acid and carbazole).
- Evaluation of differences between first melt temperature and successive melt temperatures.
- Evaluation of results obtained by different users.
- Development of uncertainty estimates.
- The outputs of the validation study were used to develop a standard operating procedure for characterising melting points of pure substances in the range from 35 to 250°C.

Traceability

Initially two PRTs were calibrated in terms of ITS-90 by NPL and the melting point measurement system including PRTs and TTI-7 meter was checked for measurement accuracy on a yearly basis using a UKAS accredited laboratory and traceable to SI (ITS-90).

The thermocouple in contact with the material under investigation was cross-calibrated in situ with the calibrated PRT i.e. both temperatures ($n=20$) were recorded at fixed temperatures at the beginning of the run approximately 7°C below the melting point and at the end of the run approximately 7°C above the melting point. The mean temperature difference between the thermocouple and PRT before and after the melt was calculated and used to correct the thermocouple temperature readings.

Quality control

Before doing any measurement using the melting point instrument, the PRT used for the work is checked with a second calibrated PRT at the expected melting point of the material (from literature data) under examination. The tolerance for the maximum deviation between the two PRTs was determined as 20 mK.

To determine if the melting point measuring system is functioning properly, at least one measurement is made on benzoic acid (LGC 2405). When a melting point value is within the stated uncertainty of the certified melting temperature on first melt, the melting point system is deemed suitable for melting point measurement.

As further confirmation of the performance of the melting point system, the PRT is checked at the ice/water triple point before use at regular intervals (not more than six months) to ensure that the resistance or temperature indicator reading has not significantly changed since the previous calibration of the instrument.

Results and discussion

Spatial and temporal stability of the oil bath/block

In the oil bath, measurements carried out at 52, 156.8, 200 and 250°C have shown that the temperature could vary spatially by about 90 mK (both SPRTs in the oil bath). Additional experiments demonstrated that this observed spatial variation (at 156.8°C) was due to the heater. Experiments carried out at 52°C have shown that a smaller variation was observed in the oil bath (max. about 3 mK).

Spatial variation of the block temperature was studied at 52, 156.8, 200 and 250°C and a good uniformity was obtained with a maximum spatial variation of 2.45 mK (both SPRTs in the block, depth profile studied).

Temporal uniformity was also studied and at 52, 200 and 250°C. At 52°C the maximum temporal temperature variation over 5 min was 0.6 mK in the block and 10 mK in the oil bath (both SPRTs close to position c). At 200°C the maximum temporal temperature variation over 5 min was 7.7 mK in the block and 32 mK in the oil bath (both PRTS in oil bath i.e. one SPRT in position c and second SPRT in position e, Fig. 1). At 250°C, the maximum temporal temperature variation over 5 min was 4.05 mK in the block.

For the uncertainty budget, the uncertainty due to possible temporal and spatial temperature instability of the block was estimated to 4 mK based upon this stability study.

Data treatment – cubic polynomial approach

A typical temperature curve is shown in Fig. 3.

Figure 3 shows the temperature plot for a thermocouple placed into a glass tube containing benzoic acid compared to the temperature measured by a PRT in the block of the oil bath. The first approach developed to extract features from the melting point curve was based upon an attempt to model the plateau region using a cubic polynomial i.e. $y=ax^3+bx^2+cx+d$ through the plateau section estimated visually from Fig. 3. After this first step the point of inflection was determined i.e. $y''=6ax+2b=0$ (second derivative of the polynomial was equal to 0) or x (point of inflection)$=-b/3a$. After determination of this first point of inflection, the time axis (x) was normalised setting the point of inflection

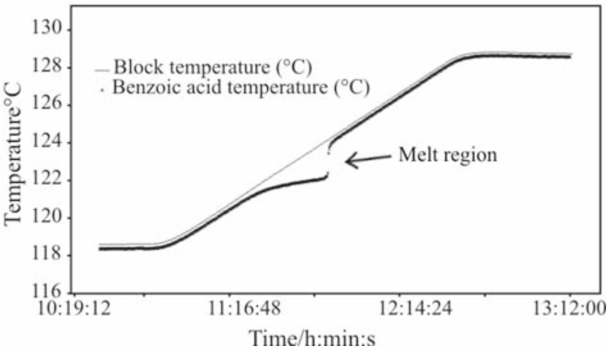

Fig. 3 Benzoic acid – temperature curve

to 0 and a further cubic polynomial was fitted through the new plateau region data. A temperature residual analysis, i.e. the difference between the predicted and experimental temperatures was carried out. The criterion for the plateau region determination is that the residuals were within ±40 mK. If this criterion was not satisfied the outliers at the end or beginning of the plateau were removed and the analysis was carried out again. The point of inflection (x) was recalculated i.e. the polynomial is $y=F(x)$, evaluated at $x=-b/3a$ to determine the temperature at the point of inflection.

To determinate the end of the plateau, a first tangent at the point of inflection of the plateau region was fitted to the plateau. The equation of the tangent is $y=a_1x+b_1$ with the slope of the tangent (a_1) equal to the first derivative ($y'=3ax^2+2bx+c$) of the cubic polynomial fitting the plateau substituting x with the point of inflection and the intercept (b_1) equals to the temperature at the point of inflection also calculated from the polynomial fitting the plateau region. A graphical representation of the tangent at the point of inflection for benzoic acid is shown in Fig. 4.

A temperature differential approach was also used to plot the tangent after the end of plateau. The tangent was plotted through the data point with the biggest temperature differential and the previous data point. The end of the plateau was calculated by determining the intersection point (x_1) between the two tangents as shown in Fig. 4. The temperature at the point of intersection is then calculated using the equation of either tangent.

The temperature at the point of inflection and at the end of the plateau were determined using this approach for two CRMs, i.e. benzoic acid and 4-nitrotoluene. The results of this approach are shown in Table 2 for 4-nitrotoluene compared to its certified melting point values (Table 3). Table 2 shows the results were reproducible with a good agreement between the temperature determined at the point of inflection (first melt, mean analyst 1 and 2, 51.56°C) and the certified mid-point temperature (51.58°C, mean LNE and NRC-CRM). No significant difference was obtained between the melting point temperature values for the first melt and successive melts. A comparison between Tables 4 and 5 for benzoic acid shows that there is not a good agreement between the temperatures determined at the point of inflection and at the end of plateau compared to the certified melting point values (mid-point and liquefaction temperatures respectively). As it was observed for 4-nitrotoluene, no significant difference was observed between first melt and successive melts. Unfortunately, this approach could not be applied to carbazole because of its melting point curve features (plateau region could not be modelled using a cubic polynomial). This problem forced the investigation of a second approach which ideally could be applied to any sample.

Data treatment – temperature differential approach

An alternative way to determine the temperature end of the plateau region only is to use a temperature differential approach, i.e. the temperature difference between two consecutive points. This approach is based upon:

- The temperature differential is around 60 mK before the plateau region and is related to the heating rate selected for the experiment (0.2°C min^{-1}).
- The plateau is defined as the region of the temperature curve where the sample temperature increases at a slower rate than the block temperature and has therefore very small differentials (±20 mK typically for benzoic acid).
- The material temperature will increase sharply when it is completely melted.

Therefore, the end of plateau temperature can be detected objectively and consistently when the temperature differential reaches a pre-determined threshold value. This approach was tested on 4 CRMs, i.e. phenyl salicylate, benzoic acid, 4-nitrotoluene and carbazole. The threshold values for the determination of the end of plateau region using this approach for each CRM

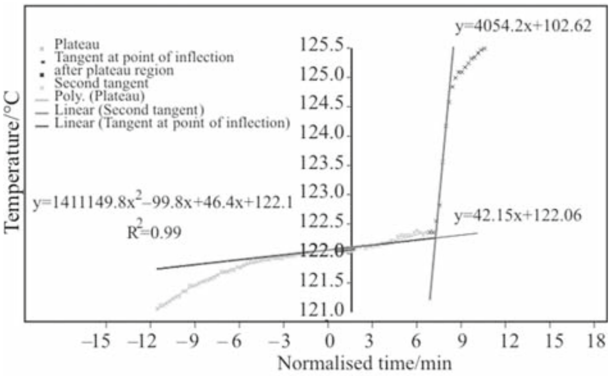

Fig. 4 Curve analysis – summary

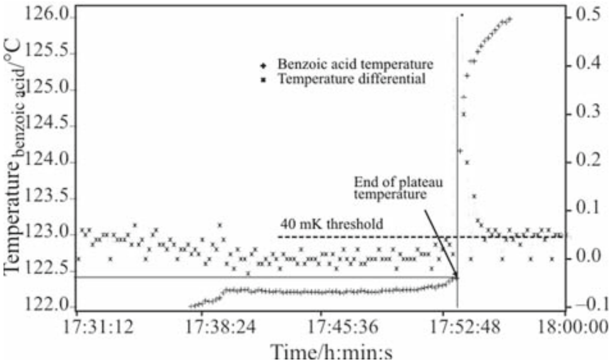

Fig. 5 Temperature differential approach – benzoic acid

were determined based upon their typical respective temperature differential over their plateau region e.g. for benzoic acid, the typical temperature differential over plateau region residual of 20 mK was doubled and set as threshold value (40 mK) as shown in Fig. 5. This approach can be applied to any melting curve and therefore sample. The threshold values determined for each CRM were:

- 200 mK for phenyl salicylate
- 40 mK for 4-nitrotoluene
- 40 mK for benzoic acid
- 100 mK for carbazole

The difference in threshold values is just an effect of the variation in typical temperature differential of the plateau region measured for each CRM.

Method validation comparing cubic polynomial and temperature differential approaches

The CRMs under investigation were dried for 24 h over phosphorus pentoxide before determining their melting point. The heating rate was 0.2°C min^{-1} unless stated otherwise. All measured melting point values determined using the cubic polynomial approach and the temperature differential approach were corrected using the correction factor determined from the in situ calibration of the thermocouple with the PRT described in the traceability section.

4-Nitrotoluene

This material was analysed previously by NRC-CRM using a similar approach. NRC-CRM determined the melting point using an air furnace taking 7 replicates of the first and second melt [8]. LNE determined the melting point values of 4-nitrotoluene using a visual method [11]. Table 2 shows the different melting point values determined using the tangent approach i.e. temperature at point of inflection and end of plateau and the temperature differential approach i.e. temperature at end of plateau for two analysts and on the first melt and successive melts.

The tangent approach could not be applied for the runs at a higher heating rate of 1°C min^{-1} because it was not possible to fit a polynomial through the plateau region. However, the temperature differential approach could be applied and no significant difference was observed between the temperatures determined at the end of the plateau using 0.2 and 1°C min^{-1} on successive melts and first melt. Table 2 also shows there are no significant differences between successive melts and first melt determination of the melting point of 4-nitrotoluene at the point of inflection, at the end of plateau using the cubic polynomial approach and the end of plateau using the differential approach. Table 3 shows the melting point results (onset, mid-point and liquefaction) obtained for 4-nitrotoluene (LGC2401) by NRC-CRM and LNE.

The results shown in Tables 2 and 3 are not directly comparable because NRC-CRM determines the melting point using a different algorithm and take the average between the first and second melt. However, Table 2 shows no significant difference between first

Table 2 Determination of the 4-nitrotoluene temperatures at the point of inflection and at the end of plateau using the tangent and temperature differential approach

4-Nitrotoluene	Corrected temperature at point of inflection/°C	Corrected temperature at end of plateau using tangent/°C	Corrected temperature at end of plateau using differential/°C
Analyst 1 first melt (*n*=4)	51.60±0.04	51.58±0.03	51.66±0.02
Analyst 2 first melt (*n*=4)	51.52±0.14	51.61±0.10	51.68±0.01
Average Analyst 1 and 2 first melt	51.56±0.1	51.60±0.07	51.67±0.02
Analyst 1 successive melts (*n*=3)	51.58±0.04	51.61±0.02	51.70±0.03
Analyst 2 successive melts (*n*=4)	51.51±0.08	51.59±0.05	51.63±0.04
Analyst 1 and 2 successive melts	51.54±0.07	51.59±0.04	51.66±0.05
Analyst 1 first melt at 1°C min^{-1} (*n*=3)	n.d.	n.d.	51.63±0.03
Analyst 1 successive melts at 1°C min^{-1} (*n*=3)	n.d.	n.d.	51.68±0.04

n: number of replicates (per analyst), n.d.: not determined

Table 4 Summary of benzoic acid melting point values determined by Analysts 1 and 2

Benzoic acid	Corrected temperature at point of inflection/°C	Corrected temperature at end of plateau/°C	Corrected temperature at end of plateau using temperature differential/°C
Analyst 1 successive melts (n=5)	122.15±0.05	122.27±0.04	122.36±0.03
Analyst 2 successive melts (n=6)	122.26±0.04	122.30±0.01	122.37±0.04
Analyst 1 first melt (n=3)	122.26±0.12	122.28±0.09	122.36±0.07
Analyst 1 successive melts at 0.1°C min^{-1} (n=3)	n.d.	n.d.	122.39±0.06

n.d.: not determined, n: number of replicates (per analyst)

melt and successive melts and therefore comparisons can be made. The temperature determined at the end of the plateau region using the temperature differential approach (51.67°C) is very similar to the liquefaction temperature reported by NRC-CRM (51.72°C) and LNE (51.70°C) in Table 3.

Benzoic acid

Table 4 summarises the different results obtained by two analysts for benzoic acid (LGC2405) which can be compared with those obtained by LNE. It is important to note that the LNE approach is different (visual method).

Table 4 shows a very good agreement obtained between the temperatures at end of plateau using temperature differential determined by Analysts 1 and 2. It is also important to note that no significant temperature differences were obtained between successive and first melts using the temperature differential approach and for the temperatures determined at 0.1 and 0.2°C min^{-1}.

Tables 4 and 5 show (as for 4-nitrotoluene) that the corrected temperature determined at end of plateau using the temperature differential approach (122.36°C) is very similar to the liquefaction temperature determined by LNE (122.37°C). The melting point of the benzoic acid was also measured by adiabatic calorimetry [12] in collaboration with the University of Oslo and found to be 122.35±0.03°C which is also in good agreement with the temperature determined at the end of the plateau using the temperature differential approach.

Table 3 4-Nitrotoluene melting point values determined by NRC-CRM and LNE

4-Nitrotoluene	Onset temperature/ °C	Mid-point temperature/ °C	Liquefaction temperature/ °C
NRC-CRM	51.385	51.552	51.72
U (k=2)	0.04	0.04	0.07
LNE	51.33	51.60	51.70
U (k=2)	0.21	0.15	0.15
Certified value	51.36	51.58	51.71
U (k=2)	0.26	0.19	0.21

Table 5 Melting point values determined by LNE (France)

Benzoic acid	Onset temperature/ °C	Mid-point temperature/ °C	Liquefaction temperature/ °C
Average (n=7; duplicate)	121.8	122.11	122.37
U (k=2)	0.28	0.22	0.22

Carbazole

Work on carbazole (LGC2409) was more challenging than the two other materials because it sublimed and showed some evidence of thermal degradation over its melting point. As was carried out for benzoic acid and 4-nitrotoluene, two analysts measured the melting point for different samples of carbazole on its first melt. However, it was observed that carbazole thermal degradation by-products were contaminating the tip of the thermocouple i.e. a black residue at the tip of the thermocouple was difficult to clean and a trend of lower melting point was observed when the thermocouple was used more than 3 times. As a result, the thermocouple was only used for 3 runs. A summary of the results obtained by the two analysts compared to certified value for the liquefaction temperature are shown in Table 6.

Table 6 shows a good agreement between the end of plateau temperature determined using the new approach compared to the certified liquefaction temperature determined by NRC-CRM.

Table 6 Summary of carbazole melting point values obtained on first melt (Analysts 1 and 2)

Carbazole	Corrected temperature at end of plateau using temperature differential/°C
Analyst 1 average and Std. dev. (n=3)	245.38±0.16
Analyst 2 average and Std. dev. (n=3)	245.45±0.03
Average Analysts 1 and 2	245.41±0.11
Certified value and U (k=2)	245.58±0.07 (liquefaction)

n: number of replicates (per analyst)

Table 7 Phenyl salicylate end of plateau temperature compared to certified liquefaction temperature

Phenyl salicylate	Corrected temperature at end of plateau using temperature differential/°C
Analyst 1 mean and Std. dev. (*n*=3)	41.95±0.04
Analyst 2 mean and Std. dev. (*n*=3)	41.98±0.09
Mean analyst 1 and 2 and Std dev	41.96±0.07
Certified value and expanded uncertainty (*k*=2)	41.85±0.05 (liquefaction)

n: number of replicates (per analyst)

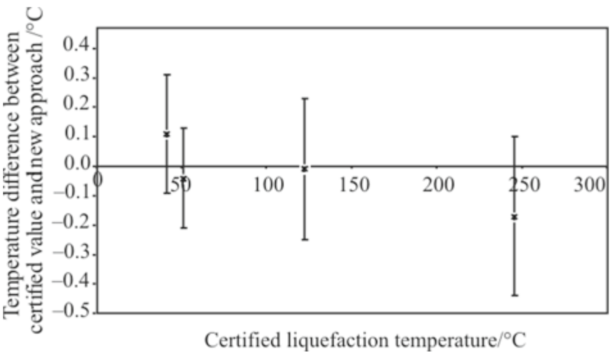

Fig. 6 Validation of the new melting point instrument (melting point values with expanded uncertainties)

Phenyl salicylate

This material was also analysed by NRC-CRM. Table 7 shows a comparison between the certified liquefaction temperature compared to the end of plateau temperature using the temperature differential approach.

Table 7 shows a good agreement between the certified value (41.85°C) and the end of plateau temperature using the temperature differential approach (41.96°C).

A graphical representation of the validation exercise is shown in Fig. 6. For more clarity, the difference between the certified liquefaction temperature and the end of plateau temperature determined using the temperature differential (plotted with expanded uncertainty (*k*=2)) is plotted.

Table 8 Uncertainty – benzoic acid

Components/°C unless otherwise labelled	Uncertainty	Divisor (uncertainty type)	Sensitivity coefficient	Uncertainty contribution/°C
Type A	1 s			
Statistical Variation - repeated plateau to plateau (1 operator, Std. dev.=0.07°C)	0.070	1.00	1.0	0.070
Statistical noise (over a few min)	0.010	1.00	1.0	0.010
Sub total – Statistical standard unertainty		1.00	1.0	0.071
Type B	worst case	when divisor 1.73		
uncertainty due to different thermocouple/PRT cross calibrations before and after melt	0.067	1.00	1.0	0.067
TTI-7 meter uncertainty	0.010	1.73	1.0	0.006
PRT uncertainty	0.006	1.00	1.0	0.006
Uncertainty due to the instability of the PRT	0.025	1.73	1.0	0.014
Plateau interpretation or plateau irregularity	0.040	1.73	1.0	0.023
Bath Condidions i.e. Effect of thermal environment	0.004	1.73	1.0	0.002
Stem Conditions or Immersion/wire inhomogeneity	0.010	1.73	1.0	0.006
Thermal lag of the thermocouple compared to the PRT (Std. dev. at 0.1°C min^{-1}–60 mK) (Thermal resistance of test material and glass/metal – ΔT i.e. non uniform T in cell)	0.060	1.00	1.0	0.06
Hydrostatic effect/mm	20.000	1.73	0.000003	0.00003
PRT self heating/mK	1.000	1.73	0.0010	0.001
Thermocouple spurious EMF/µV	0.500	1.73	0.03	0.008
Uncertainty due to the unstability of the CJC	0.010	1.73	1.0	0.006
Sub-total (non statistical)				0.095
Combined A and B (at fixed points)				0.119
Expanded uncertainty (*k*=2)/°C				0.237

CJC: Cold junction compensation

Table 9 Comparison between certified liquefaction temperature and end of plateau temperature determined using temperature differential approach

CRM	LGC	Certified value/°C	U(k=2)/°C	New approach/°C	U(k=2)/°C
Phenyl salicylate	2411	41.85	0.05	41.96	0.20
4-nitrotoluene	2401	51.71	0.21	51.67	0.17
Benzoic acid	2405	122.37	0.21	122.36	0.24
Carbazole	2409	245.58	0.07	245.41	0.27

Figure 6 clearly demonstrates there is no significant difference between the two methods and the new melting point facility using the temperature differential approach can be used to measure the liquefaction temperature of pure substances from 35 to 250°C.

Uncertainty

The following potential sources that can contribute to errors in melting point measurements were identified and assessed:

- Platinum resistance thermometer (PRT) uncertainty.
- True Temperature Indicator (TTI-7) uncertainty.
- Operator statistical variation.
- Uncertainty due to thermocouple in situ calibration.
- Bath conditions/effect of thermal environment.
- Stem conduction or immersion wire inhomogeneity.
- Plateau temperature interpretation uncertainty.
- Statistical variation.
- Statistical noise.
- Hydrostatic effect.

When the above contributions to uncertainty were considered, the overall uncertainty in temperature measurement was estimated for the four CRMs used in the validation. A detailed uncertainty budget for benzoic acid is given in Table 8.

The expanded uncertainty at the 95% confidence interval (k=2) was found to be

- Phenyl salicylate: ±0.20°C
- 4-Nitrotoluene: ±0.17°C
- Benzoic acid: ±0.24°C
- Carbazole: ±0.27°C

The uncertainty budget and associated data have been independently reviewed by appropriate staff at NPL and UKAS.

Conclusions

A melting point facility was validated using four current LGC CRMs and accredited for ISO/IEC 17025. Calibration for the determination of liquefaction temperature of pure substances from 35 to 250°C.

The facility is fully traceable to ITS-90 and an uncertainty budget was calculated. Different data processing approaches for the determination of reproducible features of the melting region were investigated and compared to traditional melting point values. A temperature differential approach was selected to determine the end of plateau region which was compared to certified liquefaction temperature of each CRM. The results of this comparison are shown in Table 9.

Table 9 shows that there was an excellent agreement between the certified liquefaction temperature values and the end plateau temperature for the four CRMs used in the validation. The uncertainty of the new approach is generally similar to the typical uncertainty reported by LNE for liquefaction temperature (0.20°C) and higher than those reported by NRC-CRM (0.05 and 0.07°C for phenyl salicylate and carbazole respectively). This difference in observed uncertainties between LGC and NRC-CRM measurements arises from the difference in methodology i.e. mean of first and second melt for NRC-CRM instead of first melt for LGC, PRT thermocouple cross-calibration used by LGC instead of single SPRT for NRC-CRM and statistical uncertainty from different operators for LGC instead of single operator for NRC-CRM.

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