

Erratum

Erratum and further comments on “Temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments” [Thermochim. Acta 346 (2000) 133–145]☆

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Abstract

Comments and corrections are made on a report entitled “temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments”. A few unnoticed mistakes that ‘survived’ the revision stages are corrected and the (new) equations are validated.

Keywords: Temperature; Differential scanning calorimetry; DMA

1. Introduction

The above paper, “Temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments”, by Alves and Mano [1], addressed an important topic in the context of the development and validation of thermal-differential scanning calorimetry (DSC), dynamic mechanical/thermomechanical analysis (DMA/TMA), etc. — data treatment procedures, for the correct assignment of materials’ transition temperatures and the quantitative interpretation of their thermal and/or thermomechanical behavior.

Unfortunately, a few unnoticed mistakes were made in the writing of some of the most critical equations, which ‘survived’ the revision stages. The opportunity is now taken to correct those mistakes, to fully validate the resulting (new) equations, and to clarify the underlying concepts and the discussion of the original results. The whole of the original experimental findings, discussion and conclusions stand as valid.

As a matter of fact, the present note is much more than an erratum and really adds to the scope of the original paper, inasmuch as the equations and procedures are here fully put to the test against the very same experimental results [1].

2. Measured temperature offsets

One significant contribution of the paper [1] indeed is the experimental study of the sample’s thermal

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environment in a typical DMA, which clearly highlighted the influence that the type of test fixture does have, through the associated sample's position relative to the sensor (thermocouple), on the actual temperature readings, which therefore, requires different thermal calibrations (in heating, cooling and isothermal experiments), depending on the type of test and sample. This has so far been a much neglected, if not entirely overlooked, aspect in DMA/TMA experiment planning and data treatment procedures.

Three different test configurations (P1–P3) have been studied in detail, and their effect on the actual sample temperature readings quantified, by means of melting runs with a very pure (99.999%) metal (In) standard. The reader will readily recognize the importance and size of the effect (up to 11°C in temperature) and the striking similarities of P2 and P3 configurations. The large negative P2/P3 to P1 measured temperature difference(s) may also be readily associated, not simply to the (not so widely) different relative sample/thermocouple positions, but also (or perhaps mainly) to the more intense heat conduction losses through the metal platform and sample tube, in configuration P1. The original discussion could not delve into extensive detail, but it should be noted here that different temperature readings (offsets) should indeed be expected even when no purge gas actually flows through the measurement cell, for both temperature scanning and isothermal runs, because in any of the situations heat is actually flowing to the outer cell cooling block and mechanical mountings, through the (still or flowing) gas, probe and sample tube. As the associated thermal resistances are not negligible, thermal lags do result, thus requiring adequate temperature corrections to obtain real, meaningful, sample temperatures. It is thus important to note that the difference of 3.5°C obtained for the In melting onsets with configurations P1 and P2, at zero helium flow rate (Fig. 8 of [1]), are not necessarily due to errors (or extrapolation uncertainties), but may be physically meaningful.

Therefore, there will generally be two contributions to the thermal (temperature) lag of the sensor relative to the tested sample, namely (i) an isothermal, sensor and gas-dependent, lag and (ii) a scanning rate-dependent (also gas-dependent) lag. Changes in the nature and/or flow rate of the purge gas, and/or in the temperature program (in its nature and/or rate), will

thus always require specific temperature calibrations, to obtain accurate data. This is why the topic is of such critical importance, but despite continuing interest and relevant contributions [2–12], general, physically sound, quantitative solutions of the problem are still pursued [1,13–16], for various phenomena and measurement techniques.

As more or less universally accepted, the first (isothermal) contribution to the thermal lag may be evaluated by extrapolation from adequate runs (preferably the melting of very pure standard materials) at very slow scanning rates. This isothermal correction may itself be temperature-dependent, and thus require more elaborate quantitative formulation and experimental measurement, but in the context of the paper of [1], as customarily done in DMA work, a one-point (temperature) procedure is adopted to evaluate the thermal lags and perform the corresponding calibrations, for the selected programs and temperature scanning rates. Therefore, the isothermal correction, ΔT_0 , is consistent with Eq. (4) of the original paper [1], i.e.

$$\Delta T_0 = T_{s,m}^0 - T_{r,m}, \quad (4a)$$

where (for In) $T_{r,m} = 156.6^\circ\text{C}$.

3. The calibration on cooling — erratum of Eqs. (5), (6) and (8)–(10)

Eqs. (8)–(10) of the paper [1] were obtained from the expressions for the thermal lags during heating and cooling experiments (Eqs. (5) and (6)), ΔT^+ and ΔT^- , which account for the effect of the scanning rate. Eqs. (5) and (6) are, in fact, incorrect. The actual (physically operating, heat flux determining) thermal lags are, of course, the difference between the real temperatures of the sample, T_r , and the corresponding temperatures read by the thermocouple shifted according to the isothermal correction, i.e. $T_s^+ - (T_{s,m}^0 - T_{r,m})$. As a result

$$\Delta T^+ = T_r - T_s^+ + T_{s,m}^0 - T_{r,m} \quad (5)$$

and

$$\Delta T^- = T_r - T_s^- + T_{s,m}^0 - T_{r,m}, \quad (6)$$

which yield the new Eqs. (8)–(10):

$$T_s^- = 2(T_r + T_{s,m}^0 - T_{r,m}) - T_s^+, \quad (8)$$

$$T_r = \frac{T_s^- - 2(T_{s,m}^0 - T_{r,m}) - a_1^+ / a_2^+}{2 - (1/a_2^+)} \quad (9)$$

and

$$T_r = T_s^- - 2(T_{s,m}^0 - T_{r,m}) - (T_{r,m} - T_{s,m}^+). \quad (10)$$

This formulation corresponds to an exact symmetry of $(T_s^+ - \Delta T_0)$ and $(T_s^- - \Delta T_0)$ relative to the real sample temperature, T_r , at each specified (heating and cooling) scanning rate, i.e. T_r is, as may be readily checked, the arithmetic average of the above shifted, true, sensor temperatures, in the absence of any extra thermal effects (like the dissipation of heats of reaction, crystallization or other material changes), which require separate quantification where necessary [13,15,16]. An alternative formulation is also possible, whereby the real sample temperatures on heating and cooling are symmetrical relative to a given true sensor temperature [13,15], but the numerical results turn out to be almost identical [13]. However, the former formulation, adopted in [1], is physically to be preferred [13], because it effectively guarantees exactly the same local heat flux value in both heating and cooling modes, as required by heat transfer theory and indeed implied in Eqs. (7) of [15] and [1].

In order to confirm the validity of the final equations, the data in Figs. 7 and 11 and Table 1 have been treated as indicated below. For a one-point calibration, $a_2^+ = 1$, and Eq. (10) may thus be used to calculate the

real values of T_{\max} observed in the DMA experiments on cooling, while Eq. (5) will give the real sample temperatures on heating. We recall that the $T_{s,m}^+$ values are the observed melting temperatures of indium, at each of the (heating) scanning rates.

The calibrations on heating and cooling obtained with the above equations are shown in Fig. 1 of this note. The results of the calibration on heating are the same as those of Fig. 12 of [1]. They show a small (just over 1°C) decrease of the glass transition (as measured in [1] from the maximum of $\tan \delta$) with the scanning rate. On the other hand, the results in cooling show a not so small, but smooth decrease of the glass transition with decreasing scanning rates. These variations (in both heating and cooling modes) may actually be somewhat amplified (the higher the scanning rate), if one accounts for the effect of the sample's thermal resistance, yielding higher (lower) than measured true sample temperatures on cooling (heating). Almost identical numerical results are obtained by the alternative method [15] referred to above.

According to the manufacturer of Perkin-Elmer DMA-7e, the temperature is measured with an error of 1°C. The calibration performed according to the above equations has itself errors, that have been quantified in [15] and increase with the scanning rate in use. Despite the errors involved in the measurements, the predicted variations on heating and cooling (Fig. 1), suggest the applicability to dynamic

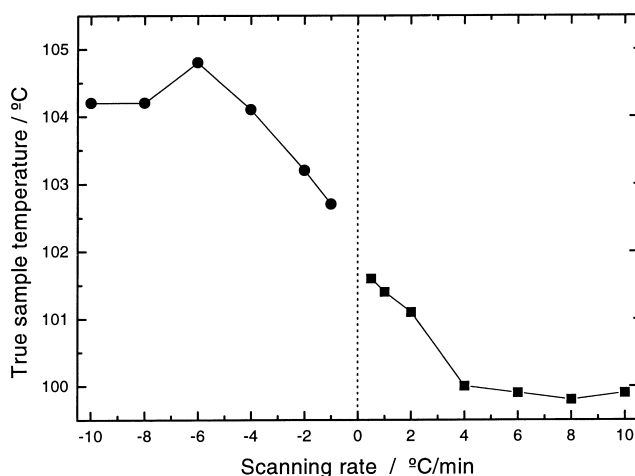


Fig. 1. Calibration on heating, according to Eq. (3) of [1], and on cooling, according to Eq. (10), for data shown on Fig. 12 and Table 1 of [1]. The isothermal correction was $\Delta T_0 = 2.8^\circ\text{C}$ at 156.6°C .

mechanical analysers of the proposed temperature calibration method.

4. Additional small corrections

As the reader may have already noted, two other small corrections are still due: (i) ‘electromotive force’ should replace ‘electrical resistance’ in the first line of page 137 and (ii) on page 143, the expression for the testing frequencies that ensure adequate resolution within ΔT is, of course, $\omega \gg \beta/\Delta T$.

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Comments on “Temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments” by Natália M. Alves and João F. Mano, *Thermochimica Acta*, 346 (2000) 133-145

ESTE É O TEXTO ORIGINAL DO COMENTÁRIO QUE ESTAVA PRONTO A SER SUBMETIDO

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Abstract

Comments and criticisms are made on a paper entitled "Temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments". The paper contains some relevant results, namely the effect on instrument calibration of the purge gas flow rate and of the sample's position in different experimental setups. It also shows that, in dynamic mechanical (DMA) experiments, the thermal lag between the sample and the sensor is symmetrical in heating and cooling experiments. However, as shown here, the paper contains various erroneous or imprecise statements, quotations from the technical literature that cannot be found therein, misinterpretations of previously published work and wrong equations (that have not been applied to treat the data and, if applied, would yield physically unrealistic results). To help the readers of *Thermochimica Acta* and young researchers that may inadvertently fall into serious difficulties if applying some of the paper's concepts and most of its equations, a physically correct quantitative treatment of the paper's very same experimental results is also offered in this contribution, based on other, previously published, work.

Introduction

The purpose of the above paper was to develop and present a methodology to be used for instrument (DMA/TMA) calibration on heating, cooling and isothermal scans [1]. It also made explicit the possible extension of the method to other thermal analysis techniques, such as differential scanning calorimetry (DSC) and even rheometry, for possible use in the study of polymer crystallization under shear.

The paper acknowledges that “*one of the most important experimental requirements is the precise knowledge of the specimen temperature during the measurement of the physical variables*”. To fulfil this requirement, one needs a precise understanding and discrimination of the different phenomena involved. Analyses and data corrections should be worked out for each type of phenomena and any developed methodology must be checked against experiments. Otherwise, a set of eventually erroneous procedures and/or equations could be proposed, published in the scientific literature, and then spread, without giving any real and useful contribution to scientific knowledge. Every statement made should be proved or duly quoted from their authors and every derivation or model must, wherever possible, be checked against experiments. This should be the aim and organization of any scientific paper submitted for publication in a reputable journal of wide readership, such as *Thermochimica Acta*.

The paper [1] contains various imprecise or erroneous statements. For example, it is referred that “*the sensor in the furnace is located close to, but separate (by a gas gap) from, the sample*”. This statement is made as a generalization for all thermal analysis techniques. It is not literally true in DSC and DTA, where the temperature sensor is, in most cases, in direct physical contact with the oven and/or sample. In a DMA,

necessarily of course, the temperature sensor is in fact located at a certain distance from the sample being analysed.

As a consequence (of this *gas gap*), the paper states that “*the difference between the real temperature of the sample and the temperature read by the sensor is seldom zero due to the existence of a thermal inertia between the sample and the sensor*” and this statement is quoted as made by Hatakeyama and Quinn [2]. As may be readily checked, in no page whatsoever of this book is such a statement made !

Inertia is, by definition, the property of matter by which it tends to continue in its present state. The thermal inertia of the system (sample, oven, sensor), should be, as it is in many cases, as small as possible. Otherwise, it would be impossible to perform thermal analysis experiments similar to those described in the paper. What does effectively exist is a set o thermal resistances.

Another example of imprecise reference to the literature is in the discussion about the thermal lag inversion on heating and cooling experiments. In reference [18], quoted in [1], no explicit symmetry arguments were presented, although in its Note 2 [3] it is stated that the sample temperature on cooling is higher than the indicated temperature, by opposition to what happens in a heating experiment. The hypothesis of the symmetry on the thermal lags was, as stated in [1], first analysed by Schick and Höhne, but they finally concluded that “for power compensated DSC a symmetry in temperature correction between heating and cooling mode is not valid” [4].

The first specific and conclusive statement that symmetry should and does exist (at least approximately) between the thermal lags on heating and cooling experiments was by the authors of this note [5], but not in the way proposed in [1], i.e. by equations (5) and (6) of the paper, which, as shown below, are wrong and physically meaningless.

In the discussion that follows, we will focus on the calibration on heating, on the isothermal correction and on the calibration on cooling from heating experiments. Use will also be made of the very same experimental data of the paper to show that a previously published method for DSC calibration may also be used in DMA's, yielding results in heating and cooling experiments at different scanning rates which are physically meaningful.

Temperature calibration on heating

An equation presented in [1] for calibration with two (or more) standards is

$$T_r = \sum_{i=1}^{1 \leq m \leq n} a_i^+ (T_s^+)^{i-1} \quad , \quad (1)$$

where T_r is the real temperature of the sample, T_s^+ the temperature read by the thermocouple in a heating experiment and n is the number of standards. The paper states that, *“if one assumes a linear response between the temperature and the electrical resistance read by the thermocouple a linear regression between T_r and T_s^+ should be used, whatever the number of standards used”*. Although this is a minor point, since eq. (1) leads, for n standards, to a polynomial dependence on the sensor temperature, it may be asked why should one propose such an equation to immediately afterwards suggest its inapplicability (or that most of its terms should vanish). Much more important, however, a thermocouple does not read an electrical resistance, but an electromotive force, which is generated at the junction and is directly related to its temperature.

The isothermal correction

The paper also discusses the effect of different locations of the calibrant sample in the experimental setup. Three different experimental setups are mentioned, but we will consider here only two of them: P1 and P2. In P1, the calibrant sample is located at the bottom of the three-point bending platform, while in P2 it is located at the sample's usual position in a three-point bending experiment. After performing experiments with an indium standard at several heating rates, the conclusion was that an extrapolation of the onsets to zero scanning rate leads to different values for those two experimental setups. This extrapolation to zero scanning rate would then provide (still according to [1]) the *isothermal correction*. The strange thing is that it was explicitly expected (page 139 of [1]) that the only contribution to the isothermal correction would be the inaccuracy of the thermocouple. Based on the results with the above two experimental setups, however, it was concluded that it was not so, which should indeed have been anticipated, from the very origin and nature of the isothermal correction, as explained in the literature quoted in [1], namely [3,5 and 6] of this note. It was then hypothesised that “*the helium fluxes create temperature gradients within the system, even during isothermal conditions*”, which is correct. Since in both experimental setups the samples are at different positions, “*the thermal environment between thermocouple and the sample is different*”, which (still according to [1]) may be “*verified by doing experiments with different values of helium flow rates*”. When the extrapolation was made to zero flow rate, it was found (with undisguised surprise) that the difference between the onsets measured with the two setups, at zero scanning rate, was 3.5 °C. The reduced number of data and inaccuracies in the linear extrapolation were even offered as explanations for the difference.

As a matter of fact, it is illogical to relate the different onset temperatures at zero scanning rate for the two experimental setups to the helium flow rate. The difference may be simply explained by the different positions occupied by the samples, from which different thermal resistances (and thus different thermal lags) result, even in a situation where no forced flow of helium exists, except perhaps for extremely long times, in the absence of any other heat losses from the sample and probe fixtures. But, of course, the actual value of the zero scanning rate onset temperature difference must also be helium flow rate-dependent, as different overall sample to gas heat fluxes and transfer coefficients may then apply.

Summarising, to clarify the issue, the isothermal correction comprises *two temperature corrections*: the first one is related to the temperature read by the thermocouple itself at zero scanning rate; the second one (which is scanning rate-dependent) is the set of thermal resistances between the thermocouple and the sample (including the samples's own thermal resistance). This second set of thermal resistances comprises, inevitably, the “gas gap” between the sensor and the sample. Even if no gas is forced to flow into and out of the system, its convective motion will generate a thermal lag between the sample and the sensor. In addition, if the temperature scanning rate significantly differs from zero, transient heat transfer phenomena may develop between the sample and the sensor, resulting in a possible additional increase (difficult to quantify) of the effective thermal lag. Such high scanning rates, however, should be avoided, particularly with high inertia (like DMA) measurement cells, as the true sample scanning rate may then lag too far below the programmed one, for any reliable quantitative data treatment and interpretation.

The distinction between these two (isothermal and rate-dependent) thermal lags was discussed in detail in [5].

The calibration on cooling (ref. [1])

In establishing the basic arguments to explain the calibration on cooling from heating calibration data, the paper presents as a basic assumption the symmetry between the heating and cooling thermal lags, which have already been tested and verified by the present authors [5]. Unfortunately, that basic assumption is misinterpreted and wrongly formulated, leading to a set of erroneous equations, which have not been checked nor even used to treat the data. The conclusion that those equations “*may be applied to other DMA and TMA apparatus, or even ... to rheometers*” and that the work “*may contribute to further developments in the calibration of DSC equipments on cooling*” is thus baseless.

Equation (5) of the paper predicts, for indium at its melting temperature, a thermal lag on heating (at 4 °C/min) between the sensor and the sample of –144.5 °C ! Values used to obtain this result were measured and given in [1]: $T_s^+ = 152.5$ °C (for P1, from Fig 7, at $\beta = 4$ °C/min) and $T_s^o = 148.6$ °C (from data in the same figure). Also, if Equation (5) is made consistent with the stated, but wrong, definition (see text) of ΔT^+ , by means of two obviously missing parentheses, the (almost) equally impossible result of +152.7 °C is then obtained. All these terrible mistakes stem from a gross misinterpretation of the basic symmetry assumption, which led to physically senseless definitions (see text) of, and expressions for, ΔT^+ and ΔT^- - Equations (5) and (6).

Using again values given in the paper and Equation (10), the prediction for the onset of crystallization of indium at –4 °C/min (from the values of the calibration on heating at the same rate) would be *ca.* –201 °C ! As the melting of indium is at 156.6 °C, no further comments need to be made on the validity of the proposed calibration method.

The calibration on cooling (ref. [5])

In reference [1], a poliester resin was used to verify that there is symmetry in the thermal lags that apply to heating and cooling DMA experiments. These experiments have been performed at scanning rates from -10 °C/min to $+10$ °C/min and at a frequency of 1 Hz. The data from Figs. 7 and 11 and Table I will be used to test the method previously proposed in [5] to perform calibrations on cooling from the melting onsets of standard metals.

Since only one standard was used to perform the calibration on heating, eqs. (13) and (16) of [5] yield

$$T_r^+ = T_s + (T_{r,m} - T_{s,m}) + \Delta T_o \quad , \quad (2)$$

and

$$T_r^- = T_s - 2\Delta T_o - (T_{r,m} - T_{s,m}) \quad , \quad (3)$$

where T_r^+ and T_r^- are the real sample temperatures on heating and cooling at a specified rate for a given measured (sensor) temperature, ΔT_o is the isothermal correction (calculated at the indium melting temperature for a constant purge gas flow rate) and $(T_{r,m} - T_{s,m})$ corresponds to b^+ in [5], which is the rate-dependent difference between the real melting temperature of the calibration standard and the melting temperature read by the sensor. A slightly different formulation has also been tested [6,7], whereby the already mentioned symmetry explicitly results, instead, in T_r being the exact arithmetic average of T_s^+ and T_s^- , in the absence of any extra thermal effects (like the dissipation of heats of reaction, crystallization or other sample changes), which have to be separately quantified where necessary.

The calibrations on heating and cooling obtained with the above two equations are shown in Fig. 1. The results of the calibration on heating are the same as those of Fig. 12 of [1]. They show a small (just over 1 °C) decrease of the glass transition (as measured in [1] from the maximum of $\tan \delta$) with the scanning rate. On the other hand, the results in cooling show a not so small but smooth decrease of the glass transition with decreasing scanning rates, which is as physically expected, and thus more easily interpreted.

According to the manufacturer of Perkin-Elmer DMA-7e, the temperature is measured with an error of 1°C. The calibration performed according to eqs. (2) and (3) above has itself errors, that have been quantified in [5] and increase with the scanning rate in use. Despite the errors involved in the measurements, the small variations predicted for the glass transition temperature seem physically reasonable, at least on cooling, thus suggesting the extensibility to dynamic mechanical analysis of the method previously proposed by the present authors [5] for the calibration of differential scanning calorimeters.

Other errors/imprecisions may still be identified in the same paper, like the loss of mass said to accompany a Curie transition in the calibration of a thermobalance, the claimed decrease in the sample's loss of mass above 130 °C (Figure 2 of [1]), the lumped, very inaccurate, reference to the variation of a_1^+ and a_2^+ (Eq. 1) with the scanning rate, the value of a_1^+ itself (on page 137), and the expression for the minimum testing frequency for adequate resolution within ΔT (on page 143). The latter, however, looks like being a simple misprint.

CONCLUSIONS

1. The temperature calibration method proposed in reference [1] is invalid and physically baseless.
2. The temperature calibration method previously developed by the present authors for DSC's has sound physical foundations and is extensible to, and quantitatively valid for, other thermal analysis techniques, like DMA.

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Figure caption

Figure 1. Calibration on heating, according to eq.(2), and on cooling, according to eq. (3), for data shown on Fig. 12 and Table I of [1]. The information for the calibration on heating was that applying to the experimental setup P2 (Fig. 7 of [1]). The data in the same figure was used to calculate the isothermal correction, $\Delta T_o = 2.8$ °C at 156.6 °C.

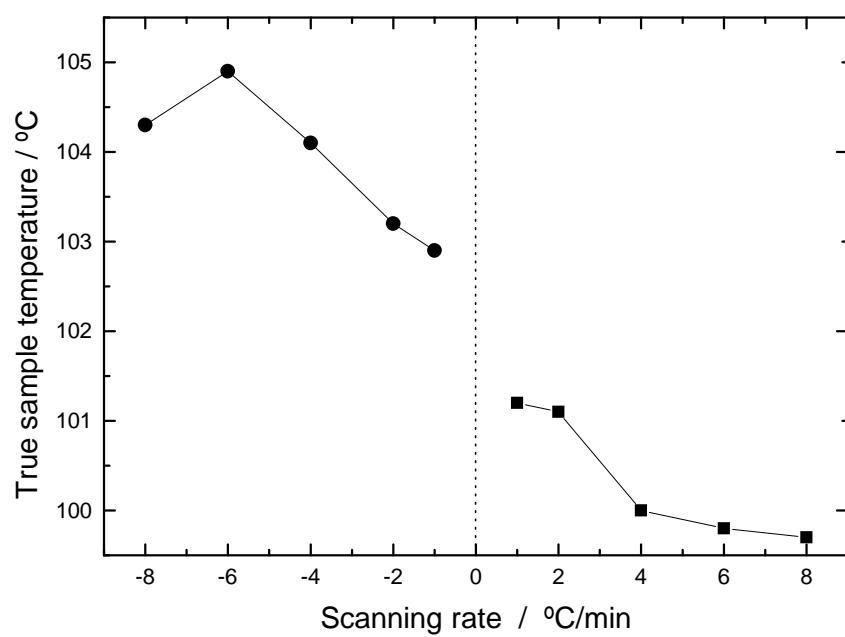


Figure 1