# A METHOD FOR DETERMINING THE COEFFICIENT OF VOLUME THERMAL EXPANSION OF PETROLEUM PARAFFINS

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## Introduction

Volume changes in solid paraffins due to temperature changes notably affect their so-called functional properties that define the technology of their application. However, data in the literature on the coefficient of volume expansion $\beta$ for paraffins are scarce and partly contradictory. This is caused, on the one hand, by the fact that the reported data are averages for a given temperature range. For other substances, average values do not usually cause notable inaccuracies. In solid petroleum paraffins, however, a modification change takes place within the temperature range between the point of solidification and ambient temperature, this change being accompanied by an approximately 3% change in specific volume [1, 2]. The hexagonal modification is stable at higher temperatures, the rhombic modification at lower temperatures. Consequently, different values for the coefficient of volume expansion will be obtained when calculated from specific volumes (densities) measured within a wide temperature range including the change of modification, and from specific volumes measured within narrower temperature ranges. Hence, the average coefficient of volume expansion does not describe the expansion (contraction) course of solid paraffins with satisfactory accuracy, since during the change of modification the coefficient of volume change must necessarily increase, and the extent of this increase must be the greater, the narrower the temperature range in which the modification change takes place.

On the other hand, the discrepancies between the data reported by different authors are also due to the fact that these data refer to different paraffin samples. It is well known that petroleum paraffins are mixtures of different hydrocarbons, and their composition depends on the origin of the crude from which they are won and on processing technology. The composition of the paraffin sample, in turn, substantially affects the change of modification and can even lead to its total absence. Thus, composition may have a notable effect on volume expansion.

The absence of reliable data was the incentive for my attempt to develop a method for determining the coefficient of volume thermal expansion of petroleum paraffins that eliminates the inaccuracy caused in the case of solid paraffins by the use of average coefficients. On the other hand, the method was tested by determining the coefficient of thermal expansion of some petroleum paraffins manufactured in Hungary within the temperature range in which solid paraffins are usually being applied in practice, i.e. between the point of solidification and ambient temperature. It was attempted to base the method on a relationship of general validity, so that the method could be extended to the determination of the coefficient of thermal expansion of any liquid or translucent solid having a low melting point, for which the application of usual procedures involves difficulties owing to modification changes or other causes.

### Principle of the method

The coefficient of volume thermal expansion $\beta$ is defined by the differential equation [3]:

$$\beta = \frac{1}{V^\circ} \left( \frac{\partial V^\circ}{\partial T} \right)_p \tag{1}$$

where $V^0$ is the specific volume, T the temperature and $P$ the pressure.

The method is based on graphical differentiation of Eq. (1). For this purpose, the temperature *vs.* specific volume diagram of the paraffin sample must be plotted. The slope of the tangent at any point of this curve will then yield the value of $\left( \frac{\partial V^\circ}{\partial T} \right)_p$, and division by the specific volume will yield $\beta$.

Specific volume being the reciprocal of density, the next step is to calculate the density values for different temperatures. Making use of the Lorentz-Lorenz equation [4]:

$$r_L = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \tag{2}$$

where $r_L$ is the refractivity, $n$ the refractive index and $d$ the density, this can be done by measuring the refractive indices at different temperatures (for translucent substances, this is feasible in the solid state too) and substituting the measured values into:

$$d_2 = d_1 \left( \frac{n_1^2 + 2}{n_1^2 - 1} \right) \cdot \left( \frac{n_2^2 - 1}{n_2^2 + 2} \right) \tag{3}$$

where $d_1$ is the known density value of the sample for one given temperature $t_1$.

The relationship (3) between density and refractive index at the temperatures $t_1$ and $t_2$ is based on the fact that $r_L$ is practically independent of the temperature and of the aggregation state of the molecules.

Subscript 1 indicates a temperature where the paraffin sample is in the liquid state, so that both refractive index and density are readily measurable. Subscript 2 indicates lower temperatures where the paraffin sample is in the solid state. At these temperatures, only the refractive indices can be measured accurately, whereas the densities will be calculated by means of Eq. (3). In practice, refractivity indices in the solid state are best measured as follows: the thermostated prisms of the refractometer are first adjusted to a temperature higher than the solidification point of the paraffin sample and melted paraffin is introduced. Subsequently the temperature is gradually and slowly reduced and measurements of the refractive indices in the solid state are taken. These are less sharp than in the liquid state, but can readily be measured after some practice.

It should be noted that — due to birefringence — two refractive indices are measured at each temperature in the solid state. Their mean value according to POPE [5] will be substituted into Eq. (3):

$$\bar{n} = \frac{2n_o + n_e}{3}$$

where $\bar{n}$ is the mean refractive index, $n_o$ the refractive index of the ordinary ray and $n_e$ the refractive index of the extraordinary ray. It should be noted that the refractive index of the extraordinary ray has the higher value.

## Experimental results

The method was tested with macrocrystalline paraffins and their mixtures. The paraffins were products of the solvent extraction paraffin plant at the Dunai Kőolajipari Vállalat (Duna Petroleum Co.) in Százhalombatta, Hungary. Sample No. 1 was obtained from the deparaffination product of the light fraction of Romashkino crude, sample No. 2 from the middle fraction of the same crude. Sample No. 3 is a 1 : 1 mixture of samples No. 1 and 2. The characteristics of the samples are listed in Table 1.

## Practical application of the method

The practical application of the method is illustrated on the example of sample No. 1.

The first step is the measurement of the density and refractive index of the melted paraffin. The values measured at 80 °C were $d_{80} = 0.7630$ and $n_{80} = 1.4280$ (Table 1).

### Table 1

Characteristics of the samples used in experiments

|                                              | Sample 1 | Sample 2 | Sample 3 |
|----------------------------------------------|----------|----------|----------|
| Point of solidification, °C                  | 52       | 58       | 54       |
| Refractive index at 80 °C ($n_{80}$)         | 1.4280   | 1.4293   | 1.4285   |
| Density at 80 °C ($d_{80}$)                   | 0.7630   | 0.7760   | 0.7645   |
| Molecular weight                             | 365      | 385      | 375      |

Refractive indices at lower temperatures (Table 2) were measured by gradual cooling of the refractometer. At the point of solidification (52 °C) the refractive index of the liquid phase (1.4385) is still observable, but the two refractive indices of the solid phase ($n_0 = 1.4730$ and $n_e = 1.5215$) also appear.

The refractometer is then further cooled and both refractive indices are read within narrow temperature intervals. The changes in the refractive
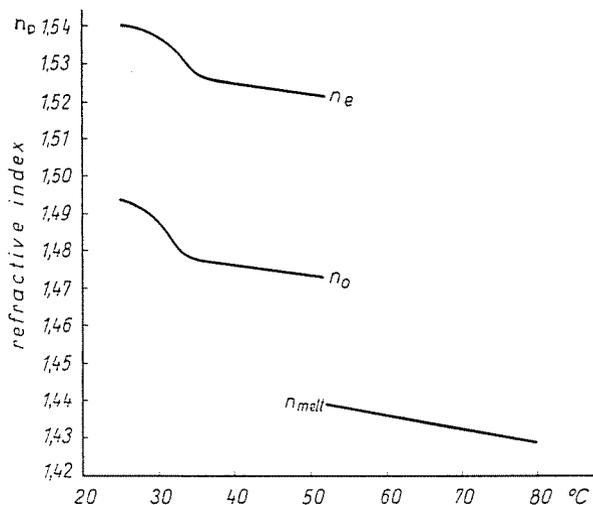


Fig. 1. Temperature dependence of the refractive index of petroleum paraffin sample No. 1

indices as a function of temperature are shown in Fig. 1. The means of the refractive indices for each temperature are then calculated using Eq. (4). By substituting these values into Eq. (3), the density of the paraffin sample for the given temperature is obtained. Its reciprocal value yields the specific volume.

**Table 2**

Refractive indexes, densities and specific volumes
of sample No. 1 at different temperatures

| t, °C | $n_{melt}$* | $n_o$* | $n_e$* | $\bar{n}$** | $d$** | $V^o$** |
|---|---|---|---|---|---|---|
| 20 | | 1.4945 | 1.5410 | 1.5100 | 0.8871 | 1.1273 |
| 25 | | 1.4930 | 1.5400 | 1.5086 | 0.8850 | 1.1299 |
| 27 | | 1.4925 | 1.5395 | 1.5081 | 0.8843 | 1.1308 |
| 28 | | 1.4920 | 1.5390 | 1.5076 | 0.8835 | 1.1319 |
| 29 | | 1.4900 | 1.5385 | 1.5061 | 0.8813 | 1.1347 |
| 30 | | 1.4880 | 1.5380 | 1.5046 | 0.8791 | 1.1375 |
| 31 | | 1.4850 | 1.5370 | 1.5023 | 0.8758 | 1.1418 |
| 32 | | 1.4815 | 1.5350 | 1.4993 | 0.8713 | 1.1477 |
| 33 | | 1.4795 | 1.5320 | 1.4970 | 0.8679 | 1.1520 |
| 34 | | 1.4780 | 1.5285 | 1.4948 | 0.8646 | 1.1566 |
| 35 | | 1.4775 | 1.5270 | 1.4940 | 0.8635 | 1.1581 |
| 37 | | 1.4765 | 1.5255 | 1.4928 | 0.8617 | 1.1605 |
| 40 | | 1.4760 | 1.5240 | 1.4920 | 0.8605 | 1.1621 |
| 45 | | 1.4745 | 1.5230 | 1.4906 | 0.8584 | 1.1649 |
| 50 | | 1.4735 | 1.5220 | 1.4896 | 0.8569 | 1.1670 |
| 52 | 1.4385 | 1.4730 | 1.5215 | 1.4892 | 0.8563 | 1.1678 |
| | | | | | (0.7800) | (1.2820) |
| 55 | 1.4375 | | | | 0.7778 | 1.2856 |
| 60 | 1.4350 | | | | 0.7739 | 1.2921 |
| 65 | 1.4340 | | | | 0.7722 | 1.2950 |
| 70 | 1.4320 | | | | 0.7692 | 1.3000 |
| 75 | 1.4300 | | | | 0.7662 | 1.3051 |
| 80 | 1.4280 | | | | 0.7630 (exp.) | 1.3106 |

\* Experimental values          \*\* Calculated values

From the data in Table 2 for $d$ and $V^0$, the diagrams $t$ *vs.* $d$ (Fig. 2) and $t$ *vs.* $V^0$ (Fig. 3) are plotted, the slopes of the tangents drawn to the curve in the latter figure are measured and substituted into Eq. (1) yielding the

coefficients of thermal expansion. The results are presented in Table 3 and in Fig. 4. The maximum in Fig. 4 and the inflexion point in Fig. 3 are seen to be at 31.5 °C.
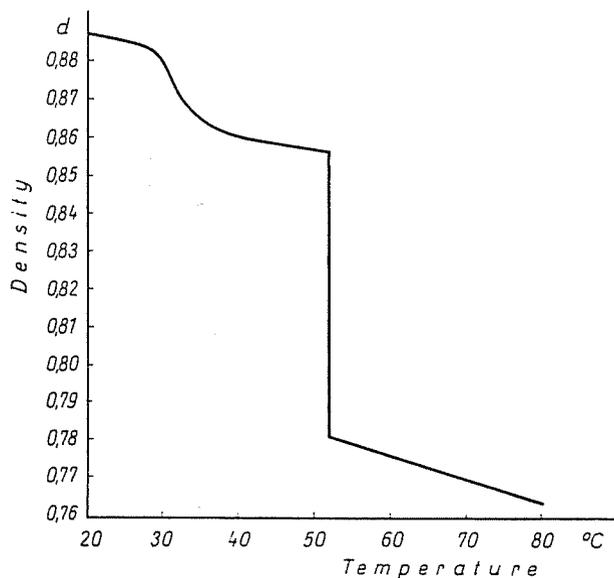


*Fig.* 2. Temperature dependence of the calculated density of petroleum paraffin sample No. 1
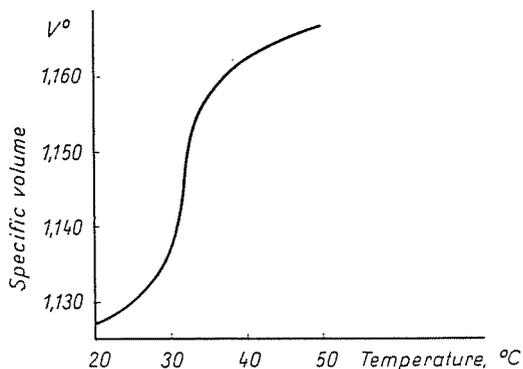


*Fig.* 3. Temperature dependence of the calculated specific volume of petroleum paraffin sample No. 1

Both Figs 2 and 3 clearly indicate the modification change of paraffin. However, the course of this transformation can best be followed on the curve representing the temperature dependence of the coefficient of volume expansion $\beta$ (Fig. 4).

**Table 3**

Coefficient of volume thermal expansion for
petroleum paraffin sample No. 1

| t, °C | Modification | $\beta \cdot 10^4$ |
|---|---|---|
| 20 | | 2.7 |
| 21 | | 3.1 |
| 22 | | 3.6 |
| 23 | rhombic | 4.4 |
| 24 | | 5.3 |
| 25 | | 6.2 |
| 26 | | 7.5 |
| 27 | | 9.5 |
| 28 | | 13.1 |
| 29 | | 22.8 |
| 30 | | 35.0 |
| 30.5 | | 44.0 |
| 31 | modification change | 51.0 |
| 31.5 | | 53.0 |
| 32 | | 48.0 |
| 33 | | 21.5 |
| 34 | | 13.7 |
| 35 | | 8.6 |
| 36 | | 7.7 |
| 37 | | 5.9 |
| 38 | | 5.1 |
| 39 | | 5.0 |
| 40 | | 4.4 |
| 41 | hexagonal | 4.2 |
| 42 | | 3.6 |
| 45 | | 3.6 |
| 52 | | 3.6 |
| 52—80 | melt | 7.8 |

Both Fig. 4 and Table 3 demonstrate that the value of $\beta$ for the hexagonal modification that is formed at the solidification point changes in a relatively small degree ($3.6 \cdot 10^{-4}$ and $5.1 \cdot 10^{-4}$ for 52 °C and 38 °C, resp.).In the temperature range where the hexagonal $\rightarrow$ orthorhombic transformation takes place (37 to 27 °C), the value of $\beta$ sharply rises, reaches a maximum value of $53 \cdot 10^{-4}$ at 31.5 °C where the rate of volume change caused by the
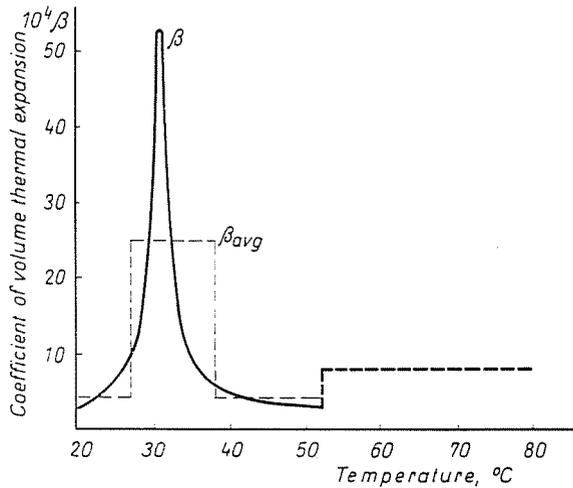
*Fig. 4.* Temperature dependence of the calculated coefficient of volume thermal expansion, petroleum paraffin sample No. 1

modification change is highest, and then sharply decreases. As soon as the transformation has become complete at 26 °C, the value of $\beta$ decreases in a smaller degree with temperature. Its value for the rhombic modification changes from $7.5 \cdot 10^{-4}$ to $2.7 \cdot 10^{-4}$ between 26 °C and 20 °C. In Table 4 the average values* of $\beta$ for the above-discussed three temperature ranges and for the liquid state are compared with the extreme values of the true coefficient of volume change.

### Table 4

Comparison of average and true coefficients of volume change

|  | $\beta$ average $\cdot$ $\cdot 10^4$ | $\beta$ true $\cdot 10^4$ |
|---|---|---|
|  | 7.8 | 7.8 |
| Hexagonal modification | 4.0 | 3.6—5.1 |
| Modification change | 25.0 | 5.1—53.0 |
| Rhombic modification | 4.2 | 2.7—7.5 |

&ast; If density values are known, a close approach for $\beta$ is obtained by using the following formula [6]:

$$\beta = \frac{d_1^2 - d_2}{2(t_2 - t_1)d_1 d_2} \cdot$$

This is the differentiated form of Eq. (1) and yields the average coefficient for the temperature range ($t_2$ to $t_1$). In practice, however, it is difficult to determine the density and specific volume of solid paraffin.

The average coefficient for the temperature range in which the modification change proceeds differs by more than 200% from the maximum value of the true coefficient. This same average coefficient is about six times the average coefficients for the hexagonal and rhombic modifications, resp., whereas the maximum value of the true coefficient in the range including the modification change is almost twentyfold of the coefficient for the rhombic modification at 20 °C.

### *Effect of mixing macrocrystalline paraffins on the coefficient of volume change*

When two petroleum paraffins having different points of solidification are mixed, the range covering the number of carbon atoms contained in the individual n-hydrocarbons that constitute the mixture will widen as compared to those of the initial paraffins. Consequently, since the temperature where the modification change proceeds differs for each individual n-hydrocarbon [7], the temperature range in which the modification of the mixture changes will also become wider as compared to the initial paraffins. Hence, the sharp increase of the coefficient of thermal expansion within the range where modification changes occur will be moderated, this having a favourable effect on the functional properties of paraffins.

In Fig. 5, the temperature dependence of the $\beta$ values for samples No. 1 and 2 and for their 1 : 1 mixture (sample No. 3) is plotted ($\beta$ values fo samples No. 2 and 3 were determined similarly to those of sample No. 1). The figure indicates that the coefficient of thermal expansion for sample No. 2 changes to an even greater extent than that of sample 1. The $\beta$ value at 41 °C ($120 \cdot 10^{-4}$) is the fortyfold of the value at 58 °C. In contrast, the dependence of the $\beta$ value on temperature is notably slighter for the mixture (Sample 3) than for either of the two starting materials. Its maximum is at 35 °C ($30.5 \cdot 10^{-4}$), this being only the tenfold of the minimum value in the studied temperature range.

It may thus be concluded that by mixing two paraffins having different points of solidification, a petroleum paraffin having the desired point of solidification and at the same time, a relatively more uniform coefficient of thermal expansion can be obtained.

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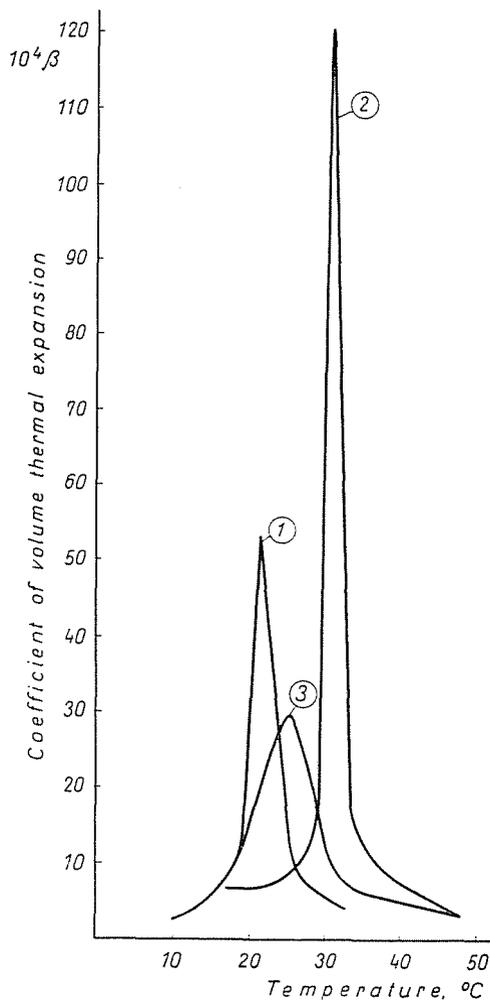
*Fig. 5.* Temperature dependence of the calculated coefficients of volume thermal expansion
for samples No. 1 and No. 2 and their 1 : 1 mixture (sample No. 3)

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## Summary

A method was developed for determining the temperature dependence of the coefficient of volume thermal expansion $\beta$ for solid petroleum paraffins. Based on the constancy of refractivity, the method consists in measuring refractive indices at different temperatures. The method allows to eliminate inaccuracies arising when usual methods are applied to petroleum paraffins.

Experimental data indicate that $\beta$ values for the hexagonal and rhombic modifications change from $3 \cdot 10^{-4}$ to $7 \cdot 10^{-4}$. However, in the temperature range where transformation of the modification takes place, $\beta$ values can increase by a factor of 20 to 40. This temperature dependence can substantially be reduced by mixing paraffins having different points of solidification.

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