



## **A NEW METHOD FOR THE MICRODISTILLATION OF LIQUIDS USING QUASI-ISOTHERMAL QUASI-ISOBARIC THERMOGRAVIMETRY**

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### **Abstract**

A method is described for the microdistillation of liquids using quasi-isothermal quasi-isobaric thermogravimetry. The liquidus curve determined under quasi-equilibrium conditions gives useful information about the composition and some thermal properties of the sample. The method could be attractive for the mineral oil, lacquer, biological and organochemical industry.

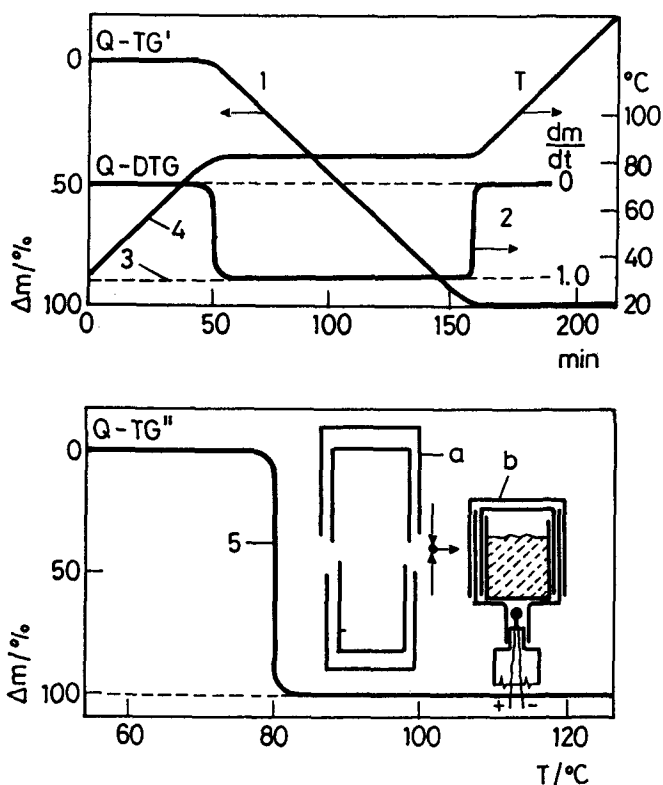
**Keywords:** microdistillation of liquids, quasi-isothermal quasi-isobaric thermogravimetry

### **Introduction**

About forty years ago, while developing the derivatograph [1] Paulik, Paulik and Erdey constructed a new instrument [2] and proposed a new technique by which the distillation curve of a liquid system can be determined by thermogravimetry. Even though the preliminary experiments of Paulik, Erdey and Gál [3] seemed promising, because of some experimental difficulties the method was not spread widely. Recently, the quasi-isothermal quasi-isobaric technique [4-6] offered a new opportunity to overcome these difficulties. Starting from the principle of this technique the intention of the authors of the present paper was to develop a new experimental method for the determination of the distillation curve of liquid systems. The reliability of the method was checked by comparing the experimental data of pure liquids as well as those of some binary mixtures with the corresponding literature data. The practical applicability of the method, developed for model systems, is under further consideration.

## The principle of the method

The liquid sample (100–1000 mg) was weighed in the inner part of so-called labyrinth sample holder [4–6] that consisted of 2–3 tightly fitting upper and lower crucibles. The sketch of the labyrinth sample holder ( $a$  = open and  $b$  = closed) and the distillation curves of benzene are presented on Fig. 1. The weight change of the heated liquid was measured on the balance of a Derivatograph C [5] as a function of time (curve 1) or temperature (curve 5). For this purpose the thermobalance Derivatograph Q [6, 7] is suitable as well. The heating regulator of the derivatograph increases the temperature of the furnace (curve 4) linearly, as it is usual in thermogravimetry up to the point where the weight change (curve 1 or 5) of the sample begins and the weight change rate (curve 2) does not reach the preslected level (line 3). Thereafter, until the end of the process the heating is regulated by the weight change rate (by the DTG



**Fig. 1** Distillation curves for benzene and the sketch of the labyrinth sample holder: 1 - weight change, 2 - weight change rate, 3 - the upper level of the weight change rate, 4 - temperature change as a function of time, 5 - weight change as a function of the liquid temperature. The labyrinth sample holder in the open ( $a$ ) and in closed state

signal) which establishes automatically a temperature difference between the sample and the furnace on a level that ensures the process to take place at a very low and constant rate. The accuracy of the method depends on the choice of an adequate level, which corresponds, among others, to the given sample mass ( $dm \cdot dt^{-1} = 0.2\text{--}2 \text{ mg} \cdot \text{min}^{-1}$ ;  $\Sigma \Delta m = 50\text{--}1000 \text{ mg}$ ). The special construction of the labyrinth sample holder [4–6] makes it possible that in the very beginning of the experiment the vapor of the sample expels the air present within the sample holder. The vapor streaming out through the narrow channel system prevents the air moving to the inner space, and, in this way a so-called 'self-generated' atmosphere is formed. So, the distillation process, except in the very beginning and the end of the measurement, proceeds under the conditions of a physicochemical quasi-equilibrium (isothermic, isobaric, equilibrium vapor-composition, atmospheric (cca 100 kPa) pressure) and the temperature of the liquid corresponds to the equilibrium temperature (curve 4). In this technique, the temperature of the system is regulated on the basis of the feedback principle, by the distillation process itself. Hence, the measured temperature changes in accordance with the equilibrium composition of the system, i.e., the weight change of the sample as a function of the temperature (curve 5) represents the progress of a quasi-equilibrium distillation process.

## Experimental

The measurements were carried out on a computerized Derivatograph C (Hungarian Optical Work, Budapest) [5]. The computer linearizes the non-linear signal of the thermocouple and makes its cold junction independent on room temperature as well. However, for a precise temperature determination, the temperature measurement system of the instrument has to be calibrated. The calibration procedure was carried out by measuring the boiling point of distilled water and the melting point of a reagent grade of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Besides, the boiling temperatures of some reagent grade liquids were determined too. The mean values of the parallel measurements showed a linear dependence on the theoretical temperatures (Fig. 2). By a least-square data-fitting method, the coefficients of the linear relation have been determined and they served as the factors for automatic temperature correction.

The sample masses were 70–80 mg. The heating rate in the non-isothermic period was  $10 \text{ deg} \cdot \text{min}^{-1}$ , while the weight change rate in the quasi-isothermic period was set to  $dm \cdot dt^{-1} = 1.0 \text{ mg} \cdot \text{min}^{-1}$ ,  $\Sigma \Delta m = 100 \text{ mg}$ .

The experiments were performed using reagent grade chemicals purified by distillation. The purity only in the case of *n*-propanol was questionable and was controlled by gas chromatography. It was found that the sample contained traces of isopropanol.

Figure 1 shows the distillation process of benzene as a function of time (curve 1, 2 and 3) or temperature (curve 5). The distillation curves of acetone (curve 1), methanol (curve 2), ethanol (curve 3), benzene (curve 4), *n*-propanol (curve 5), distilled water (curve 6) and formic acid (curve 7) are shown in Fig. 3. The binary systems of methanol-*n*-propanol (Figs 4 and 5), water-*n*-propanol (Figs 6 and 7) and water-formic acid (Figs 8 and 9) of differ-

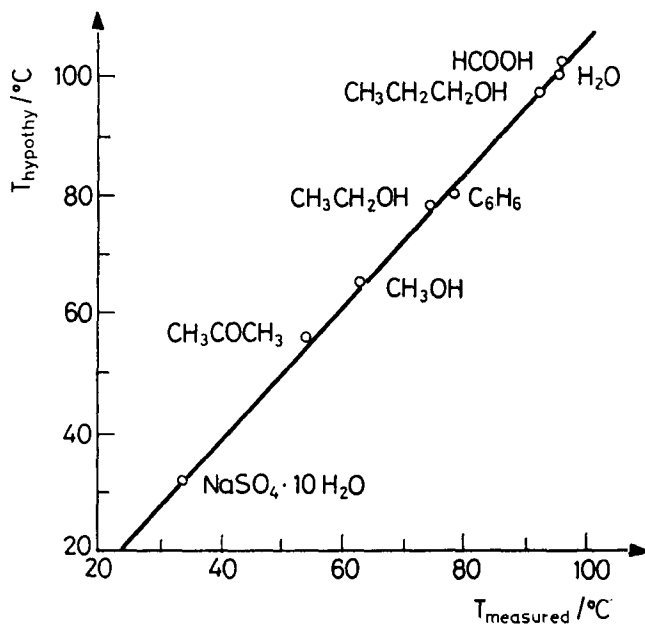


Fig. 2 The temperature calibration line with the experimental boiling temperatures and melting points of some reagent grade chemicals

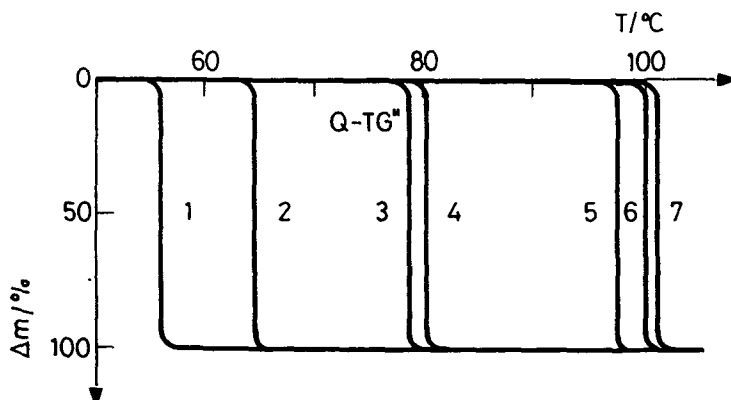
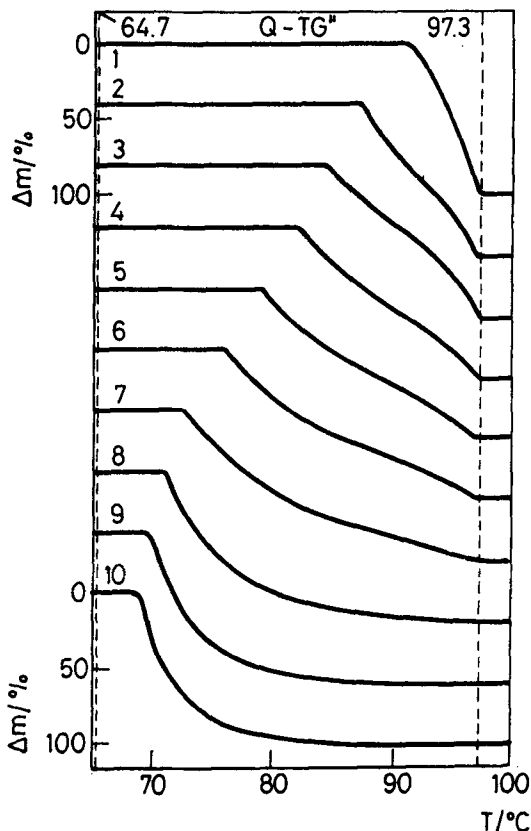


Fig. 3 Q-TG'' curves of some liquids: 1 - acetone, 2 - methanol, 3 - ethanol, 4 - benzene, 5 - *n*-propanol, 6 - distilled water, 7 - formic acid

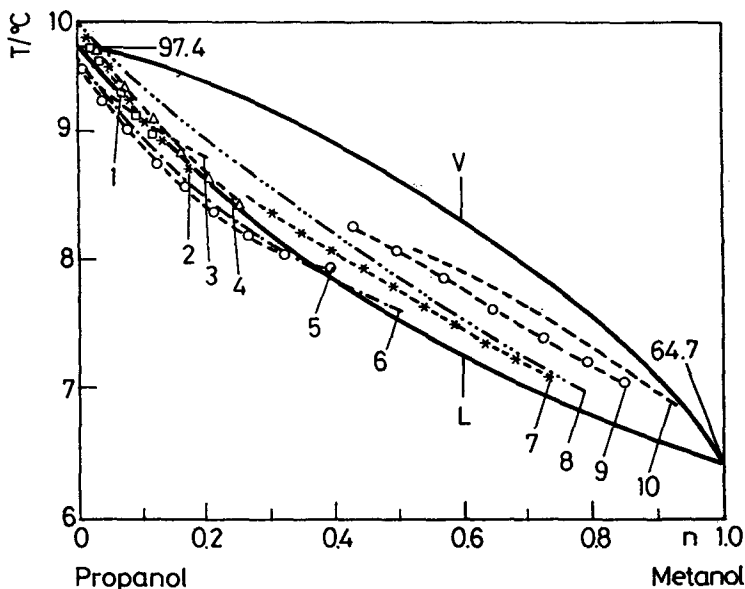
ent compositions were investigated, too. These systems were chosen because they represent the distillation process of the three basic types of binary liquid systems.



**Fig. 4** Q-TG<sup>n</sup> curves for the methanol-*n*-propanol systems of different starting compositions. The mole fraction of propanol (*n*) for curves: 1 - 0.93; 2 - 0.83; 3 - 0.80; 4 - 0.75; 5 - 0.50; 6 - 0.41; 7 - 0.27; 8 - 0.22; 9 - 0.15; 10 - 0.08

In the case of pure liquids the accuracy of the method can be checked by comparing the experimental isothermic boiling points with the data given in the literature, while for the binary systems it can be done only by calculation of the liquidus curve from the measured data. This calculation was needed, because in the multicomponent systems with changing temperature the composition of the liquid (curve *L*) and the vapor (curve *V*) phase changes continually but in a different way (Figs 5, 7 and 9). As a consequence, the progress of the distillation process changes with the changing composition of the sample (curves 1–10 in Figs 4–9). The *L* and *V* curves in Figs 5, 7 and 9 were constructed on the basis

of the literature data for the methanol-*n*-propanol [8], *n*-propanol-water [9] and water-formic acid [10] systems.



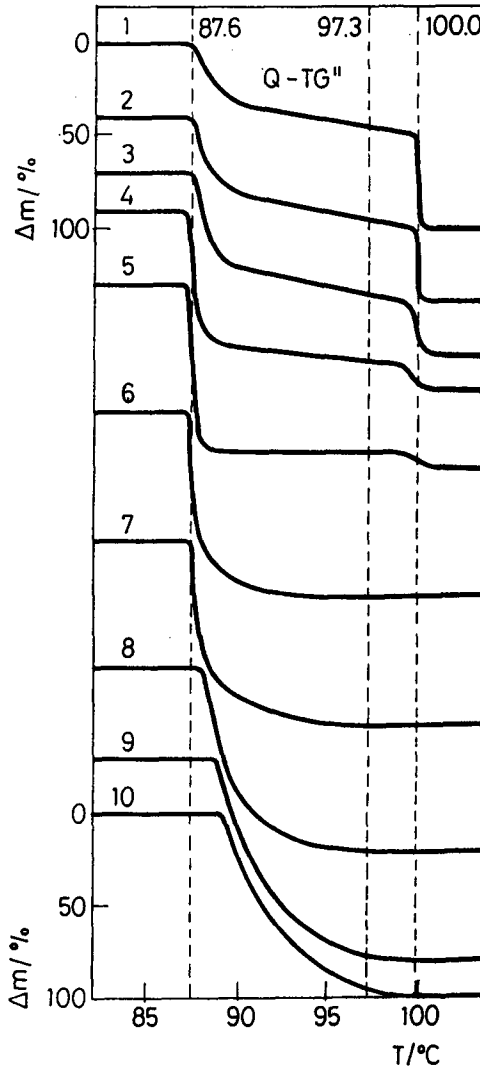
**Fig. 5** The temperature change as a function of the liquid (L) and vapor (V) phase composition for the system methanol-*n*-propanol. Curves 1–10 were obtained on the basis of data presented in Fig. 4

The experimental liquidus curves were calculated as follows. All the Q-TG curves as a function of temperature were divided into 10–15 intervals. In these intervals the mean value of the temperature and the corresponding weight change were determined. On the basis of these values and from the data of the L and V curves in Figs 5, 7 and 9 the composition of the corresponding liquid phase was calculated for each respective interval taking the preceding composition as a starting value for the calculation of the next one. This set of data represents the composition change of the liquid phase as a function of temperature (curves 1–10 in Figs 4, 6 and 8), i.e., the liquidus curve of the given system. The courses of liquidus curves for each starting composition (1–10), together with the experimental data determined by classical physical methods are presented in Figs 5, 7 and 9. These figures show to what an extent the distillation process can be monitored by quasi-isothermic quasi-isobaric thermogravimetry.

## Discussion

As can be seen from Figs 2 and 3, in the case of pure liquids the evaporation of the sample takes place under quasi-isothermic conditions practically at the

boiling temperatures given in the literature, except the very beginning and end of the process. This observation is supported by the fact that the mean value of the boiling points of 3–5 parallel measurements of different liquids falls in the interval of  $\pm 0.2^\circ\text{C}$  around the line presented in Fig. 2. The deviation of the individual values of the parallel measurements from the mean value is also about  $\pm 0.2^\circ\text{C}$ . The equilibrium temperature variation (the isothermic part, Fig. 1, curve 4) was within  $\pm 0.2^\circ\text{C}$ , while the variation of the weight change rate



**Fig. 6** Q-TG'' curves for the water-*n*-propanol binary system of different starting compositions. The mole fraction of water (*n*) for curves: 1 - 0.91; 2 - 0.88; 3 - 0.83; 4 - 0.72; 5 - 0.64; 6 - 0.46; 7 - 0.43; 8 - 0.39; 9 - 0.29; 10 - 0.22

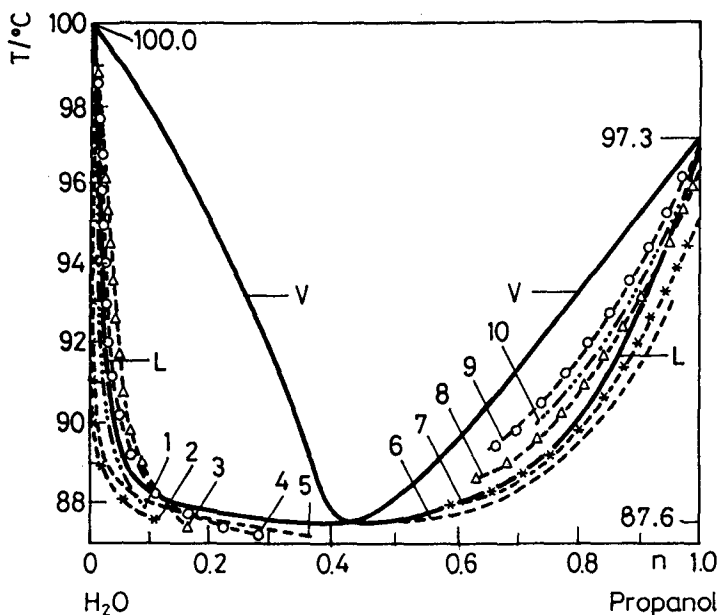


Fig. 7 The temperature change as a function of the liquid (L) and vapor (V) phase composition for the system water-*n*-propanol. Curves 1–10 were obtained on the basis of data presented in Fig. 6

( $dm \cdot dt^{-1} = 1.0 \text{ mg} \cdot \text{min}^{-1}$ ) amounted to  $\pm 0.1 \text{ mg} \cdot \text{min}^{-1}$ . As for the weight change, only 5% of the total weight change falls to lower temperatures at the beginning and 5% to higher temperatures at the end of the process.

The accuracy and the precision of the method seem satisfactory, especially when taking into account that the boiling point of a liquid determined by various precise methods [11] differs more significantly. For example, in the case of *n*-propanol, the literature [9, 12–14] gives 97.0, 97.1, 97.2, 97.4 or 97.8 °C as a boiling point.

It is necessary to emphasize, that the purpose of this work was not to develop a new method for the determination of the boiling point of pure components, to control the already known boiling temperatures, or for studying a vapor-liquid equilibrium. The presently described quasi-isothermic quasi-isobaric thermogravimetry can give, in a relative easy way, useful information about the distillation process of multicomponent systems, e.g., practical information about the composition of the liquid and some physical properties of the sample. The application of the method is anticipated in biochemical, lacquer, mineral oil and organochemical industry. Quasi-isothermic quasi-isobaric thermogravimetry offers a possibility to analyze samples with minute quantity (e.g., essential oils, forensic samples, etc.). The classical stationary methods [11] are not suitable



for that kind of analysis, instead, dynamical fractional distillation techniques are used for such purposes. However, the accuracy of these techniques is not satisfactory, probably because the applied heating method causes a rapid evaporation of the sample, and the fractional distillation process does not proceed under equilibrium conditions, resulting in an incomplete separation of the components.

The reliability of the method can be judged on the basis of Figs 5, 7 and 9. As can be seen from the curves 1–10 and the corresponding liquidus ( $L$ ) and vapor ( $V$ ) curves taken from literature, it is obvious that the quasi-isothermic quasi-isobaric distillation proceeds practically under equilibrium conditions.

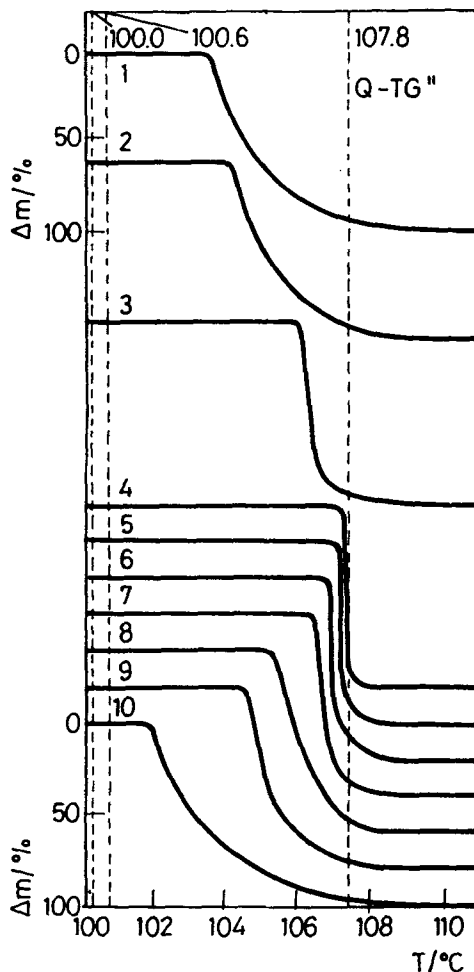


Fig. 8 Q-TG'' curves for the formic acid-water binary system of different starting compositions. The mole fraction of formic acid ( $n$ ) for curves: 1 - 0.90; 2 - 0.80; 3 - 0.70; 4 - 0.64; 5 - 0.59; 6 - 0.55; 7 - 0.41; 8 - 0.32; 9 - 0.26; 10 - 0.16

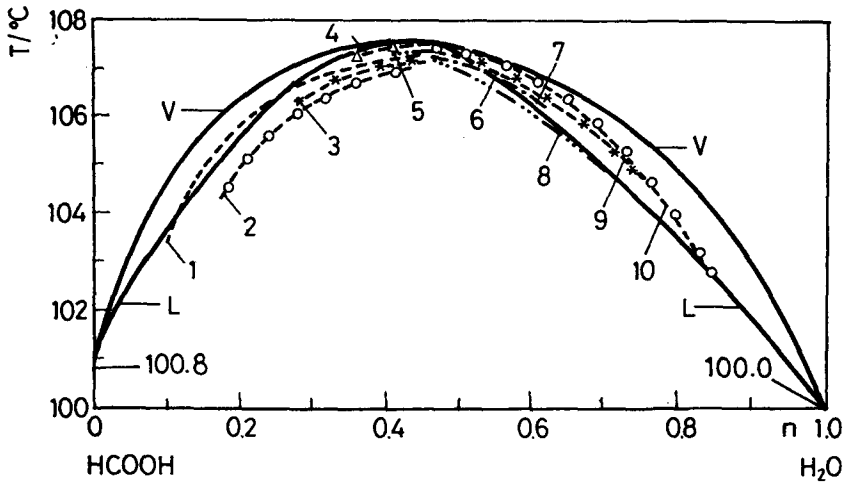


Fig. 9 The temperature change as a function of the liquid (L) and vapor (V) phase composition for the system formic acid-water. Curves 1–10 were obtained on the basis of data presented in Fig. 8

The experiences gained in this research show that the accuracy of the measurement can be improved by increasing the sample mass (500–1000 mg), or by decreasing the weight change rate (e.g.,  $dm \cdot dt^{-1} = 2 \text{ mg} \cdot \text{min}^{-1}$ ;  $\Sigma \Delta m = 1000 \text{ mg}$ ). To accomplish the calculation of the liquidus curve, the effect of the atmospheric pressure change could be taken into account, too. However, the most important factor from the aspect of the accuracy of the measurements is a careful calibration of the temperature measuring system of the instrument.

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In memory of late Prof. J. Paulik co-founder of the theory, on which the science of thermal analysis was built.

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**Zusammenfassung** — Es wird eine Methode zur Mikrodestillation von Flüssigkeiten unter Anwendung quasiisothermischer quasiisobarer Thermogravimetrie beschrieben. Die unter Quasigleichgewichtsbedingungen bestimmte Liquidus-Kurve liefert nützvolle Informationen über die Zusammensetzung und einige thermische Eigenschaften der Probe. Diese Methode kann von Interesse für die Mineralöl-, Lack-, Bio- und organochemische Industrie sein.