

EXPERIENCES WITH THE USE OF DSC IN THE DETERMINATION OF
VAPOR PRESSURE OF ORGANIC COMPOUNDS

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This paper describes the arrangement of measuring apparatus for vapor pressure determination by means of DSC according to the dynamic method (measurement of boiling temperatures at various pressures). Measuring conditions, main test parameters, typical disturbances and measuring errors are discussed. In the measuring range accessible (0.1 to 7000 kPa / -30 to 600°C), certain boiling points and vapor pressure curves plotted therefrom agree very well with values specified in the literature. Extrapolation of these vapor pressure curves to the pressure range up to 0.1 mPa gives approximate values, the orders of magnitude of which are in agreement with those measured by means of other methods. Vapor pressure curves of oleochemical substances are presented.

Introduction

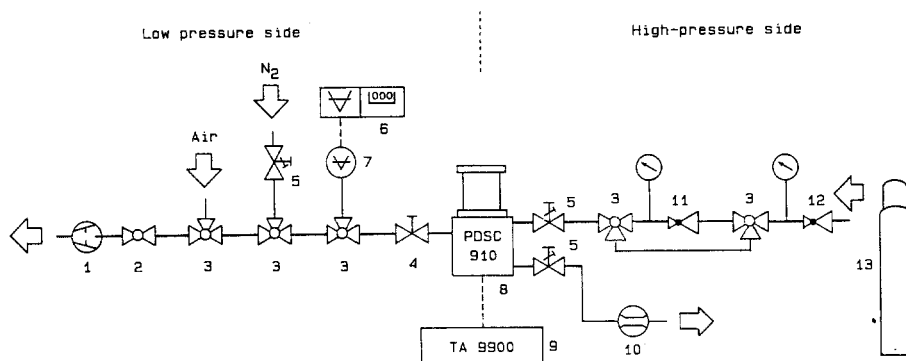
The vapor- or saturation pressure is an important physical parameter for the characterization of substances. It is one of the values required by the legislator for the notification of new chemicals according to the Chemicals Law. Vapor pressures and vapor pressure curves, however, are also needed in everyday work in the chemical industry, for example, in product development for product optimization by substitution of individual substances, in process engineering, as well as in plant engineering for pilot plant planning and plant layout. Vapor pressures of interest lie in a wide range, which extends over several powers of ten.

For the determination of vapor pressures, we use DSC (differential scanning calorimetry) according to the dynamic method, by which the boiling temperature is measured at various pressures. From 6-8 individual measurements carried out at various pressures, a vapor pressure curve $\log p = f(1/T)$ can be plotted. This procedure has been known for 20 years and has been published in various variants (boiling

capillary, DTA, DSC [1-4]). This paper gives a description of the arrangement of our measuring apparatus, which enables boiling temperatures of all kinds of compounds to be measured in the pressure range from 0.1 to 7000 kPa and at temperatures between -30 and $+600^{\circ}\text{C}$. The way to optimal measurements is shown by variation of the main test parameters when determining the boiling temperature. Boiling point determinations and vapor pressure curves of organic compounds will be introduced and discussed in the following.

Experimental Procedure

Fig. 1 shows a schematic diagram of the arrangement of our measuring apparatus. It consists of a Du Pont 9900 thermal analyzer and a DSC pressure cell. For measurements in the



1. Rotary vane vacuum pump
2. Stop cock
3. Three-way cock
4. Shut-off valve
5. Dispensing valve
6. Electronic vacuum gage
7. Vacuum measuring cells 0.1-20 kPa / 1-200 kPa
8. DSC pressure cell
9. Du Pont 9900 thermal analyzer
10. Flow meter
11. Pressure-reducing valve + manometer 0.1- 2 MPa
12. Pressure-reducing valve + manometer 0.5-20 MPa
13. N_2 bottle as pressure source up to 7 MPa

Fig. 1 Arrangement of apparatus for vapor pressure determination by DSC

pressure range from 0.1 to 100 kPa, the low-pressure side is used. The system is evacuated with a rotary vane pump; the desired operating pressure is regulated with nitrogen via a reducing valve. The pressure is measured by means of an electronic vacuum gage (Membranovac 1 VS, manufactured by Leybold-Heraeus). With this apparatus, absolute pressure can be measured. It has two measuring heads, for pressure ranges from 0.1 to 20 kPa and from 1 to 200 kPa. Below 0.1 kPa, the error in pressure measurement becomes too large, so that this value is the lowest limit that is measurable with this test set-up.

Optimization of the procedure

In the DSC diagram, a boiling process is indicated in the form of an intensive endothermal signal. The boiling point is determined as the onset temperature. The main problem when determining the boiling point is pre-boiling vaporization of the test substances in the course of the heating process. To prevent vaporization prior to boiling, it is recommended in the literature [4,5] to use sealed pans with pinholes (0,02 - 0.8 mm in diameter) in their lids. When preparing pans with small pinholes by means of manual tools in our laboratory, we obtained difficultly reproducible results, whereas the use of pans with larger holes promoted pre-boiling vaporization. We succeeded in solving this problem by putting steel balls of 1.6 mm in diameter, serving as "valves", on top of the sealed pans with larger pinholes (diameter 0.5 - 0.8 mm). This enables reproducible measurement of the boiling process in the pressure range from 5 to 7000 kPa.

Fig. 2 shows boiling point determinations of analytical-grade toluene by means of different pan configurations. Curve a results from a measurement using an open pan. With the beginning of the heating process, vaporization already sets in, and at approx. 80°C, the toluene has vaporized completely. In the case of a sealed pan with a pinhole of 0.7 mm in diameter (curve b), vaporization starts at approx.

50°C; only part of the sample vaporizes, and, although somewhat randomly, an onset temperature can be established. The sealed pan with the steel ball serving as "valve" (curve c) shows the least sample vaporization, from approx. 70°C onwards, and enables very precise determination of the onset temperature. The reference pan contained high-purity indium ($T_m = 156.6^\circ\text{C}$) for temperature calibration. From curve c, the boiling point of toluene is determined as 111°C , which agrees fairly well with the value of 110.6°C that is reported in the literature [6].

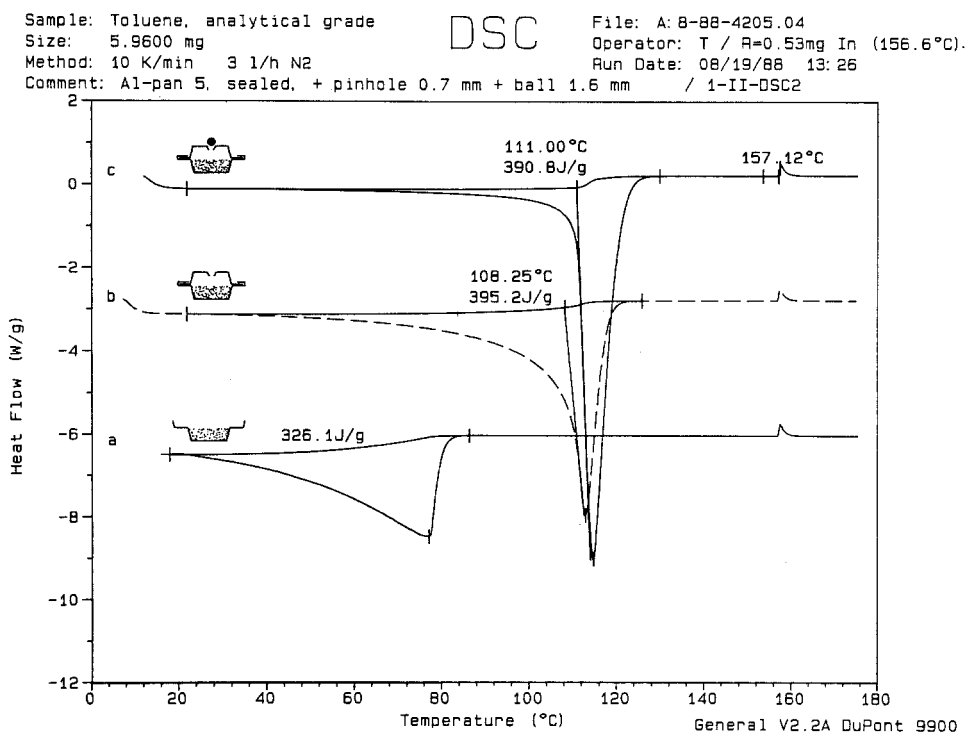


Fig. 2 Boiling curves of toluene

Further tests served to determine the appropriate sample amount and heating rate. When using sample amounts of 5 - 10 mg and heating rates between 10 - 20 deg/min, it became evident that our pan configuration gives measurements of

good reproducibility. Disturbances during measuring, due to delay in boiling and clogging of the "valve", became visible by characteristic deviations of the boiling curve. An interference-free diagram can often be obtained by the addition of inert boiling chips such as silicium carbide.

Wrong sample sizes also make themselves clearly felt. Too small a sample amount promotes vaporization prior to boiling. Too large a sample amount, however, results in overheating. The negative slope of the vaporization peak will then make the onset temperature appear too high. The same is the case with high heating rates. Too low heating rates, however, promote pre-boiling vaporization and give lower boiling points.

For all measurements in the vacuum range we use a special heat-conducting paste to improve the transfer of heat between the cell bottom and the measuring pan.

Results and Discussion

By adhering to the test procedure and parameters described, the boiling temperatures of any given substance, provided that it does not react chemically below its boiling point (decomposition, rearrangement), can be determined with our measuring system. Decompositions, for example, can be identified by changes in the peak shape, which is extremely wide and flat. In Table 1 the experimentally established boiling points of various pure organic substances and the corresponding values specified in the literature [6] are compared. The measuring accuracy is ± 1 deg.

Boiling ranges can be determined in the same way (onset and offset of the vaporization peak). Table 2 gives a comparison between the boiling ranges determined for five benzene fractions and the manufacturer's specifications.

Making allowance for the accuracy of the measurements, one can see that the boiling ranges are within the limits guaranteed by the manufacturer.

Impurities influence not only the melting temperature, but also the boiling temperature. The same applies to oleochemical substances, which are mostly mixtures of homologes (Fig. 3). Model tests carried out with a C12 fatty alcohol, to which other fatty alcohols of differing chain

Table 1 Boiling points of pure organic substances

Substance	Boiling point Measured °C	Boiling point Literature [6] °C	ΔT deg
Diethyl ether	34.7	34.6	0.1
Acetone	56.6	56.5	0.1
Cyclohexane	81.4	80.7	0.7
n-Heptane	99.0	98.4	0.6
(Water	99.7	100.0	- 0.3
n-Decane	175.0	174.1	0.9
Benzoic acid	249.8	249.2	0.6
n-Pentadecane	270.1	270.5	- 0.4
Dibutyl phthalate	341.0	340.0	1.0
Octadecanol	349.6	349.5	0.1

lengths had been admixed, always show a lowering of the melting temperature. Depending on the boiling temperature of the component added, the boiling temperature remains constant or decreases or increases. For the determination of boiling temperatures, it is therefore important to have as comprehensive information as possible available on a substance's structure and composition from spectroscopic and chromatographic analyses in order to be able to judge whether or not the data established (boiling temperature / boiling range) are plausible.

Sample: C12 fatty alcohol 99.3% DSC File: A: 8-88-0726Z.01
 Size: 6.5350 mg Operator: St/ V=1.54mg In (156.6°C)
 Method: 10 K/min 31/h N2 Run Date: 08/29/88 15:04
 Comment: Al-pan 5, sealed, + pinhole 0.7 mm + ball 1.6 mm 1-II-4

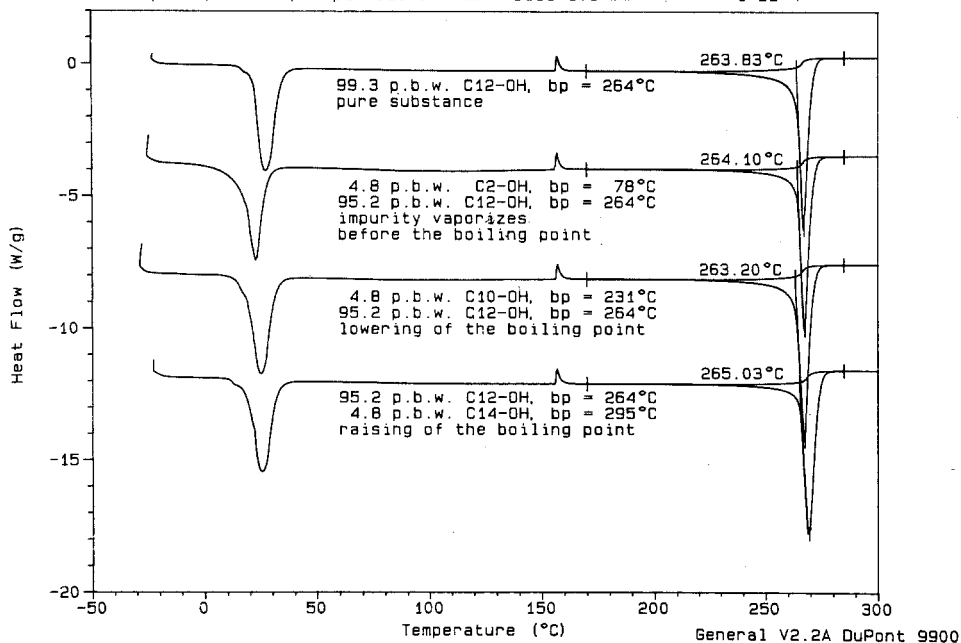


Fig. 3 Melting/boiling curves of oleochemical homologe mixtures

Table 2 Boiling ranges of benzene fractions, technical grade

Boiling range, manufacturer's specifications °C	Boiling range, measured °C
60 - 95	75 - 92
80 - 110	92 - 107
100 - 140	112 - 134
135 - 175	145 - 173
145 - 200	160 - 195

In the measuring range accessible here, the boiling temperatures determined at various pressures give vapor pressure curves that agree very well with data specified in the literature [7], as can be seen from the toluene example (Fig. 4). In this pressure range, the DSC method is a very accurate and precise procedure for the determination of vapor pressure curves. Of a number of oleochemical substances with unknown vapor pressures the required data were established by using this technique. Fig. 4 shows the vapor pressure curves of two fragrances, isopalmitic acid, and stearic acid as examples.

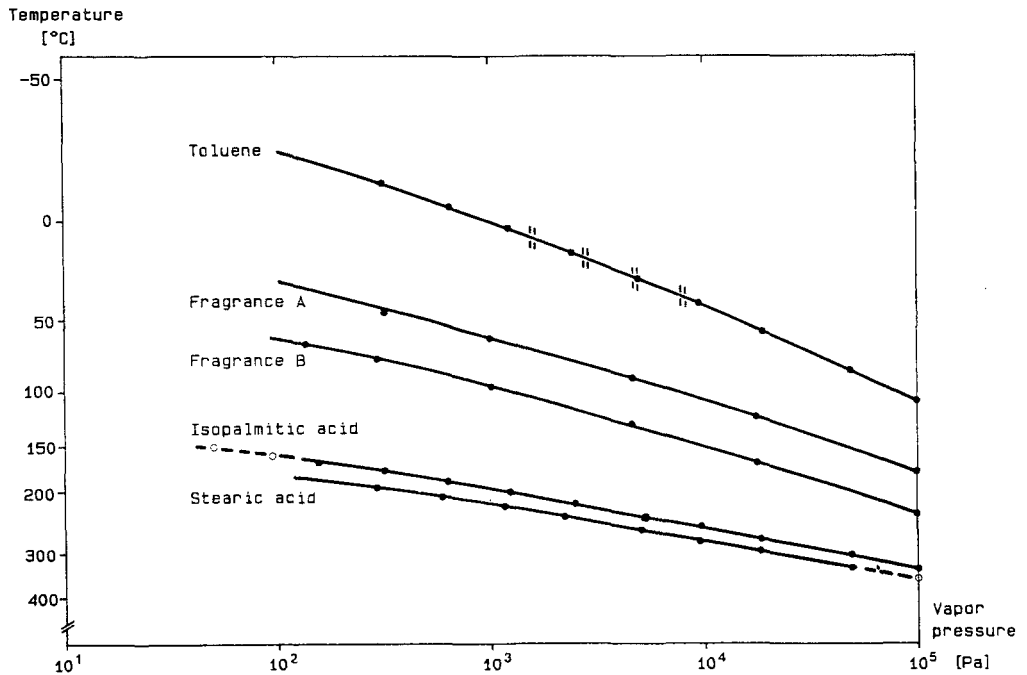


Fig. 4 DSC vapor pressure measurements; \circ DSC values, \parallel values measured according to the dynamic method [7]

In the interesting temperature range from 10 to 50°C, many substances have vapor pressures of 0.1 to 1000 mPa. For the determination of vapor pressure curves in these pressure

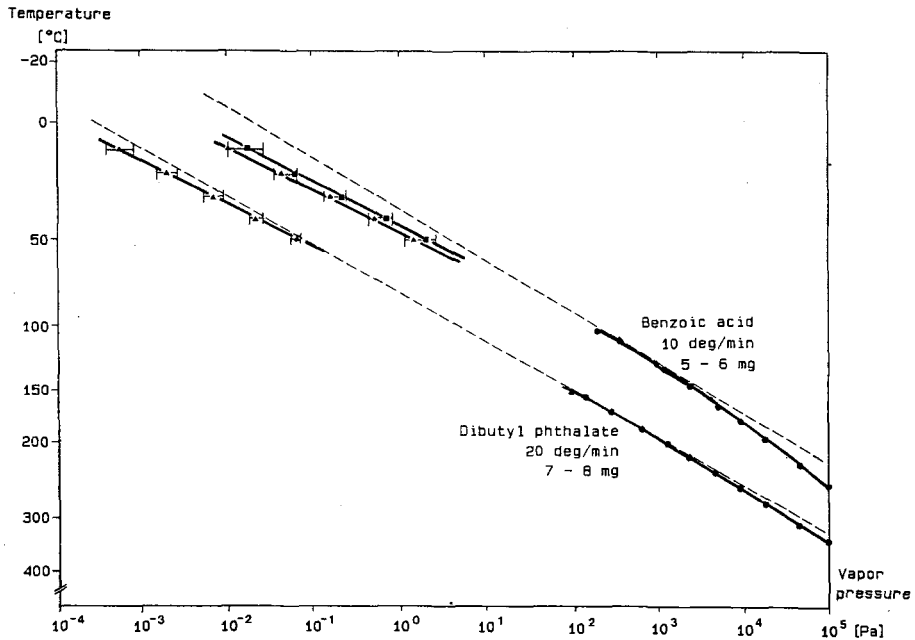


Fig. 5 DSC vapor pressure measurements versus methods with other measuring ranges

- Gas saturation method [7]
- △ Vapor pressure balance [7]
- DSC values

ranges, measurements according to the gas saturation method (0.1 to 1000 mPa) and the vapor pressure balance method (1 to 1000 mPa) are proposed in the EEC Guidelines [8]. For benzoic acid and dibutyl phthalate, the corresponding literature values [7] are shown in Fig. 5. In addition, the measurements obtained in the pressure range from 0.1 to 100 kPa by using the DSC method are given. When these curves are extrapolated linearly over a range of 5-6 powers of ten to the lower pressure range up to 0.1 mPa, there are differences between the measured values and the extrapolated ones, but the orders of magnitude are fairly well in agreement. Thus the DSC method can also be used as a technique for the approximate determination of vapor pressure curves at very low pressures.

References

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Nr. L 251 / 13 - 36 v. 19.9.84
Abschnitt A.2. Siedepunkt, Siedebereich
Abschnitt A.4. Dampfdruck.

Zusammenfassung

Der Aufbau eines Meßplatzes zur Dampfdruckbestimmung mit der DSC nach der dynamischen Methode (Messung der Siedetemperaturen bei verschiedenen Drücken) wird beschrieben. Meßbedingungen, wesentliche Versuchsparameter, typische Störungen und Meßfehler werden diskutiert. Im zugänglichen Meßbereich (0,1 bis 7000 kPa / -30 bis 600°C) bestimmte Siedepunkte und daraus ermittelte Dampfdruckkurven stimmen sehr gut mit Literaturangaben überein. Die Extrapolation der Dampfdruckkurven in den Druckbereich bis 0,1 mPa liefert näherungsweise Werte, die mit nach anderen Verfahren gemessenen Werten in der Größenordnung übereinstimmen. Dampfdruckkurven von fettchemischen Substanzen werden vorgestellt.

Резюме - Описана измерительная аппаратура для определения давления паров, используя динамический метод ДСК /измерения температур кипения при различных давлениях/. Обсуждены условия измерения, основные проверочные параметры, типичные неполадки и ошибки измерения. Точки кипения и кривые давления пара, измеренные в интервале давлений 0,1-7000 кПа и при температурах от -30° до 600° , хорошо согласуются с литературными данными. Экстраполяция кривых давления пара до давления 0,1 мПа дает приближенные значения, порядок которых согласуется с таковыми, измеренными другими методами. Приведены кривые давления пара для дымящих химических веществ.