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DIFFERENTIAL SCANNING CALORIMETRY TO MEASURE THE PURITY OF POLYCYCLIC AROMATIC HYDROCARBONS

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The application of differential scanning calorimetry (DSC) for purity determination is well documented in literature and is used amongst others in the analysis of pure organic crystalline compounds. The aim of this work is to examine whether the DSC method for purity determination consistently produces values for the purity of polycyclic aromatic hydrocarbons (PAHs) which are sufficiently accurate as required for the certification of reference materials. For this purpose, 34 different existing PAH certified reference materials were tested. The DSC results are shown to be consistent with the results obtained by other methods assessing the organic impurities content in PAHs, like gas chromatography (GC), high performance liquid chromatography (HPLC) and mass spectrometry. Significant differences between the measured values and the certified purity values were observed only in a limited number of cases.

Keywords: *certified reference materials, DSC, polycyclic aromatic hydrocarbons, purity*

Introduction

PAHs (polycyclic aromatic hydrocarbons) constitute a range of organic compounds. The PAH molecules consist of at least two fused benzene rings substituted by N, O or methyl, hydroxyl or nitro groups. The compounds occur naturally in crude oil and its derivatives, but they are also formed during incomplete combustion of fossil fuels and forest fires. The physical and chemical properties of the individual PAH vary. In vivo and in vitro experiments have shown that various PAHs are potent mutagens and/or carcinogens [1, 2]. PAHs can accumulate in human and animal tissues containing fat. Therefore, they form an important class of environment contaminants. The properties of some PAHs can make them highly mobile throughout the environment, and deposition and re-volatilization are distributing them between air, soil and water. Current European legislation like Regulation (EC) No. 850/2004 on persistent organic pollutants, the Water Framework Directive 2000/60/EC and Directive 2004/107/EC concerning the content of As, Cd, Hg, Ni and PAHs in ambient air require EU Member States to monitor the content of PAH compounds in different compartments of the environment.

Comparability and traceability of the PAH monitoring results require certified reference materials (CRMs). Therefore, the European Commission produced a group of PAH CRMs of high purity. Such pure PAHs generally exist as colourless, pale yellow or white crystalline solids. During certification, the purities of these candidate RMs were determined by different laboratories using independent analytical methods, namely gas chromatography with flame ionisation detection or mass spectrometry (GC-FID and GC-MS), high performance liquid chromatography with UV detector (HPLC-UV) and direct inlet mass spectrometry. Certification reports which contain information regarding the CRM's synthesis and characterisation are accessible from the website of the Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre of the European Commission [3]. In the certification exercises DSC was used for studying homogeneity because of the good repeatability of the DSC results. Also, DSC is used for monitoring the stability of the certified values, after certification. There were some doubts about the validity of the DSC results for certification measurements related to the ability of the method to detect all impurities. Today, DSC results are used more often. This paper intends to demonstrate whether the DSC purity determination method is indeed sufficiently reliable and fit-for-purpose when used on PAHs.

The DSC purity determination method was established using melting point observations revealing a relation between a substance's melting point and its purity (Kofler [4], 1920). The method is used to solve problems in different fields for example pharmacy [5]. The further development of this method is based on a number of assumptions: impurities and the main compound are forming a simple eutectic system (impurities need to be soluble in the liquid phase and insoluble in the solid phase), the system is under constant pressure, the con-

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tent of impurities is low and the heat of fusion is independent from temperature. Also, it is required that there are no additional transitions or heat-induced effects such as decomposition in the temperature range of melting. DSC purity results are expressed in mol% and are a direct estimate of the purity of the main compound. This is different from chromatographic results, which are based on the separation and detection of particular impurities. As DSC cannot detect all impurities when solid solutions are formed, this method cannot be used as a sole criterion of purity [6]. Plato [7] gave several examples of compounds giving erroneous values because of non-ideal crystal structures or due to impurities showing a similar structure as the matrix compound formed during synthesis. A NIST Special Publication mentions DSC as a SI traceable colligative technique to determine purity of high-pure (neat) organic materials [8], but recommends comparing DSC purity with results obtained by other measurements techniques (mainly chromatographic: gas chromatography, high performance liquid chromatography and thin layer chromatography). New RMs for calibration and validation of DSC instruments and methods were recently described by Archer [9].

The optimisation of the DSC purity determination method was done by Blaine *et al.* [10] using a NIST purity standard – phenacetin doped with *p*-aminobenzoic acid – in 1984. As a result of their investigations, the experimental parameters influencing purity results were assessed: specimen size, heating rate, level of impurity. An optimal specimen size (1.7 mg) and heating rate (0.5–2°C min^{-1}) were deduced. Repeatability and reproducibility were assessed during interlaboratory tests (8 laboratories and 6 different models) and published in an ASTM standard [11]. Estimated criteria for judging the acceptability of results for this method based on repeatability and reproducibility standard deviations were <0.068 and 0.26 mol%, respectively. The introduction of more accurate technical solutions in modern DSC instruments allows taking into consideration the effect of thermal resistance between sample and thermocouple (thermal lag), thus improving the accuracy of the purity calculations. The so-called Tzero$^{\text{TM}}$ technology used in the TA instruments Q1000 differential scanning calorimeter allows for measurement of thermal resistance and capacitance during calibration and to correct the melting peak for thermal lag related errors [12].

Evaluation of the trueness of a method using certified reference materials (CRMs)

Evaluation of trueness is known to be one of the most important sources of uncertainty within the uncertainty budget of analytical methods. The most common procedure to assess trueness consists of measuring CRMs and calculating the method bias by comparing the obtained value with the certified value. It was our aim to evaluate the DSC method performance according to ERM Application Note1[13] by comparison of purity results obtained by DSC on PAH CRMs with their certified value. The method compares the difference between the certified and measured values with the uncertainty of this difference (the combined uncertainty of certified and measured value). The certified value is taken from the certificate. For the PAH CRMs used in this investigation, the certified values were obtained assessing and combining the results of methods other than DSC.

The difference between the mean measured value and the certified value is the method bias (Δ_m), and can be calculated according to Eq. (1):

$$\Delta_\text{m} = c_\text{m} - c_\text{CRM} \tag{1}$$

where c_m is the mean measured value, and c_CRM is the certified value. The uncertainty of Δ_m is u_Δ. This value is calculated from the uncertainty of the certified value, given in the certificate (u_CRM) and the uncertainty of the measurement result (u_m), expressed as a standard deviation of the average, according to Eq. (2):

$$u_\Delta = \sqrt{u_\text{u}^2 + u_\text{CRM}^2} \tag{2}$$

The value of u_m is calculated using Eq. (3):

$$u_\text{m} = \frac{s}{\sqrt{n}} \tag{3}$$

where s is the standard deviation of results and n is the number of repetitions. The expanded uncertainty of the difference between measured and certified value, corresponding to a confidence interval of approximately 95%, U_Δ, is obtained by multiplication of u_Δ with a coverage factor (k), usually equal to 2. To evaluate method performance, Δ_m is compared with U_Δ. If one finds $|\Delta_\text{m}| \le U_\Delta$, the difference between measurement result and certified value is not significant.

Using this approach for the DSC method the assumption was made that the DSC purities expressed in mol/mol (or mol%) are equivalent to purities expressed in g/g (or mass%), as on the certificate of the PAH CRMs. This would imply that the molecular mass of the impurities is the same as the molecular mass of the examined sample. In case of a low impurity level, this assumption is not very critical. It must also be acknowledged that certain assumptions are made when performing chromatographic and mass spectrometric data evaluations.

Experimental

A Q1000 differential scanning calorimeter (TA Instruments-Waters LLC, New Castle, USA) equipped with an autosampler and a RCS cooling device was used for purity determination. The Tzero^{TM} cell constant and temperature calibrations (according to the producer's recommendations using empty DSC cell, sapphire and indium with certified purity) were performed before the measurements to estimate thermal resistance and capacitance. Measurements were done under an atmosphere of nitrogen (flow rate 50 mL min^{-1}). The PAH samples were weighed accurately using a micro-balance with readability 0.001 mg in standard aluminium crucibles taking sample masses between 1.5 and 2 mg, closed with an appropriate aluminium lid and crimped. An empty crucible and lid of the same type were used as reference. The heating rate was 1°C min^{-1} and measurements were done in triplicate.

Results and discussion

In total, the purity of 34 different PAH CRMs was measured. Table 1 lists the data of all tested compounds: melting onset temperatures obtained with the DSC tests, certified purities and corresponding uncertainties taken from the CRM certificates, DSC purity calculated as mean from 3 replicates, and the uncertainties (u_m) related to the mean values, calculated using Eq. (3) and also the inorganic impurities content. The last column gives the inorganic impurity as indicated on the CRM certificates.

For four materials, it was observed from the DSC curves (Figs 1–4) that they are unstable near their melting point. For all other compounds the results of Table 1 were used to calculate the Δ_m and U_Δ values, which are presented in Fig. 5. For 19 of the remaining 30 materials, no significant difference was found between certified and measured values. For the 11 other substances the raw purity results from DSC deviate significantly from the certified values ($\Delta_m<U_\Delta$). This indicates that the raw DSC results do not necessarily always provide a true assessment of the sample purity, as was mentioned in the introduction. The following discussion will provide general conclusions and will explain possible reasons for the deviations.

Method repeatability

When comparing the uncertainty of the certified value (u_{CRM}) and the standard uncertainty of the DSC results (u_m), it is clear that the main contribution to U_Δ (Eq. (2)) stems from u_{CRM}. The good repeatability of the DSC purity determination method was well-known previously and is confirmed by the u_m data in Table 1.

Interference between melting and decomposition or other thermal transitions

Four of the examined compounds have shown to be unstable near their melting point. They started to decompose (coronene Fig.1, and picene, Fig. 3) or show the presence of an unresolved peak in the melting area (benzo[*g*,*h*,*i*]fluoranthene, Fig. 2 and 1-nitropyrene, Fig. 4). Coronene and picene are PAHs with relatively high melting temperatures (437 and 366°C respectively). They were unstable during melting. In the case of picene the melting onset was very sharp, but decomposition occurred soon after the peak maximum was reached (Fig. 3).

1-nitropyrene (Fig. 2) was obtained by nitrification of pyrene in the presence of dioxane and HNO_3 at 70°C. In the DSC curve two partially separated peaks with close melting points are visible. The two peaks can be attributed to the isomers, detected as impurities with molecular mass (*m*/*z* 247) or pyrene (being raw material for synthesis) having a similar melting point

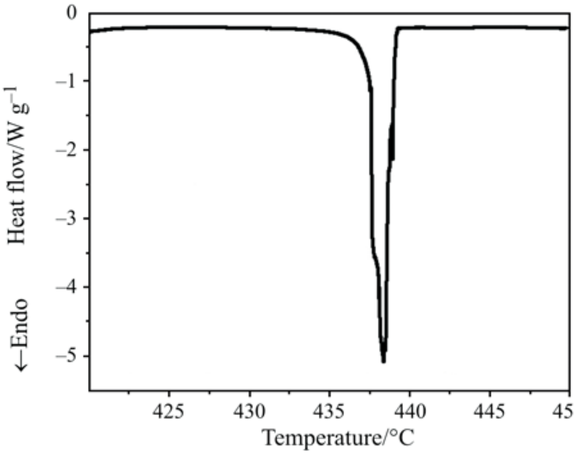

Fig. 1 DSC scan of coronene (heating rate 1°C min^{-1})

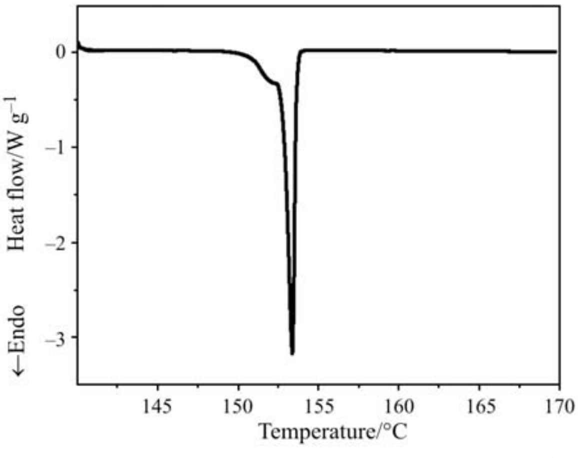

Fig. 2 DSC scan of 1-nitropyrene (heating rate 1°C min^{-1})

Table 1 Results of DSC purity measurements on 34 different PAH CRMs

CRM-code	Compound name	T_m/°C	$c_m \pm u_m$/ g g^{-1}	$c_{CRM} \pm u_{CRM}$/ g g^{-1}	Inorganic impurity/ g g^{-1}
BCR-340	Benzo[*b*]naphtho[*1,2-d*]furan	42.8	0.9983±0.0001	0.997±0.003	0.024
BCR-306	1-Nitronaphthalene	55.8	0.9989±0.0003*	0.996±0.003	0.000
BCR-134	Benzo[*c*]phenanthrene	66.0	0.9987±0.0004	0.997±0.002	0.0011
BCR-307	2-Nitronaphthalene	75.1	0.9974±0.0001	0.997±0.003	0.0022
BCR-337	Dibenzo[*d*,*b*]furan	81.6	0.9996±0.0001*	0.990±0.006	0.0041
BCR-341	Benzo[*b*]naphtho[*2,1-d*]furan	100.4	0.9988±0.0001	0.996±0.003	0.0023
BCR-158	Benz[*c*]acridine	108.2	0.9994±0.0001	0.998±0.001	0.0011
BCR-140	Benzo[*c*]chrysene	125.4	0.9978±0.0001	0.995±0.005	0.0027
BCR-157	Benz[*a*]acridine	129.7	0.9990±0.0001	0.998±0.001	0.0011
BCR-342	Benzo[*a*]fluorenone	133.7	0.9987±0.0001	0.998±0.002	0.0010
BCR-308	9-Nitroanthracene	147.3	0.9995±0.0001*	0.997±0.003	0.0019
BCR-139	Benzo[*g*,*h*,*i*]fluoranthene	(149)	–	0.994±0.003	
BCR-305	1-Nitropyrene	(153)	–	0.997±0.002	
BCR-266	7*H*-Dibenzo[*c*,*g*]carbazole	156.6	0.9993±0.0001*	0.997±0.002	0.0010
BCR-271	Benz[*a*]anthracene	160.4	0.9995±0.0001*	0.998±0.002	0.0011
BCR-310	3-Nitrofluoranthene	161.9	0.9970±0.0001	0.996±0.003	0.0022
BCR-338	4*H*-Cyclopenta[*d*,*e*,*f*]phenanthren-4-one	170.8	0.9998±0.0001*	0.996±0.003	0.0021
BCR-312	2-Nitro-7-methoxynaphtho[*2,1-b*]furan	187.3	0.9997±0.0001	0.998±0.002	0.0017
BCR-270	Triphenylene	198.1	0.9997±0.0001*	0.997±0.001	0.0013
BCR-155	Dibenz[*a,c*]acridine	204.2	0.9997±0.0001	0.998±0.001	0.0011
BCR-152	Dibenz[*a*,*i*]acridine	210.3	0.9995±0.0001	0.998±0.001	0.0010
BCR-309	6-Nitrochrysene	213.4	0.9991±0.0001*	0.989±0.003	0.0002
BCR-154	Dibenz[*a*,*j*]acridine	219.6	0.9992±0.0001	0.998±0.001	0.0011
BCR-343	3-Hydroxybenzo[*a*]pyrene	223.8	0.9980±0.0001	0.994±0.006	0.0016
BCR-265	Dibenzo[*a*,*e*]fluoranthene	232.4	0.9994±0.0001	0.998±0.001	0.0010
BCR-133	Dibenzo[*a*,*e*]pyrene	244.5	0.9989±0.0001	0.996±0.004	0.0010
BCR-339	6*H*-benzo[*c*,*d*]pyren-6-one	251.2	0.9987±0.0002	0.989±0.001	0.0075
BCR-269	Chrysene	253.8	0.9997±0.0001*	0.992±0.003	0.0015
BCR-311	6-Nitrobenzo[*a*]pyrene	255.2	0.9993±0.0001	0.998±0.002	0.0020
BCR-138	Dibenz[*a*,*h*]anthracene	266.6	0.9996±0.0001*	0.990±0.003	0.0013
BCR-267	Indeno [*1*,*2*,*3-cd*]fluoranthene	269.2	0.9997±0.0001	0.998±0.002	0.0016
BCR-159	Dibenzo[*a*,*h*]pyrene	317.1	0.9990±0.0001*	0.992±0.002	0.0015
BCR-168	Picene	(366)	–	0.998±0.003	
BCR-272	Coronene	(437)	–	0.998±0.001	

T_m, melting onset temperature (average from 3 DSC tests, repeatability <0.1°C), values indicated in parentheses are taken from literature; c_{CRM}, certified purity, u_{CRM}, certified uncertainty, c_m, mean measured value, u_m, uncertainty of the measurement result; -, no results due to decomposition; * – result for which $|\Delta m| > U_\Delta$, indicates a significant bias [11]

(154-156°C). The shape of the resulting DSC curve makes it impossible to calculate the purity.

According to the literature melting temperature for pure benzo[*g*,*h*,*i*]fluoranthene (Fig. 4) is 149°C. The melting point obtained by DSC is about 130°C and two peaks partially resolved are also present in the graph. The significant decrease of the melting temperature and broadening of the peak could be caused by the presence of impurities. The presence of such impurities was confirmed during the certification of the CRM using mass spectrometry. Possible impurities are fluoranthene substituted by a methyl group (*m*/*z* 216) and benzophenantrene, which is a substrate of the benzo[*g*,*h*,*i*]fluoranthene synthesis (*m*/*z* 228). In this case DSC is not a good method for purity analysis either because of the presence of two

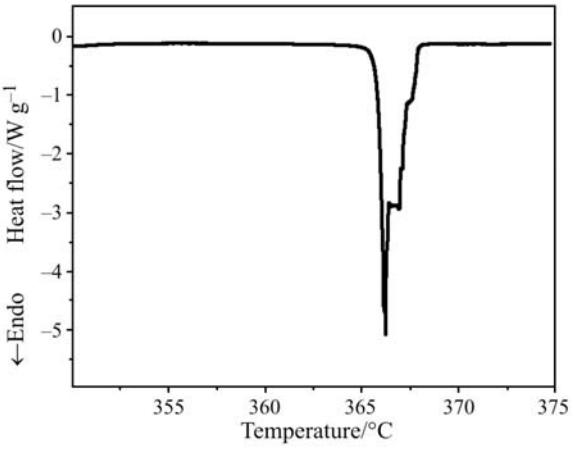

Fig. 3 DSC scan of picene (heating rate 1°C min^{-1})

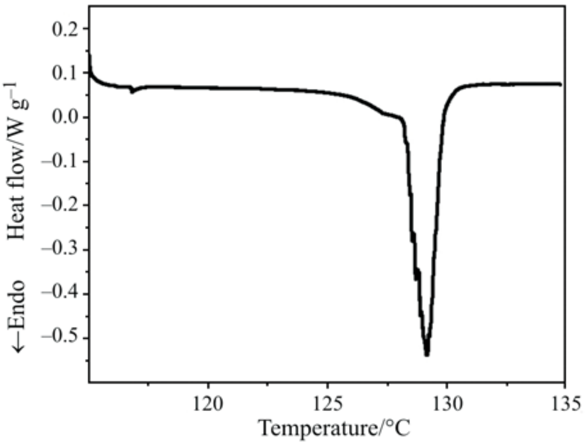

Fig. 4 DSC scan of benzo[*g*,*h*,*i*]fluoranthene (heating rate 1°C min^{-1})

partially resolved peaks and traces of decomposition during melting.

Method selectivity

Figure 5 shows that all bias values Δ_m are positive: for each of the tested PAH CRMs, the certified value is lower than the value measured with the DSC purity determination method. This indicates indeed that, as for most methods that are used to assess purity, the DSC method does not necessarily reveal the presence of all kinds of impurities. One example shows the inorganic impurities. Most inorganic substances are not dissolved in liquid organic compounds, due to the polar nature of the ions into which the inorganic substance is decomposed. The inorganic impurity content of the tested CRMs was determined during the certification using sulphated ash content (values shown in Table 1). Therefore, it was decided to correct the impurity values measured using DSC, with the inorganic impurity values mentioned in the certificate. The result of this correction is presented in Fig. 6, which reveals that for almost all (28) of the 30 examined PAH CRMs, the DSC purity values agree considerably better with the certified value after correction for inorganic impurity. The correction reduces the average bias Δ_m from 0.19 to 0.15%. For two materials (BCR-339, 6*H*-benzo[*c*,*d*]pyren-6-one, and BCR-337, dibenzo[*d*,*b*]furan), the correction of Δ_m for the inorganic impurity renders their $\Delta_m < U_\Delta$. The inorganic impurities for these compounds were high: 0.0041 and 0.0075 g g^{-1}, respectively.

As a conclusion, we observe that after elimination of the compounds showing decomposition or interfering thermal transitions, and after correcting for inorganic impurity, only 4 (6-nitrochrysene, chrysene, dibenz[*a*,*h*]anthracene, dibenzo[*a*,*h*]pyrene) out of 30 PAH compounds which allowed DSC purity determination, show a significant method bias ($|\Delta_m| > U_\Delta$), indicating. This observation supports the use of DSC purity measurements in the certification of reference materials. On the other hand, it is obvious that for the few materials with a significant bias, the

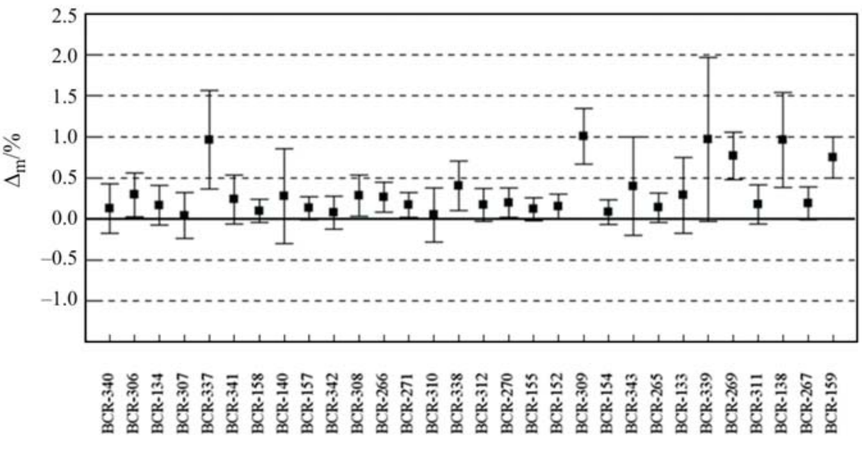

Fig. 5 Bias values Δ_m for all tested PAHs. The error bars correspond with the values U_Δ (Eq. (2)). The graph reveals that for most of the tested PAHs $U_\Delta > \Delta_m$

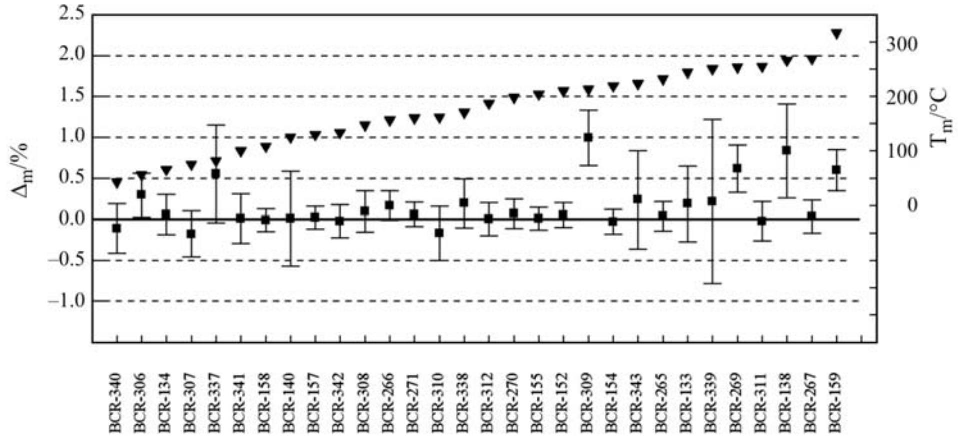

Fig. 6 Corrected bias values (corrected for inorganic impurities; squares) for all tested PAHs, ranked according to their melting onset temperature (triangle – right-hand Y-axis; Table 1). The error bars correspond with the values U_Δ (Eq. (2)). The graph reveals that for most of the tested PAHs $U_\Delta > \Delta_m$

purity determined with DSC is higher than the certified purity obtained with other methods. This must be caused by the non-detection of some of the impurities by the DSC method. It remains therefore a valid recommendation to use multiple techniques based on independent physico-chemical principles for the determination of certified purity values of PAH CRMs.

Conclusions

The trueness of the DSC measurement results for PAH purity determination was assessed by measuring 34 PAH certified reference materials. The method bias was calculated by comparing the obtained value with the certified value. The method bias was insignificant for most PAH CRMs, especially after correcting the DSC results for the certified inorganic impurity content of the CRMs. Some compounds could not be measured because of their decomposition during melting, or because of interference of another thermal transition with the melting peak. A significant bias was found for only 4 out of the 30 remaining compounds. In each of these cases, DSC results indicate a higher purity than the certified purity. This suggests the presence of impurities that are not detectable with DSC. It has been shown that the DSC purity determination method, performed with standard crucibles, provides accurate measurements of the organic impurity content for most PAHs, although additional purity determination methods must be applied to exclude possible overestimation of the true purity.

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