A10.1. Measurement of the thermal properties of a cosmetic product

An industrial enterprise wanted to know the thermal properties of a cosmetic product of pasty constitution. It was therefore necessary to choose methods of measurement adapted to the specificity of the material.

Using a differential calorimeter, we first performed a measurement of the specific heat, which is advisable for any study if we have this type of equipment.

Next, we must measure another quantity which is thermal conductivity, diffusivity or effusivity. Given the “sticky” nature of the material, we avoided the hot wire and hot strip methods, the flash method also seems difficult to implement practically with this type of material. We therefore opt a priori for an asymmetric centered hot plate method with realization of a thin-edged frame to contain the paste under a controlled thickness. We will perform a steady-state measurement to estimate thermal conductivity and then a confirmation measurement in transient regime to estimate thermal effusivity.

A10.1.1. Specific heat

The specific heat $c$ (J kg$^{-1}$ K$^{-1}$) of the samples was measured by a Setaram calorimeter μdSc3.

A preliminary verification of the calibration of the device was carried out with sapphire, the specific heat of which was measured between 20°C and 90°C and compared with the reference values (see Figure A10.1). The maximum deviation observed is 0.6%.
The results obtained for the cosmetic product sample are given in Table A10.1. The accuracy of the measurement is estimated at 3%.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>20°C</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
<th>80°C</th>
<th>90°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$ (J kg$^{-1}$ K$^{-1}$)</td>
<td>1808</td>
<td>1964</td>
<td>2068</td>
<td>2075</td>
<td>2038</td>
<td>2001</td>
<td>1931</td>
<td>1868</td>
</tr>
</tbody>
</table>

**Table A10.1. Values of the specific heat $c$ (J kg$^{-1}$ K$^{-1}$) measured by the Setaram calorimeter μdSc3**

The density was measured by weighing a container of known volume, empty and then filled with water, and finally with the pasty product. The value thus obtained is:

$$\rho = 1070 \text{ kg m}^{-3}$$

**A10.1.2. Thermal conductivity**

The thermal conductivity was measured in steady state by the asymmetric centered hot plate method [JAN 17, DAM 16, JAN 10]. The device used, which has been placed in a climatic chamber maintained at a temperature $T_a$, is shown schematically in Figures A10.2 and A10.3. The section of the samples and of the heating element is $0.102 \times 0.102$ m$^2$.

Thermal conductivity was calculated as:

$$\lambda = \frac{e}{T - T_1} \left[ \frac{R_{el}}{s} J^2 - \frac{\lambda_0}{e_0} (T - T_0) \right]$$
where:

- $e$ is the thickness of the PVC frame (and thus of the pasty product);
- $\frac{R_{el}}{S}$ is the ratio of the electrical resistance to the section, calibrated with a material of known properties (see [JAN 17]);
- $I$ is the intensity;
- $\lambda_0$ is the (known) thermal conductivity of extruded polystyrene;
- $e_0$ is the thickness of extruded polystyrene.

**Figure A10.2. Schematic diagram of the experimental device**

**Figure A10.3. View of the device used for holding the pasty product**
We first performed a 3D digital simulation under COMSOL of the device to check that the temperature at the center of the heating element was not affected by the edge effects due to the presence of the PVC frame and by convection and radiation heat transfer on the side walls.

According to the established results [JAN 17], in order to carry out a measurement at an average temperature $T_0$ we have imposed the following temperature values: $T = T_m + 5^\circ C$; $T_0 = T_1 = T_m - 5^\circ C$ and $T_a = T_m + 3^\circ C$.

The experimental results are reported in Table A10.2. The thermal conductivity is constant over the temperature range $[20^\circ C; 50^\circ C]$ and has the value:

$$
\lambda = 0.206 \text{ W m}^{-1} \text{ K}^{-1}.
$$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$T_0$</th>
<th>$T_1$</th>
<th>$e_0$</th>
<th>$e$</th>
<th>$\lambda_0$</th>
<th>$I$</th>
<th>$T_m$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\circ C$</td>
<td>m</td>
<td>m</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>A</td>
<td>$^\circ C$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.02</td>
<td>14.88</td>
<td>15.25</td>
<td>0.01875</td>
<td>0.0156</td>
<td>0.0278</td>
<td>0.19</td>
<td>20.0</td>
<td>0.206</td>
</tr>
<tr>
<td>40.3</td>
<td>29.6</td>
<td>29.91</td>
<td>0.01875</td>
<td>0.0156</td>
<td>0.0278</td>
<td>0.195</td>
<td>35.0</td>
<td>0.206</td>
</tr>
<tr>
<td>55.67</td>
<td>44.9</td>
<td>45.14</td>
<td>0.01875</td>
<td>0.0156</td>
<td>0.0278</td>
<td>0.195</td>
<td>50.3</td>
<td>0.205</td>
</tr>
</tbody>
</table>

**Table A10.2. Measured values of the thermal conductivity**

### A10.1.3. Thermal effusivity

To confirm the results of the first two devices, we used the device shown in Figure A10.2 for an evaluation of the results of the transient hot plate. For this purpose, we have fixed the intensity passing through the resistance to a value which allows a temperature rise of the order of $10^\circ C$ to be obtained in 180 s and we have recorded the change in temperature $T(t)$ from the start of heating with a time step of 0.1 s. It has been shown previously that, after a certain time (depending on the thermal capacity $C_h$ of the heating element) and during the time when the semi-infinite medium hypothesis is valid, the curve $T(t) = f(\sqrt{t})$ can be assimilated to a straight line with a slope $\alpha$. The thermal effusivity $E$ can then be estimated by equation (4.2.11):

$$
E = \frac{2\phi_0}{\alpha\sqrt{\pi}} - E_i
$$

where $E_i$ is the thermal effusivity of the extruded polystyrene in our case and $\phi_0$ the heat flux produced by the Joule effect in the heating element.
Preliminary measurements of specific heat by DSC, density and thermal conductivity by the centered hot plate method allowed us to calculate the effusivity value of extruded polystyrene at 20°C:

\[ E_i = \sqrt{0.0302 \times 39.3 \times 1212} = 37.9 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2} \]

The experimental curves \( T = f(t) \) and \( T = f(\sqrt{t}) \) obtained with the product to be characterized are given in Figure A10.4.

A first estimate was made by calculating the slope of the curve \( T = f(\sqrt{t}) \) over the entire recording interval, i.e. [0; 290 s]. We have thus obtained the value \( E = 624.3 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2} \), the estimation residues, i.e. the difference \( T_{exp}(t) - T_{mod}(t) \) are shown in Figure A10.5(a). It is found that they are neither flat nor centered on the zero value over the entire estimation interval, but a horizontal plateau is observed between 50 s and 150 s. The estimate is then resumed by reducing the interval to [50 s; 150 s] for calculating the slope of the curve \( T = f(\sqrt{t}) \). We then obtain \( E = 625.0 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2} \) and flat residues centered on zero over the chosen estimation interval, shown in Figure A10.5(b). It will be noted, however, that in this particular case the first value was very close to the final result, which is not always the case.

The knowledge of the effusivity, the density and the thermal conductivity makes it possible to estimate the specific heat by: \( c = \frac{E^2}{\rho \lambda} \) which allows us to obtain:

\[ c = \frac{625^2}{1070 \times 39.3} = 1772 \text{ J kg}^{-1} \text{ K}^{-1} \]

Figure A10.4. Examples of experimental curves \( T = f(t) \) and \( T = f(\sqrt{t}) \)
This value should be compared with that measured by DSC, namely: 
\[ c = 1808 \text{ J kg}^{-1} \text{ K}^{-1} \]. The difference is only 2%. The last two measurements carried out with a very simple device of the asymmetrical hot plate type could thus alone make it possible to measure the thermal properties of this product sufficiently accurately.

**Figure A10.5.** Estimation residues realized on a) [0; 290 s] and b) [50; 150 s]