PURITY DETERMINATIONS BY THERMAL METHODS

A symposium
sponsored by ASTM
Committee E-37 on
Thermal Measurements
Baltimore, MD, 25 April 1983

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Foreword

The symposium on Purity Determination by Thermal Methods was held in Baltimore, Maryland, 25 April 1983. The symposium was sponsored by ASTM Committee E-37 on Thermal Measurements. R. L. Blaine, E. I. du Pont de Nemours and Company, and C. K. Schoff, PPG Industries, presided as symposium cochairmen and are coeditors of this publication.

Related ASTM Publications

Standardization of Technical Terminology: Principles and Practices. STP 806 (1983), 04-806000-42

Thermal Insulations, Materials, and Systems for Energy Conservation in the '80's, STP 789 (1983), 04-789000-10

Manual on the Use of Thermocouples in Temperature Measurement, STP 470B (1981), 04-470020-40

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Introduction

This symposium on Purity Determinations by Thermal Methods and the resultant Special Technical Publication of the same title commemorate both past accomplishments and promise of future progress. This symposium is held on the tenth anniversary of Committee E-37. It commemorates the issuing of the first Standard Test Method undertaken by the Committee. And the symposium itself is the first sponsored by the Committee.

It was June of 1973, one decade ago, when the formation meeting was held for the new ASTM Committee E-37 on Thermal Analysis (later Thermal Measurements) in Philadelphia. This formation meeting was attended by 82 specialists in thermal analysis, from government, industry, and academia, many of whom remain active in the work of the Committee today. It was clear from the earliest days of the Committee that there was much interest in the calorimetric purity method based upon the differential scanning calorimetry technique. And so a task group aiming at producing a Standard Test Method was initiated on this important analytical technique beginning in 1975. The details of the generation of that test method, issued as E 928 in this year of the decade anniversary of the Committee formation, are described in the paper by task group chairman, Dr. C. M. Guttman.

The calorimetric purity method, however, was more than the first test method to be initiated by the Committee. It was the vehicle whereby the members of the Committee, new to ASTM procedures, grew to trust each other's viewpoint and to appreciate the ASTM consensus standards generation process. This initiation process, while being slow and deliberate, paved the way for other test methods to follow, and, indeed, in later stages, to actually pass the calorimetric purity method and issue previous to the calorimetry purity method.

No contemplation of the activities of the first decade of Committee E-37 would be appropriate without mentioning the contributions of its chairman. Dr. E. M. Barrall (IBM Corporation, San Jose, California) was the first chairman elected by the membership. A change in Dr. Barrall's corporate responsibilities soon after election, however, dictated a by-election in which Dr. P. K. Gallagher (Bell Laboratories, Murray Hill, New Jersey) became the new chairman of the committee. Dr. Gallagher's gentle but efficient administrative hand guided the committee through its infancy and toddler stages. The late Dr. O. Menis (National Bureau of Standards, Gaithersburg, Maryland) and Dr. S. A. Moros (Hoffman-La Roche Inc., Nutley, New Jersey) chaired the committee through its childhood and adolescent years as it began to glimpse what benefits would result from commit-

tee maturity. Finally, under the chairmanship of Dr. R. L. Blaine (Du Pont Company, Wilmington, Delaware), the committee reached young adulthood as the training times of previous chairmen yielded the fruits of newly generated Standard Test Methods.

While these committee chairmen provided the administrative leadership for the Committee E-37 in its first decade, far more praise falls on the shoulders of the individual members of the committee, particularly the task group and subcommittee chairman. The contributions of these individuals are too numerous to count but represent the real present and future strength of this committee.

The material contained in this STP reflects two important aspects of ASTM activities: codification and documentation of the collective wisdom of the committee in a technical field and exploitation of new concepts and techniques.

The papers by Dr. W. P. Brennan and co-workers and Dr. C. M. Guttman lay the understanding and outline the historical perspective of the calorimetric purity method. Authors Dr. C. M. Guttman and J. E. Hunter, III, and co-workers provide detailed information leading to an estimation of the precision and accuracy of the established test procedure. Authors O. Lim and co-workers, and J. P. Elder compare the results obtained by the dynamic calorimetric purity procedure with those obtained by other techniques both for model systems and for actual materials of commercial interest. An analytical technique is most useful when the limits of its applicability are well known. The papers by Dr. A. R. McGhie and J. E. Hunter, III, and co-workers help define some of these limits. And, finally, Dr. S. A. Moros details the work to generate a set of Standard Reference Materials for further exploration in the future.

An additional set of papers explores other thermal techniques for examination of material purity by a variety of thermal measurements. Dr. D. D. Pollock explores the temperature dependence of certain electrical properties as a key to the determination of purity for high-purity silver. Dr. G. T. Furukawa and coworkers document the use of cryoscopy for the purity determination of highly pure benzene. Dr. H. G. Wiedemann and co-workers explore a new simultaneous technique of thermomicroscopy and differential scanning calorimetry. And, finally, Dr. W. Smykatz-Kloss reviews the application of differential thermal analysis for the identification of "impurities" in minerals.

This symposium and Special Technical Publication is dedicated, then, to those pioneers who initiated the committee's activities a decade ago, to those members who have contributed to its progress in that decade, and to its present members as they work together to produce new and better Standard Test Methods.

Roger L. Blaine

E. I. du Pont de Nemours and Company, Wilmington, DE 19898; symposium co-chairman and coeditor.

Calorimetric Purity

William P. Brennan,[1] *Michael P. DiVito,*[1] *Richard L. Fyans,*[1] *and Allen P. Gray*[1]

An Overview of the Calorimetric Purity Measurement

REFERENCE: Brennan, W. P., DiVito, M. P., Fyans, R. L., and Gray, A. P., **"An Overview of the Calorimetric Purity Measurement,"** *Purity Determinations by Thermal Methods, ASTM STP 838*, R. L. Blaine and C. K. Schoff, Eds., American Society for Testing and Materials, 1984, pp. 5–15.

ABSTRACT: The well-known effect of impurities on the melting behavior of crystalline compounds provides the basis for the determination of the purity of these compounds by differential scanning calorimetry (DSC). In the Perkin-Elmer DSC method for the determination of the purity of crystalline compounds, the van't Hoff equation is used to describe the rate of melting of a compound as a function of sample temperature. The presence of an impurity will broaden the melting peak of the compound and lower the final melting point from T_o, the melting point of a 100% pure compound, to T_m, the melting point of the impure mixture. If careful sample preparation and slow scanning rates are employed to approach thermodynamic equilibrium, accurate estimation of the true purity of a compound can be determined.

The recommended DSC procedure involves the use of a relatively small sample size consistent with homogeneity, the tightest possible encapsulation to minimize temperature gradients within the sample, and the slowest possible scanning rate to approach equilibrium conditions. Also, it is recommended that the melting curve be analyzed over a range of fraction melted (usually 10 to 50%), where the curve is least sensitive to possible gradients in the instrument-sample system.

KEY WORDS: differential scanning calorimetry, crystalline compounds, impurities, van't Hoff equation, melting behavior

The determination of the absolute purity of organic materials by differential scanning calorimetry (DSC) has been an accepted technique in the pharmaceutical and chemical industries since the development of the DSC in the early 1960s. Gray described in detail the thermodynamic theory for the determination of purity by DSC as early as 1966 [*1*, *2*]. Since then, a host of other researchers have critically evaluated this technique for accuracy, reproducibility, and ease of

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use, as well as for the sample variables and instrument parameters which are associated with this technique [*3–26*].

The purpose of this paper is to review the well established calorimetric purity technique as described by Gray and others, as well as to review the recent advances in the determination of the purity of organic materials using sophisticated new instrumentation and advanced computer software programs.

Methods of Purity Determination

In a review on the subject of purity analysis, Barnard et al [*7*] discuss the major methods for the practical analysis of high-purity chemicals. Some of the major techniques discussed include elemental analysis, thin layer chromatography, gas chromatography, phase solubility, and differential scanning calorimetry (DSC).

Providing careful sample preparation and instrument optimization, DSC has proven to be a rapid, accurate, and precise technique for the analysis of the purity of many different types of materials.

Of course, as with any analytical technique used for the determination of purity, DSC is by no means without its potential errors and limitations. However, provided certain sample preparation and instrument variables are understood and carefully controlled, the determination of purity by DSC provides reliable results in a very small amount of experimental time.

Theory of the Calorimetric Purity Method

The determination of the purity of an organic compound by DSC is based upon the well-known fact that the presence of even minute amounts of impurity in a material broadens its melting range and lowers the final melting point of the material from T_o, the melting temperature of an infinitely pure material, to a lesser temperature, T_m. An example of these effects is clearly demonstrated in Fig. 1, which shows the DSC traces of three benzoic acid samples of different purities performed on a Perkin-Elmer DSC-4. As the DSC theory predicts, as the impurity content in the benzoic acid increases, the melting point decreases, and the range of melting broadens. Notice that even minute differences in the impurity content of the samples results in distinct differences in the DSC melting peak shape and final melting temperature.

In many situations, the comparisons of the peak shapes and melting points of unknown materials to known standards, as shown in this figure, can be used routinely for the qualitative assessment of the minimum purity of a material. This technique provides a rapid qualitative testing procedure and is especially useful for many quality control applications where it is only necessary to determine if a sample has a certain minimum purity.

In other more demanding situations, however, the exact mole percent purity (or impurity) of a material is required. With these situations in mind, Gray first described the use of power compensated DSC for the quantitative assessment of

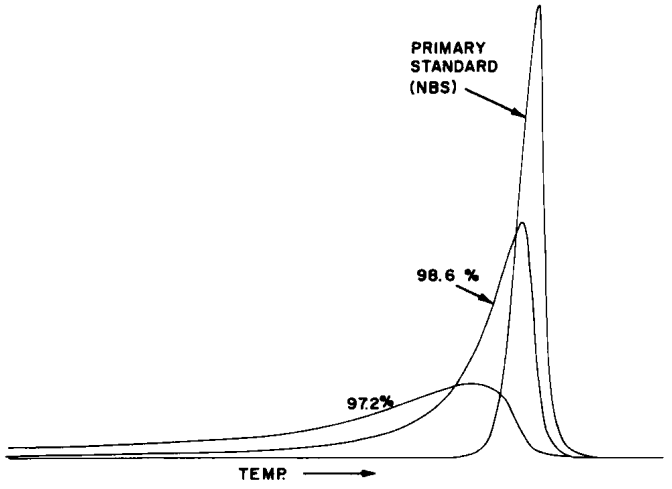

FIG. 1—*Effect of purity on DSC melting peak shape and melting temperature of benzoic acid.*

the purity of organic materials. This overview would not be complete without a general review of Gray's theoretical discussion on the dynamic DSC purity technique [*1*, *2*]. The quantitative assessment of the purity of an organic material requires the knowledge of three important sample parameters:

Melting point
Heat of fusion (ΔH_f)
Analysis of the DSC melting peak shape

Differential scanning calorimeters provide both accurate temperature and calorimetric measurements, thus permitting the simple determination of each of these three important sample parameters from a single dynamic DSC experiment.

DSC measures directly the amount of energy absorbed or emitted by a sample (dq/dt), which can be expressed by the following simplified expression (Eq 1)

$$\frac{dq}{dt} = \frac{dT_s}{dt} \times \frac{dq}{dT_s} \tag{1}$$

where

dT_s/dt = scanning rate, K/min, and

dq/dT_s = heat capacity of the sample or the energy required to accomplish a transition, J/K (cal/°C).

The heat capacity term in this expression provides important information about the shape of a melting peak and, therefore, is the most important term here. From the van't Hoff equation, which describes the rate of melting of a compound as a function of sample temperature, the following relationships describing the heat flow to or from a sample and the melting point depression of a sample due to the

presence of an impurity, (Eqs 2 and 3) can be then obtained

$$\frac{dq}{dT_s} = \frac{\Delta q(T_o - T_m)}{(T_o - T_s)^2} \tag{2}$$

where

Δq = total heat of fusion of the sample, joules (calories);

T_o = melting point of a 100% pure material, K;

T_m = melting point of sample system, K;

$(T_o - T_m)$ = melting point depression due to impurity, K; and

T_s = sample temperature, K.

The melting point depression due to an impurity $(T_o - T_m)$ can be expressed as

$$(T_o - T_m) = \frac{RT_o^2X_2}{\Delta H_f} \tag{3}$$

where

R = molar gas constant, 8.314 J/mol K (1.987 cal/mol °C);

X_2 = mole fraction of the impurity; and

ΔH_f = molar heat of fusion, J/mol (cal/mol).

From these basic van't Hoff relationships (Eqs 2 and 3) the theory of the determination of the purity of a sample by DSC can now be derived. To do this, we integrate Eq 2, which results in an expression which describes the fraction of material reacted (melted in the case of purity) at any sample temperature on the melting curve (Eqs 4 and 5)

$$F = \frac{T_o - T_m}{T_o - T_s} \tag{4}$$

By rearranging this equation

$$T_s = T_o - \frac{T_o - T_m}{F} \tag{5}$$

where

F = fraction melted, and

T_s = sample temperature, K.

The theoretical discussion is now nearly complete. By substituting Eq 3, which defines the melting point depression due to an impurity, into Eq 5, the now familiar linear equation used by Gray for the determination of purity by DSC can be obtained (Eq 6)

$$T_s = T_o - \frac{RT_o^2X_2}{\Delta H_f} \cdot \frac{1}{F} \tag{6}$$

Since Eq 6 is a linear equation, a plot of the sample temperature (T_s) versus the reciprocal of the fraction of material melted at that temperature ($1/F$) should give a straight line with a slope equal to the melting point depression $RT_o^2X_2/\Delta H_f$ and a Y intercept of T_o. This linear plot is referred to as a van't Hoff plot, a typical example of which is shown in Fig. 2. The fraction of material melted at any sample temperature is determined directly from the dynamic DSC scan and is proportional to the peak area under the curve up to that temperature. By generating this van't Hoff plot from a series of sample temperatures and fraction melted results in the range from approximately 5 to 60% melted, it is a relatively simple procedure to obtain values for T_o, the slope of the line, and finally, the direct determination of the mole fraction of impurity from Eq 6.

Sample Preparation for Dynamic Purity Determinations

As previously mentioned, the determination of the purity of a material by DSC has been shown to be a rapid, accurate technique by a host of researchers for many different types of materials [*1–26*]. As with any analytical technique, and especially in those techniques which measure the small differences between materials as in the case of purity, superb instrument response and sample preparation are a must. The preparation of sample materials for the determination of purity by DSC as well as optimum instrument operating techniques are listed next. A short explanation of each item will follow.

Moderate to slow scanning rates.
Small sample size.
Proper sample encapsulation.
Correction for thermal resistance.

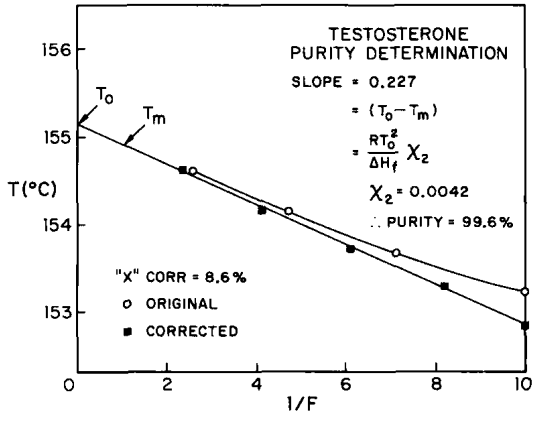

FIG. 2—*Typical van't Hoff plot for the calculation of purity by DSC.*

C_o, the heat capacity contribution of the sample pan and sample.
Proper temperature selection for the analysis.
van't Hoff linearization.
Thermal history of materials.

Scanning Rates

Since the van't Hoff equation is based on equilibrium conditions existing during the melting of the sample, scanning rates of less than 5 K/min and preferably less than 2.5 K/min are recommended [*1*, *8*]. These scanning rates will ensure equilibrium during melting.

Sample Size

Sample sizes of 1 to 5 mg are recommended for the determination of purity by dynamic DSC studies [*1*]. This sample size will allow equilibrium conditions during melting while not contributing any significant thermal resistance to the measurement system.

Sample Encapsulation

It is recommended that samples be encapsulated in hermetically sealed volatile sample pans, since many materials demonstrate a significant vapor pressure at or near their melting point [*8*]. Additionally, the samples should be tightly encapsulated in the sample pan to prevent bubbling or movement of the sample as melting proceeds, since this movement can result in changes in the melting peak shape. Tight encapsulation is best accomplished by sealing the material between two volatile sample pan bottoms, or by placing an aluminum disk on top of the sample before sealing [*2*].

Correction for Thermal Resistance

The only significant thermal resistance in a DSC is that between the sample pan and sample holder, designated as R_o, provided the sample size and sample encapsulation techniques just described are adhered to. In a DSC, there is a small temperature difference between the true sample temperature and the temperature of the sample holder as a result of this thermal resistance. This temperature difference is proportional to the thermal resistance constant. Since this thermal resistance is known and reproducible from run to run, it can be easily calculated and used to correct sample temperatures for "thermal lag." A complete description of the procedure for calculating this constant for the Perkin-Elmer DSC is described by Gray [*1*] and involves the determination of the slope of the onset of a melting curve of a pure material such as a high purity indium metal standard. Using the slope of this onset line, the thermal resistance can be calculated from the following equation (Eq 7)