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1.   Introduction

Paraffin waxes tend to display differing expansion behaviour according to their composition. It is known from the literature [1-3] that the volume of paraffin waxes increases by up to 10 % on heating up to the melting point. Depending on their composition, paraffins first form a hexagonal crystal structure, which rearranges into an orthorhombic lattice on cooling. In the higher molar mass paraffin waxes or those with a very broad molar mass distribution, the hexagonal phase may be absent. The solid phase transformation is linked with both the evolution of heat and an additional volume contraction of several percent. It is assumed that the solid phase transformation and the associated changes have significant effects on the properties of paraffin waxes relating to applications technology. The aim of these investigations is therefore to determine the volume change of paraffin waxes in the range of solid phase structural transformation.
In principle, a range of standard procedures is available for determining the heat expansion coefficients of materials. The main methods among them are dilatometric procedures [4]. Here the heat expansion or contraction in one dimension is measured with a distance sensor. The distance sensor presses on the sample in order to enable a firm contact with a force that cannot be arbitrarily reduced. A procedure such as this can only be used with major restrictions on strongly elastic samples and this is especially true for paste-like samples [5,6]. Another suitable method involves pycnometric measurements [7]. These have the advantage that the volume expansion is determined from the change in density and therefore does not depend on the shape (and dimensional stability) of the samples investigated. However, commercially available pycnometers are not designed for temperature conditioning operations, and quantitative determination of the thermal density changes proves to be extremely laborious [6]. All optical procedures, particularly the highly sensitive interferometric versions, fail due to the fact that temperature conditioning of the sample is not possible during the measurement [8]. It was possible to show that, with the aid of dip tube measurements, paste-like samples can be reproducibly characterized with respect to dilatory temperature behaviour [9].

2.   Measuring method

For this reason, the decision was taken in favour of a procedure in which the volume expansion of solid, partially dimensionally unstable samples takes place via a determination of the filling height. Water and the paraffin wax sample floating in it can be temperature-conditioned with a reaction vessel from Normschliff via a C6 CS LAUDA thermostat. In order to read out the volume, a pipette (disposable serological polystyrene pipette, sterile, 5 ml) was attached for each sample. An analogue thermometer was used to check the temperature in the vessel. During this process, randomly shaped paraffin test pieces with a weight of 10 g $\pm$ 9 mg were added to a large volume of liquid (430 ml) compared with that of the paraffin wax.

The filling height resulting from the expansion of the liquid and the expansion of the sample is measured as a function of temperature. The measuring scale of the filling tube was subdivided into 100-µl steps. Differences in the 10 µl range were detected without any difficulty.

The samples were each heated in 5-degree steps. The heating rate was 1.6 K/min (30 °C – 35 °C) and dropped with rising temperature to 1.05 K/min. From the time of the (manual) temperature setting on the thermostat, the samples were conditioned for approx. 20 minutes with stirring until the desired measuring temperature was attained in the water bath. After this period, it was also certain that the sample piece was evenly at the measuring temperature. An essential factor for the accuracy and reproducibility of the measurements was the absence of air bubbles on the sample surface. For this reason, it was necessary to use smooth samples. Attempts to measure paraffin wax chips failed due to the non-reproducible number of air bubbles adhering to the surface. In order to secure the absence of air bubbles, only water which had been standing for some time and which had been previously heated and cooled down was used for the investigations.

3. Characterization of the samples investigated

During the investigations, 9 paraffin wax samples were compared in terms of their expansion behaviour. These included fully refined macrocrystalline paraffin waxes, an intermediate paraffin wax and a plastic microcrystalline paraffin wax with the following parameters (Tab. 1):

Table 1: Compilation of the parameters for the paraffin wax samples investigated

	Type	CP* [°C]	Pen (25°C)[#] [1/10 mm]
Sample 1:	Spindle oil paraffin wax	50.5	19
Sample 2	Neutral oil-2-paraffin wax	56.5	19
Sample 3	Microwax	71.5	26
Sample 4	Neutral oil-1-paraffin wax A	55.5	18
Sample 5	Intermediate paraffin wax	65.5	18
Sample 6	Neutral oil-1-paraffin wax B	55.0	18
Sample 7	Neutral oil-1-paraffin wax C	55.0	18
Sample 8	Neutral oil paraffin wax A	57.5	18
Sample 9	Neutral oil paraffin wax B	56.0	19

*: Congealing point (DIN ISO 2207)
[#]: Needle penetration at 25°C (DIN 51579)

In addition to this, thermoanalytical investigations were conducted to further characterize the paraffin waxes. To this end, the melt curves of all samples were measured by means of differential scanning calorimetry (DSC). In the experiments, aluminium oxide was used as a reference, argon as the atmosphere and nitrogen as a coolant. The heating rate was 10 K/min and measurements were taken at a temperature of -10°C to 100°C. Identical initial weights were taken for all paraffin waxes (10 mg) in order to obtain comparable results (Figure 1).
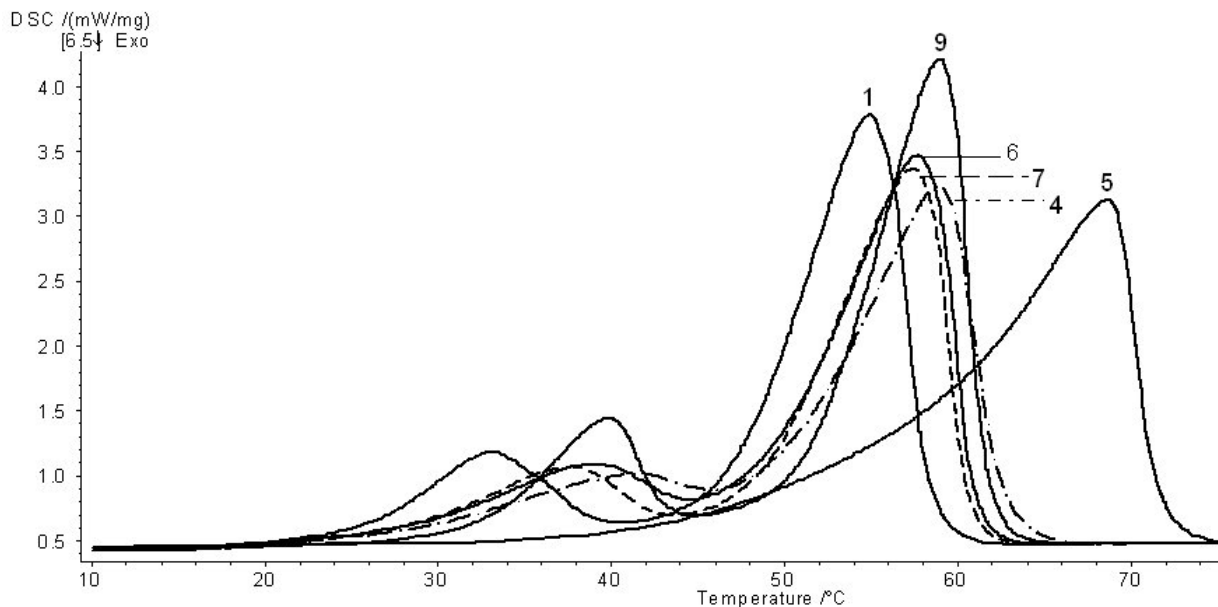
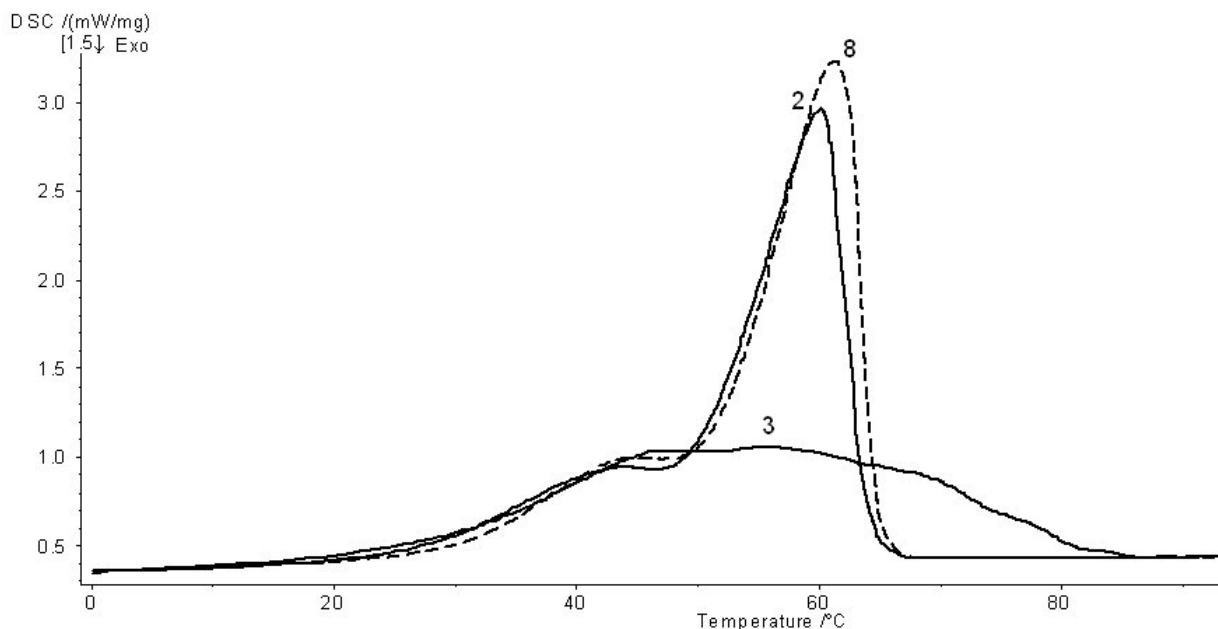**Figure 1a):**   DSC curves of paraffin waxes 1, 4, 5, 6, 7 and 9

Figure 1b):   DSC curves of paraffin waxes 2, 3 and 8

In addition to the large melt peak, paraffin waxes 1, 4, 6, 7 and 9 exhibit another peak at lower temperature. This smaller peak is caused by the transformation of the hexagonal crystal structure into the orthorhombic structure. In paraffin waxes 2 and 8 the crystal structure transition coincides with the melting and only exhibits a shoulder on the melt peak. The intermediate paraffin wax (No. 5) and the microwax (No. 3) show no crystal structure transformation peak.

4. Investigation of the temperature expansion behaviour of paraffin wax samples at phase transformation temperatures

First the expansion of 430 ml of water (full reaction vessel) was measured in ml within a temperature range from 30°C to 70°C. This provided a reference. It was now possible to measure the expansion of water with the paraffin wax samples in the reaction vessel. A 10 g piece of the appropriate sample was always used for this purpose. For further details of the evaluation and calibration procedure see [9]. The reaction vessel was heated in 5 K steps up to the individual final temperature, which lay just below the congealing point of the paraffin wax concerned. As sample 3 (microwax) was dimensionally unstable even at temperatures just above ambient, only the temperature range from 30 °C to 45 °C was investigated in this case.

The investigations of the paraffin waxes yielded two principally different patterns of expansion curve. Most samples exhibited a plateau response (Figure 2a), i.e. two regions with more pronounced volume expansion and an area between with a flat shape were identified. This is shown for samples 1, 4, 5, 6, 7 and 9 in Figure 2a. Samples 2, 3 and 8, on the other hand, exhibited a constant rise in the volume with temperature (Figure 2b).
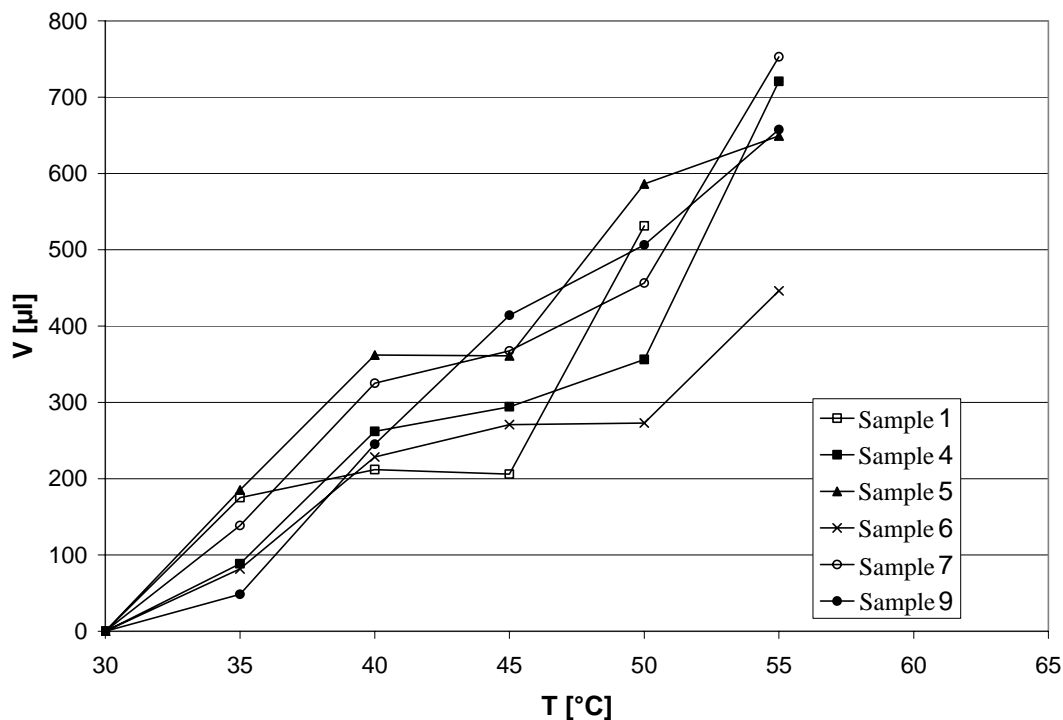

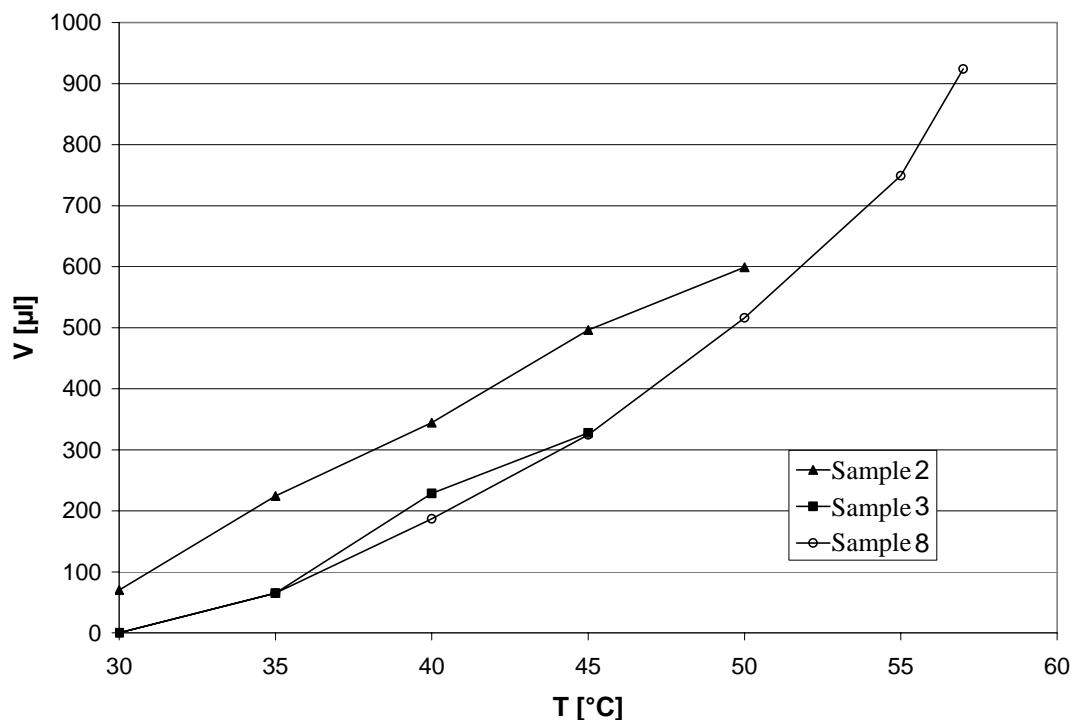**Figure 2a):** **Volume change in the samples with 2 phase transitions and plateau course**

Figure 2b): **Volume change in the samples with a constant rise in the temperature expansion behaviour**

The evaluation takes account of the previously determined volume of pure water in the measuring equipment as a function of the temperature as well as the volume of the paraffin wax specimen at the starting temperature. Under these constraints, the linear expansion coefficient of the paraffin is calculated with the aid of the equation [3]

$$\alpha_{Par}(T) = \frac{V_{Par}(T) - V_{Par}(T_o)}{3(T - T_o)V_{Par}(T_o)}$$

Here T_o is the starting temperature of 30 ^{o}C. The volume of the paraffin wax specimen at the starting temperature was determined separately and was approx. 10 cm^3. The calculated expansion coefficients of the paraffin waxes investigated are shown in Table 2. Expansions in the range of 1 to approx. 4 % were determined.

Table 2: **Expansion coefficients of the investigated samples in the temperature range from 30 °C up to the individual final temperature**

Sample name	α_{Par} [K^{-1}]	Max. expansion in the temperature interval [%]	Max. expansion in the phase transformation region [%]	Max. contraction in the phase transformation region [%]	Final temperature of the investigation [°C]
Sample 1	0.89×10^{-3}	2.67	0.62	- 5.9×10^{-2}	50
Sample 2	0.80×10^{-3}	2.80	not defined	none	55
Sample 3	0.73×10^{-3}	1.83	not defined	none	50
Sample 4	1.00×10^{-3}	3.40	1.00	none	54
Sample 5	0.75×10^{-3}	3.00	0.83	- 1.0×10^{-2}	60
Sample 6	0.65×10^{-3}	2.15	0.65	none	53
Sample 7	1.09 10^{-3}	3.60	1.09	none	53
Sample 8	1.14×10^{-3}	4.22	not defined	none	57
Sample 9	0.91×10^{-3}	3.09	0.82	none	54

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With the exception of sample 5, the measured expansion curves correlate in their trend with the results from the DSC measurements. This becomes apparent through a comparison of Figure 1a) with 2a) as well as 1b) with 2b). Samples that exhibit DSC curves with two peaks show two separate sharp increases in volume in the corresponding temperature ranges. The samples with only one DSC peak show a constant volume expansion. This observation gives rise to the conclusion that the first sharp increase in volume is caused by the change in crystal structure and the second sharp increase by the onset of melting in the paraffin wax. The intermediate paraffin wax (No. 5) represents a special case. The molecular composition and the material properties of such paraffin waxes are located in the transition area between microwaxes and macrocrystalline paraffin waxes. The volume expansion thus detects a further phase change that cannot be recorded with the DSC measurement.

In general the expansions obtained are relatively low in the phase transformation area, as can be seen from Table 2. Interestingly, some samples exhibit a minimal but clearly measurable contraction (Samples 1 and 5). One possibility of explaining this may be overlapping of the thermal expansion and the simultaneous volume reduction by a change in the crystal structure.

Within the limits of measuring accuracy, a hysteresis (see [9]) was detected in the thermal expansion. The path of the heating curve deviates from the path of the cooling curve. The heating or cooling rates here were not identical, with average values of 1.33 K/min and 0.18 K/min respectively. The results show that even with moderate heating and cooling rates at the respective temperatures, no identical crystal structures are attained that would thus result in different expansion curves. Within the investigations it was not possible to unambiguously clarify whether the hysteresis effects are due to non-identical temperatures in the sample pieces or to kinetic delay of the phase transformation. To this end, work has been started on developing an automated procedure for further investigations in which it will be possible to measure the temperatures on the inside of the specimen. This procedure is described below.

5. Automation of the measuring procedure

One disadvantage of the existing measuring setup proved to be the necessary time and personnel input that is required for a complete measuring cycle. The objective was to refine the measuring station so as to achieve a fast computer-controlled measuring setup that performs the measurements independently after the experimental preparations and presents the relevant results.
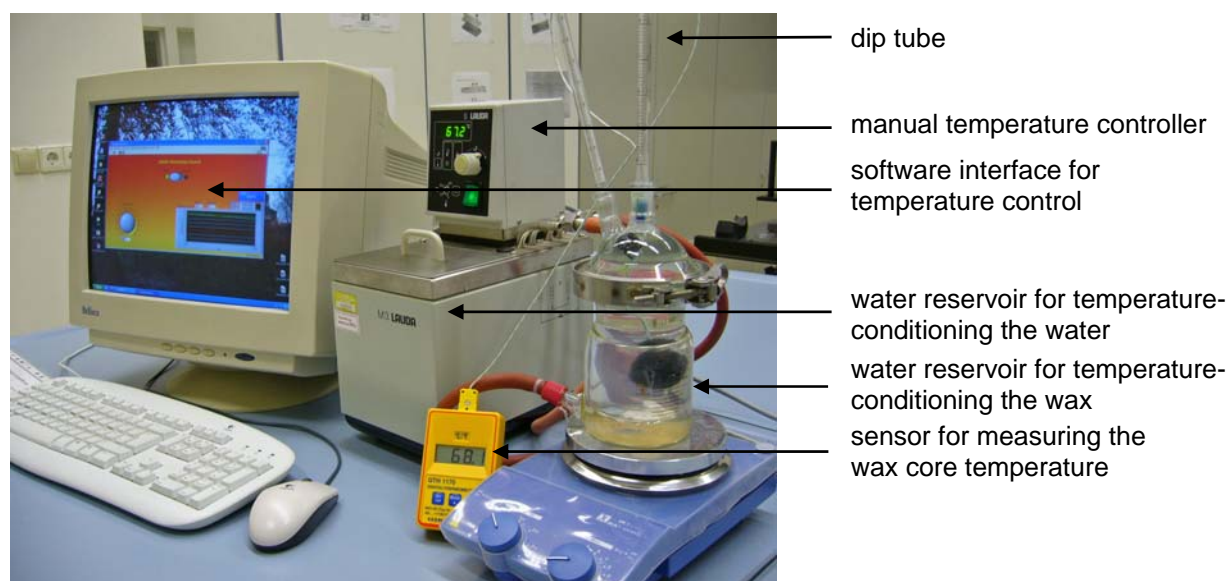

Figure 3: **Computer-controlled routine measuring station**

To achieve this, the existing thermostat was converted from manual operation to a computer-controlled system and a software module was programmed for temperature control of the surrounding water in LabVIEW 7. Consequently it is now possible to heat up the paraffin wax sample under investigation precisely, in accordance with a previously defined temperature-time profile. Heating rates are possible of up to 2.7 K/min here and cooling rates of up to 0.33 K/min.
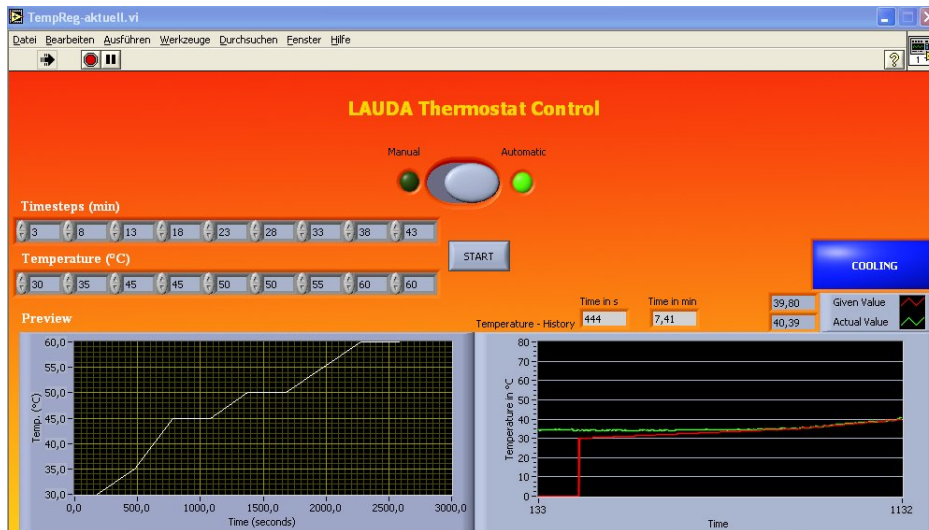

Figure 4: **Monitor display of the software for temperature control**

Five temperature sensors and one level sensor unit have been integrated into the measuring apparatus (Fig. 3). The temperature of the water is measured in the thermostat and in the water surrounding the sample. Furthermore, three sensors are located in the wax sphere and thus provide a precise image of the temperature distribution inside the sample.

The measuring station software (Fig. 4) records these sensor data via a USB measuring laboratory connected to the computer and controls the targeted heating of the sample. It calculates the average temperature on the inside of the sphere from the three temperature measurements and gives a warning if the standard deviation is too great.

These data together with the readings from the ultrasonic sensor, which is intended to record the volume expansion in future, are set off against the reference data and issued as the resulting temperature-volume chart. The data acquired are also stored as a file for later processing.

In order to shorten the duration of the experiment, it is necessary to run the experiment continuously and have a high heating rate. Here it is assumed that the paraffin sample is not heated completely throughout its volume and therefore does not have the same temperature everywhere. Consequently, an average wax temperature is used, with the temperature deviation inside the sample not being allowed to exceed 2 K otherwise an error larger than 5 % results.

In order to determine the mean temperature, a spherical sample holder (Fig. 5) was developed with integrated sensors.
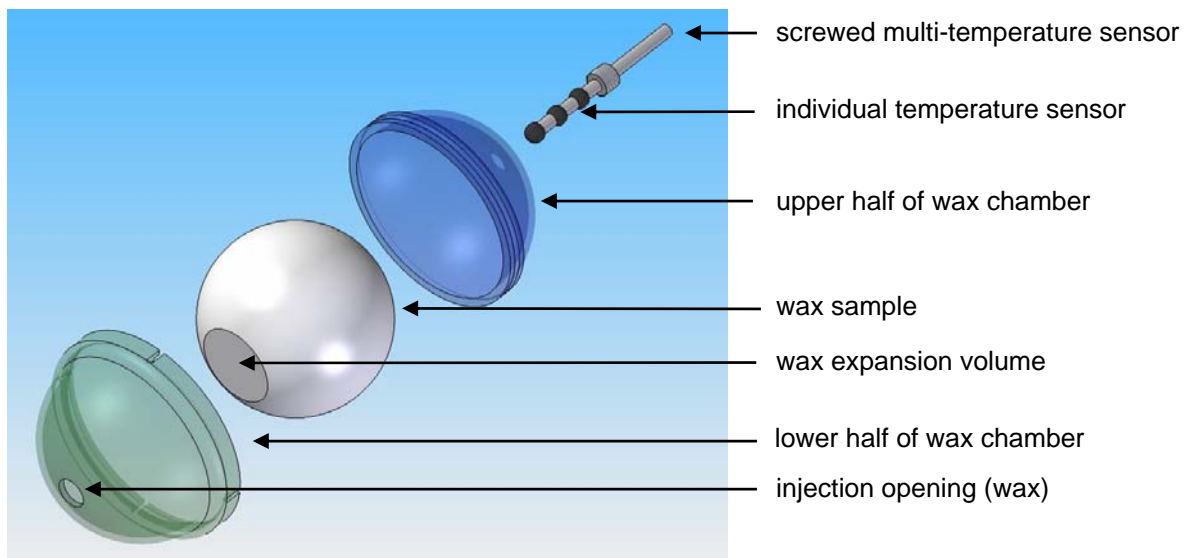
Figure 5: Exploded diagram of wax expansion chamber

The previously heated paraffin sample is injected into the hollow sphere at the start of the experiment in liquid form. After the sample has solidified, it is integrated into the measuring apparatus free of air bubbles. As was previously the case, work is carried out with degassed water and preceding reference measurement. The expansion is still currently measured manually via a graduated dip tube, which is replaced by an ultrasonic sensor with 0.2 mm measuring accuracy in further investigations.

The experimental procedure is divided into two parts: in the first part, the paraffin wax sample is heated rapidly and the volume expansion recorded. During this stage, the expansion behaviour of the sample is identified and particularly interesting temperature ranges are determined. In the second part, the temperature-time profile is adapted to the sample concerned and relevant areas are now examined more slowly. This yields a more accurate expansion graph with minimized errors.

In initial experiments it was shown (illustrated by Sample 5 in Fig. 6) that even with the heating cycle shortened from 4 hours to 1 hour, the passage of the curve is recorded correctly in qualitative terms.
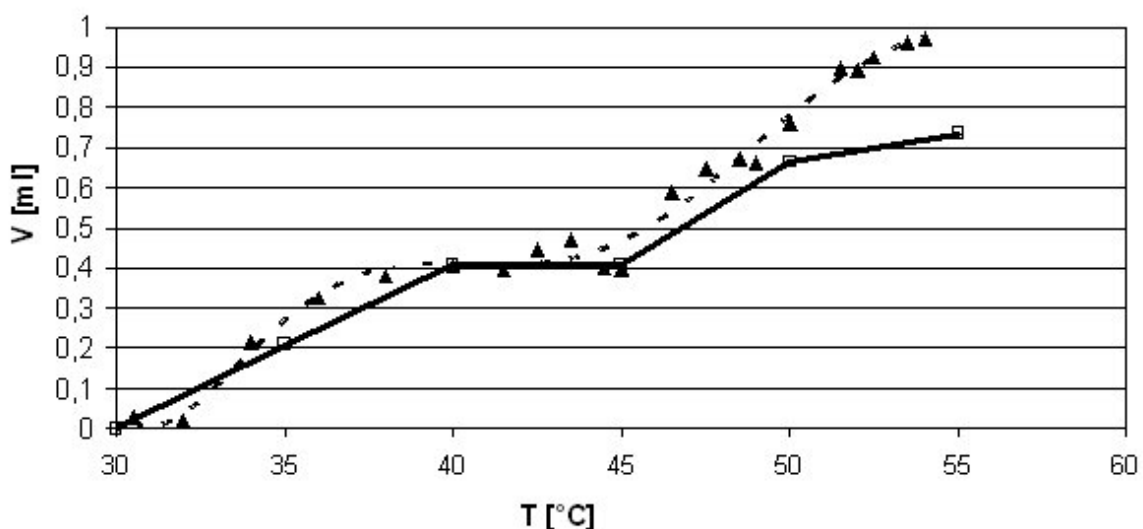

Figure 6: Standardized volume change of Sample 5 with standard procedure (hollow squares, continuous line) and in the automated measuring procedure (solid triangles, broken line)

We shall report on the results of the further measurements at a later point in time.

6. Summary

These investigations have shown that it is possible to determine volume changes in solid paraffin waxes at different temperature using the measuring method developed. The measuring method used has proven to be uncomplicated and representative for the measurement of mouldable substances. The method can be used to display patterns of expansion and contraction. It was shown that the phase changes of the paraffin waxes determined with DSC (crystal structure transformation, melting) are associated with significant volume changes. The essential steps to automate the measuring procedure were implemented and thus reduce the input of personnel and time into the investigation. As a result, a new measuring procedure is available that facilitates the targeted development and selection of paraffin waxes for applications in which volume changes dependent upon temperature represent a decisive criterion.

Acknowledgements

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