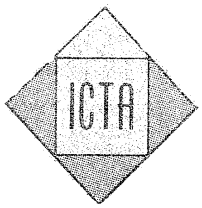


Certificate

ICTA Certified Reference Materials

for Thermogravimetry

certified by the

International Confederation for Thermal Analysis

distributed by the

United States National Bureau of Standards

as

GM 761

Nickel and Four Magnetic Alloys

These Certified Reference Materials are certified for calibration of temperature scales in thermogravimetry.

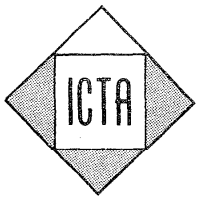
The National Bureau of Standards distributes a number of materials certified by recognized standards organizations, professional societies, or other government agencies.

The National Bureau of Standards has ascertained that the certifying organization is a recognized non-profit professional society one of whose objectives is to improve the reliability of measurements. The sponsoring organization is solely responsible for the quality of the material and for the accuracy of the statements and data related to this certified reference material.

Certificate

ICTA Certified Reference Materials
for Thermogravimetry

certified by the
INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS



and distributed by the
United States National Bureau of Standards
as
GM-761

This certificate describes the testing and evaluation program of these Certified Reference Materials (CRM). It also provides an analysis of the data and their relation to the mechanical design of the balance as an aid to the user of the CRM in interpretation of his own data.

The mean values for the defined points are given in table 2.

The overall and participant means for the several materials are given in tables 2-6.

Comparisons by instrument type are given in tables 10-14.

This certificate was prepared for the ICTA by
Paul D. Garn, Oscar Menis and Hans-Georg Wiedemann
of the
Committee on Standardization
International Confederation for Thermal Analysis

Members of the committee are:

P. D. Garn	R. C. Mackensie	F. Paulik
K. Heide	H. G. McAdie	J. P. Redfern
H. Kambe	O. Menis	O. T. Sørensen
G. Lombardi	H. R. Oswald	H.-G. Wiedemann
	T. Ozawa	

380-LA-014

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I. INTRODUCTION

A. Background

In this certificate information is presented to enable the user of ICTA Certified Reference Materials for Thermogravimetry, GM-761, to obtain optimum temperature measurement accuracy in thermogravimetry.

A useful dynamic temperature standard exhibits the following characteristics:

(a) it has an easily detected and reproducible thermal effect, i.e., provides an easily measurable and sensitive signal;

(b) it undergoes its thermal change rapidly enough to be measured on commercially available dynamic instruments; and

(c) it is stable enough to permit its convenient use under the normal operating conditions of the instrument.

These materials are not intended to, and may not, meet the criteria for equilibrium temperature standards. Their values are based on dynamic measurements and incorporate the errors associated with them.

Dynamic temperature standards are needed in several fields of thermal analysis. These needs are quite different in character and cover a wide temperature range. The first completed task of supplying Standard Reference Materials resulted in the issuance of SRMs 758, 759 and 760 for differential thermal analysis between 100 and 1000°C. The development was carried out by the International Confederation for Thermal Analysis (ICTA) through its Committee on Standardization, in liaison with the National Bureau of Standards through O. Menis and J. P. Cali, and is described in the NBS Special Publication 260-40[1]. These materials will continue to be issued through the National Bureau of Standards Special

Reference Materials program, listed as GM-758, GM-759, and GM-760 respectively.

The range was extended to ca. 180K by testing and issuing ICTA Certified Reference Materials for measurement below 350K, GM-757. For polymer glass transition measurements, ICTA Certified Reference Material Polystyrene, GM-754, has been issued.

The materials described herein have been certified by the International Confederation for Thermal Analysis as temperature standards for thermogravimetry. This certificate was based upon the testing done by the ICTA Committee on Standardization and the data treatment and interpretation presented in this Certificate. The materials are four alloys and one metal that are magnetically permeable. In conjuction with a magnetic field, they show easily detected changes in apparent weight at the temperatures at which thermally induced disorder or change in structure eliminate or drastically reduce their magnetic properties.

B. Rationale

In thermogravimetry the commercially available instruments have a wide range of design. Sample capacities range from <1 g to ca. 150 g and full scale weight changes range from 0.01 g to 100 g. It is inevitable that different approaches are taken for measurement of the sample temperature.

A thermobalance with a low sample capacity requires an isolated temperature sensor -- a thermocouple, resistance thermometer, or other transducer -- located in the vicinity of the sample holder but not in mechanical contact with it. On the other hand, a large capacity thermobalance enables connection of thermocouple leads from the stationary to the "moving" system. In this case the weight change range may be limited at the lower end by the reproducibility of any restraint from the connection. If the balance is held near a null

position by weight adjustment or a restoring force, the effect of the connection can become negligible. Further, many thermobalances are operated very frequently in vacuum; in this case the heat transfer is by radiation so the relation of the temperature of the sample to that of the sensor is different from that observed in air or a controlled atmosphere. The convective/conductive transfer of heat is the major process at low and moderate temperatures. The relative transfer by convection/conduction as compared to radiation depends not only upon the temperature but also upon the materials -- especially surfaces -- in the space between the heater and sample holder or temperature sensor so a suitable quantitative discussion is not appropriate in this Certificate.

The facts that

(1) substantial differences in measured temperature response can arise even for a given thermobalance, and

(2) differences in measured temperatures also arise from variations in measuring positions in different thermobalances

lead directly to the need for temperature standards by which the data from different experiments or different laboratories can be related or compared with confidence.

Each of these reference materials undergoes a measurable change in magnetic properties at a reproducible temperature. This change requires no discrete enthalpy increment and therefore does not disturb the temperature relationship between the sample holder and temperature sensor. Consequently, each provides a clear indication on the weight change record when the *specimen* reaches the temperature of this change, the temperature being indicated by the *sensor* can be noted and a measure of the systematic error found.

II. HISTORICAL

A. Brief Outline

The problem of temperature calibration of thermobalances was a part of the agenda of the ICTA Committee on Standardization from its first meeting in 1966. Attempts were made by some of the Committee to find materials whose decomposition provided adequate reproducibility. When it became apparent that the magnetic method[2] met the needs far better than any other, the Committee undertook the evaluation of candidate materials. Nickel, iron and their alloys were tested and the results evaluated taking into consideration not only the quality of the measurements but also, so long as the measurements were suitable, the availability and ease of production of samples in an easily used form. Several other materials may be suitable but have not yet been tested by laboratories using a sufficiently varied array of instruments.

B. ICTA

Early examination of decomposition processes by task groups of this Committee involved principally inorganic carbonate and oxalate systems. Because nearly all carbonate decompositions are reversible, the temperature depends upon the carbon dioxide pressure. Except when the atmosphere is all carbon dioxide, the changing partial pressure of carbon dioxide will spread out the weight loss. This occurs because of the increase of the carbon dioxide gas within the particle, within the sample, and within the furnace.

Typically, the carbon dioxide concentration would not approach in magnitude the inert gas pressure but the *temperature* varies with *log P* so the small concentrations built up during the process have a marked effect in inhibiting the continuation of CO_2 evolution. The spreading out of the weight loss results

both from this build-up and from unavoidable non-homogeneity of the partial pressure.

The packing or dispersion of the particles is not ordinarily sufficiently reproducible to assure reproducibility of the temperature, nor is the "average" partial pressure of carbon dioxide within the sample known, determinable, or calculable. For these reasons, a set of temperature reference materials based on carbonate decompositions is not feasible.

Oxalate decompositions are also not feasible. The reasons arise from two sources -- both related to the conditions of the experiment. Most metal oxalates are prepared as hydrates. If the oxalate hydrate were to be issued as the reference material, the loss of water could not be the reference temperature for the same reasons as for the carbonate decomposition. The oxalate decomposition could not be used either, but for less obvious reasons. Oxalate decompositions are irreversible, so the partial pressure of gaseous product does not have the same influence. However, the anhydrous oxalate has just been formed; consequently its tendency to decompose to the carbonate or oxide is noticeably dependent upon the conditions of its formation, namely the degree of confinement of the water vapor.

An alternative might appear attractive -- issuance of the previously dehydrated materials, thoroughly conditioned at appropriate temperatures. Use of oxalates is still not feasible because of the ready oxidizability of oxalates. In air, depending upon the conditions of atmosphere accessibility, the endothermic process may not be evident or it may be interrupted by the exothermic oxidative process. Further, the oxidative process leads to a sudden increase in temperature, sometimes as high as 150°. It is clear that the response of a temperature sensor not within the sample would be unacceptably dependent upon its closeness to the sample and the nature of any intervening container.

The use of magnetic reference materials for temperature calibration in thermogravimetry was proposed by Norem, et al.[2] Some of the materials then proposed had apparent deficiencies for general use so members of the committee tested a number of other alloys. After the initial trials by some of the Committee, a test program, designated as the Fifth International Test Program, was undertaken. Examination of the data and comments from this test program led to a decision to make some changes in the protocol and undertake a new program, designated as the Sixth International Test Program.

Some of the participants from the Fifth ITP were unable to take part in the Sixth ITP. Their contributions are recognized by acknowledgement in Section X. Some new participants were found to augment the efforts of those who took part in both programs.

C. General

A different approach was taken by the American Society for Testing and Materials (E.37) and by the International Standards Organization (TC-61). Each organization was principally concerned with polymeric materials, ASTM E.37 with polyethylene terephthalate and ISO TC-61 with polyvinyl chloride and polymethylmethacrylate. In each case, a wide range of data was reported. A detailed discussion of these programs is not appropriate in this document because -- due to the inherent differences in instruments -- there is an atmosphere effect somewhat similar in variability to the oxalate case described above.

III. THE SIXTH INTERNATIONAL TEST PROGRAM

A. Organization

The Sixth ITP was organized in a manner similar to the previous programs. The several members of the Committee selected and contacted persons that were active in thermogravimetry and had a concern for data interpretation. Some of these had taken part in the Fifth ITP. The test protocol was revised to clarify procedures. A member of the Committee, H.-G. Wiedemann, was delegated the task of finding a source of materials that could be tested before purchasing. A quantity of each of the selected materials was prepared and sent to the participants with the test protocol.

The report on first sets of returns were reviewed by the Committee at its Eleventh Meeting. After consideration of the larger set of data at the Twelfth Meeting, the Committee decided to recommend to the ICTA Council that the materials be certified.

The preparation of the certificate was assigned to P. D. Garn, H.-G. Wiedemann and O. Menis. Acquisition of the initial quantity was handled by H.-G. Wiedemann. The certificate was drafted and circulated to the Committee for comment. The revised draft, at the request of H. G. McAdie, then President of ICTA, was circulated directly to the ICTA Executive Committee. Upon approval by that committee, this certificate was printed and the materials and certificate forwarded to the United States National Bureau of Standards for distribution.

The protocol for the Sixth ITP is given below with the reasons for each of the steps. The precaution of specifying the procedure in detail is essential because of the variations in practice from laboratory to laboratory. On the other hand, latitude was allowed in as many respects as possible to enable the participant to perform this service without substantial change from his ordinary measurements.

B. Protocol

The Sixth International Test Program comprised the circulation of five small discs each of four alloys and nickel to about 40 invited participants and processing/evaluating the data received from 18. The homogeneity (in magnetic behavior) of the ribbon from which the discs were cut was verified.

The specific instructions are given below with the rational for each.

1. *The operating conditions of each instrument should be those normally employed for thermogravimetric measurements.*
   The tests of these calibration materials should be realistic
2. *The accuracy of the temperature sensor should be known. The Committee prefers use of recognized temperature standards.*
   Thermocouple responses should be checked occasionally.
3. *All temperature data* T_i, T_{max}, T_e, *defined in the accompanying figure, should be reported to the nearest* 1°C.*
   These defined points were easily measured in the preliminary test program. Greater reporting accuracy is not justified by the data or their repeatability.
4. *Each material should be examined at heating rates of* 1-2°C. min^{-1} *and* 5-6°C. $min.^{-1}$.
   In many thermoanalytical techniques the measured parameters are influenced by heating rate. Even though this may be solely an instrumental effect as compared to sample related, it is necessary to determine the magnitude of any influence.
5. *A time-temperature curve from the temperature sensor should be included. Apparatus with DTG should also include the DTG curve.*
   This is a routine check for unusual behavior.

*To avoid confusion in nomenclature, the designations of these defined points were changed to T_1, T_2 and T_3.

6. *One curve of the balance with empty sample holder exposed to the magnet should be supplied, using the same sensitivity employed with the test material.*
   This is a check for any discontinuous magnetic properties of the sample support.

7. *The test material should be used as supplied. Use whatever number of pieces is needed. If there is need, ask the Chairman for instructions.*
   Homogeneity of the test material is to be preserved against any innovative pre-treatments.

8. *With the measurements a sketch or photograph of the magnet-furnace-sample arrangement should be added. (See attached sketch).*
   Some kinds of deviations or anomalies relatable to the particular arrangement might occur. The sketch or photograph will help to trace them.

9. *Platinum or its alloys should not be in direct mechanical contact with the metal sample. The thermocouple may be in direct contact with the sample holder if the design permits. If the thermocouple is not in contact with the sample support assembly, the separation should be stated.*
   The precaution concerning platinum arose from reports of possible alloying in the preliminary study. The thermocouple in contact with the sample holder should give the best measure of the sample temperature. Variation in measured temperature with distance is very probably so knowledge of the thermocouple position is essential.

10. *A minimum of 2 runs of two cycles each on separate sample should be made at each heating rate.*
    This is a routine check for reproducibility as well as inhomogeneity.

11. *For the investigations a low sensitivity of the balance should be used in order that effects of buoyancy, oxidation, etc. may be reduced vs. ferro-paramagnetic effect.*
    Any extraneous effects should be minimized to focus attention on the principal measurement.

12. *All runs should be done in oxygen-free nitrogen, dried over* $Mg(ClO_4)_2$ *or its equivalent.*

This is precautionary, to eliminate any differences in treatment which might obscure differences between balances.

13. *Results should be reported according to the recommendations for good practice defined by the Committee* (Anal. Chem. 39, 543 (1969).
This is a reminder.

14. *Send curves and data to Dr. Hans-Georg Wiedemann, Mettler Instruments AG, CH-8606 Greifensee, Zurich, Switzerland.*
The task of organizing the purchase and distribution of materials and assemblying the responses was delegated to Dr. Wiedemann, Vice Chairman of the Committee on Standardization.

IV. MATERIALS

The materials for these Certified Reference Materials were purchased from the Vacuumschmelze GMBH, Hanau, Federal Republic of Germany. They are, in ascending order of their magnetic transitions,

Permanorm 3
Nickel
Mumetal
Permanorm 5
Trafoperm

Typically, the magnetic transition temperature is highly susceptible to variations in composition such as might take plac from batch to batch; nickel is well known to be highly susceptib The Committee emphasizes that these materials are not being certified; only *these batches* of materials are certified.

V. PARTICIPANTS AND EQUIPMENT

The participants in the Sixth International Test Program are listed in Table I.

TABLE I

Participants and the Apparatus Used

Name and Affiliation	Apparatus
V. Amicarelli, Istituto Chimica Applicata, Facolta di Ingegneria, Bari, Italy	Mettler TA-1
G. D'Ascenzo, Istituto Chimico, Universita degli Studi di Roma, Rome, Italy	DuPont 951
P. A. Barnes, Chemistry Department, Leeds Polytechnic, Leeds, U. S.	Stanton-Redcroft TG 750
M. Escoubes, Laboratoire de Chimie Appliqee et Genie Chemique, Universite Lyon, Lyon, France	Setaram MTB 10-8
C. R. Foltz, R&D Center, Armstrong Cork Company, Lancaster, PA, U.S.A.	DuPont 951
P. K. Gallagher, Bell Telephone Laboratories, Inc., Murray Hill, N.J. U.S.A.	Perkin-Elmer TGS-1
B. Haglund, Coromant Research Center, Stockholm, Sweden	Mettler TA-1
P. J. Haines, Kingston Polytechnic Kingston, U. K.	Stanton-Redcroft HT-D
K. Heide, Sektion Chemie, Otto-Schott-Institut, Friedrich-Schiller-Universitat, Jena, DDR	Mettler TA-1
H. Kambe and R. Yokuta, University of Tokyo, Tokyo, Japan	Rigaku-Denki RTG and custom-built using Cahn Electrobalance

Name and Affiliation	Apparatus
H. G. McAdie and J. M. Jervis, Ontario Research Foundation, Mississauga, Ontario, Canada	R. L. Stone TGA-5B
O. Menis, U. S. National Bureau of Standards Gaithersburg, MD., U. S. A.	DuPont 951
T. Oshigama, Yaskawa Electric Manufacturing Co., Ltd., Kita-Kyushu, Fukuoka, Japan	Rigaku-Denki 8002
H. R. Oswald and J. P. Matthiew, Inorganic Chemical Institute, University of Zurich, Zurich, Switzerland	Mettler TA-1
T. Ozawa and Y. Takahashi, Electrotechnical Lab., Tamashi Branch, Tokyo, Japan	Rigaku-Denki 8002
A. Quivy and M. Harmelin, Centre d'Etudes de Chimie Metallurgique du CNRS, Vitry, France	C. I. Instruments Mark 2B
D. Stewart, Hoffmann-LaRoche, Inc., Nutley, N. J., U.S.A.	Perkin-Elmer TGS-1
H.-G. Wiedemann and E. Sturzenegger, Mettler-Instrumente AG, Greifensee, Switzerland	Mettler TA-1

VI. DATA ANALYSIS

The data were first examined by H.-G. Wiedemann, who gave a preliminary report at the Eleventh Meeting of the Committee on Standardization; complete data were not available at that time. Copies of the complete data were subsequently forwarded to P. D. Garn. Analysis of the data was discussed at a meeting of P. D. Garn, H.-G. Wiedemann and O. Menis in Gaithersburg, Md. in June, 1978 and in later correspondence, conference and telephone conversations.

The need for reference standards was immediately evident from the scatter of the data, substantially greater than anticipated. The several balance types, the variety of ways of

positioning the magnet and the diverse positions of the temperature measuring point with respect to the sample, all contributed to overall scatter.

Means for each participant were computed and transferred to cards. These were sorted in the several ways and the means and standard deviations computed for each group. Facilities at both the National Bureau of Standards and The University of Akron were used.

In every case, the data were analyzed *as received*. Any errors in interpretation or interpolation are included in the data in this certificate. The treatment is thereby representative of the inter-laboratory comparisons that would be made using these reference materials.

VII. RESULTS - TEMPERATURE DATA

A. Examination for Systematic Bias

Examination of the unweighted raw data and comparison with the means disclosed immediately that systematic bias was the major source of deviation. This was expected because of the diverse methods chosen by instrument manufacturers to provide a temperature measuring point. No extensive statistical evaluation appeared appropriate. Instead, the data from each observer were examined in terms of their relation to the means.

One set of data indicated deviations -- both high and low -- large enough to warrant close examination of the apparatus. This examination disclosed that the position of the magnet was such that the sample was in a near-zero vertical magnetic flux. The lack of magnetic field acting in the direction of the measured movement had led to inability to determine the designated points in a few cases as well as the major deviations noted above. The data were deleted.

In three other cases, the data on the highest temperature material reported by these participants differed from their other deviations both in direction and, quite strikingly, in magnitude. From the thermobalance characteristics, it was concluded that the temperature distributions changed substantially near the limit of operation of the furnace. These three data sets, two on Trafoperm and one on Permanorm 5, were deleted.

B. Examination for Random Error

The data on a given material from any one participant differed typically by 0-5° for any of the three points. Because there were no "standard" ways of arranging the magnet, comparison of identical instruments is less meaningful than in the previous test programs on DTA-DSC reference materials. It can be concluded, however, that data reproducible within a few degrees can be obtained on any one instrument.

C. Heating Rate Dependence

The data of individual participants were examined to learn whether or not a variation due to heating rate existed. In most cases the differences were small, 0-3°, much less than the systematic deviation discussed above. The differences wer not even completely consistent in sign. For these reasons the data from the two heating rates were joined in the subsequent data treatments.

One consideration which had led to the deletions of some data sets on Trafoperm and Permanorm 5 was the large apparent heating rate dependence for these whereas the same materials in other furnace assemblies yielded no similar dependence not did the lower temperature materials in the same thermobalances

An inference that the temperature distribution within the furnace asembly varies somewhat with heating rate may be drawn

and that this temperature distribution is more severe when the furnace is near its maximum operating temperature.

D. The Unweighted Means

With the exclusions noted above, the unweighted means and standard deviations were calculated from the participants' means. These are given in Tables 2-6. In only five of the 213 means did a participant's standard deviation for a given data point equal or exceed the overall standard deviation. Each of these five data sets was from an instrument which enabled a wide range of adjustment of the thermocouple position.

The several runs involved in the deleted sets were made at different times; that is, these measurements were done when work load permitted. Other instruments of the same type yielded much closer-lying data so an inference may be drawn that repositioning of the thermocouple junction from time to time led to the differences.

The small ranges of data for observers are disclosed in the means of the participants' standard deviations given in Table 7. Another measure of the typical standard deviation in a single laboratory is given by deleting the five outlying standard deviations mentioned above. It should be noted that the sum of the 15 deviations from the overall means (absolute values) was only 28°.

E. Significance of the Means

The mean values of these data are useful as reference points from which to measure the deviations found in an individual apparatus. The reference points can thereby be used to relate measurements from laboratory to laboratory -- even though different instruments are used -- because common materials, tested for homogeneity, were used.

The mean values of these data cannot be taken as an accurate measure of the magnetic transition temperature. The defined points on the TG curve in Figure 1 are necessarily arbitrary but are readily defined geometrically; they have no firm relationship in principle to the absolute value of the temperature at which the material loses its paramagnetism, even when that event occurs at a well-defined temperature. This does not detract in any way from their utility in dynamic measurements.

The test programs were necessary to insure that the participants were able to make suitable measurements. The four missing data sets are from a participant who reported only the T_1 and T_3. The T_2 can, of course, be measured without difficulty but no attempt was made to read the curves, to preserve the integrity of the *participant-supplied* data.

F. Participants Deviations from the Means

The variability of the overall data arises from instrumental parameters. This is evident from the consistent differences between any one participant's data and the overall means. Table 8 shows the mean deviation

$$\frac{\Sigma \text{ (participant mean - overall mean)}}{\text{number of measurements}}$$

for the several participants along with the standard deviations within the sets.

It is clear from the closeness of the individual data sets that the overall instrument behavior is consistent for each part cipant. Both the most positive value, an average of 10.9° above the mean values, and the most negative, an average of 13.7° below the mean value, have somewhat high standard deviation, 4.1 and 5.5° respectively, and the ranges were 5 to 19 and -7 to -24 respectively, the higher differences appearing at the higher temperatures in each case.

These increasing differences with temperature imply that substantially different temperature gradients exist in some furnaces at the lower and higher temperatures. They also demonstrate the need for calibration not simply of the thermocouple but of the *thermocouple+sample holder+heating rate* combination. The need for heating rate calibration appears to be very important when the apparatus is being used at or near its performance limits.

G. Derivative Thermogravimetric Data

Two investigators reported DTG data. Of these, one reported computer-generated values very close to the TG values. The T_1 data tended to be slightly lower for DTG. The DTG value for T_2 was typically either the same or 1° higher than the TG value. The T_3 value was generally 2-3° higher for DTG than TG, but a few data were higher and lower.

The other set of DTG data were from an electronic derivative system. The DTG data tended to be 4-10° higher than the TG values on heating and corresponding lower in cooling. The apparent *temperature* difference is presumably a *time* lag due to the capacitance in the derivative circuit. In typical RC circuits, the time constant can be adjusted to a (subjective) compromise between good sensitivity and acceptable noise. It should be possible to ascertain the typical time lag associated with the (resistance) setting in the circuit to enable a temperature correction.

The computer-derived data are typically generated from already-smoothed data; the agreement in the values reported out should be better than for an electronic derivative. The DTG values have validities no greater or less than those of the smoothed data.

H. Breadth of Deflection

A feature worth noting is the difference between the measured T_1 and T_3 which can be defined as the breadth of the

deflection. Not only are there large differences in breadths but also these have some consistencies with respect to both material and apparatus.

Table 9 shows the breadth, as measured by T_3-T_1 for the averages of investigators data. The differences among the materials are clear.

Nickel has an extremely sharp transition, which the small breadth reflects, whereas Permanorm 3 had the greatest span of measured differences, nearly five times that for nickel.

The $\Sigma(T_3-T_1)$ for each participant discloses that some had characteristically large or small breadths. Five participants had small values for one or more materials, these data were from four different instruments.

I. Sample Loading Position

Three general types of balances are readily identifiable -- the top-loaded, the bottom-loaded, and the beam-loaded, in which the terms identifies the position of the load (including sample) with respect to the beam. Even though there is no obvious direct effect arising from the load position, the question has been raised so a test of the data was indicated. The data are given, with means, standard deviations, and spans, in Tables 10-14, with as assembly of the means in Table 15.

The spans, the differences between the high and low investigator means for each group, disclose some systematic errors. The data on beam-loading have smaller spans than the others partly because only one (commercial) balance is represented. The top-loading balances were five in number, two manufacturers each represented by two models. The bottom-loading group represented six models, counting one particular model of balance separately for each different control and measuring system with which it is supplied. The separate counting is appropriate because manufacturers can position sensors differently in differen models.

In comparing the balance type means with the overall means, (Table 15), the weighting of the mean arising from the greater number of top-loading balances should be taken into account.

The deviations within a balance type can be attributed with confidence to differences in operator adjustment. Whereas the participants data in all tables are randomized, when the data in Table 6 are arranged in numerical order (to provide complete sets), the sequence of participants is precisely repeated for each of the five materials (Tables 2-6). Further, for the beam-loaded data of Tables 10-14, the same participant was consistently high, neither of the other two being consistently lowest. This suggests a systematic difference either in calibration, which can occur with any balance, or in placement of the measuring point, in this beam-loaded thermobalance.

The only balance used by as many participants as the beam-loaded DuPont instrument is the top-loaded Mettler TA-1, in which the thermocouple is fixed in a position near the sample. Table 16 shows the data for these four instruments. These data show a much smaller range than the whole group of the top-loading balances. Even so, there are ranges greater than thermocouple uncertainities. The probable sources of differences are both instrumental and personal. The instrument differences may arise from any component of the temperature measuring system and should be consistent in magnitude and direction whereas the personal variations in interpretation of curves may be either systematic or random both in magnitude and direction. The importance of systematic error is demonstrated by the similarities in the order of participants. For the ten sets of measurement of T_2 and T_3, the high → low ranking of participants was repeated precisely (accepting a tie as agreement) in nine cases. The exception was T_2 for Permanorm 3; even this change in order would occur for a shift of only 3° in the reported temperature.

The order of participants is not nearly so reproducible for T_1. Only in two of the five cases did the order coincide. However, two participants supplied all five high reported temperatures and two supplied all the low; one participant reported four of the second-highest values.

It is clear that a range of values several times the standar deviation of the individual data sets can be obtained from identical balances in different laboratories. It is also clear that the differences are largely systematic because the order of participants data is so often repeated for T_2 and T_3. The variation in reported values of T_1 may arise in part from subjective interpretation of the curve.

The existence of systematic variation even within balance types demonstrates the need for use of reference materials from a common source, and, emphasizes the importance of calibrating under programmed temperature as compared to an independent calibration of the thermocouple.

Comparing the larger groups, the consistently lower temperatures from the bottom-loaded balances are very obvious. The difference from the mean tends to increase with temperature. Some of the bottom-loaded balances have the temperature sensor below the sample holder. If there is a vertical temperature gradient in the furnace, this behavior would be the predictable result. Sorting the data in order of temperature bears this about,the same two participants reporting data invariably lower than the others. A third participant used a balance which had a support system close below the sample holder; these data were more nearly like those from other positions.

J. Cooling Data

The temperatures observed on cooling as the specimens regained their magnetic properties were virtually the same as on

heating. There is no evidence of a hysteresis that might interfere with any subsequent measurements.

K. Observation by Participants

A small number of observers supplemented their report of data with remarks on any unusual behavior. Any behavior that might tend to vitiate the data were investigated by study of related data from all laboratories. There is no question brought forward by more than one observer that remains unresolved.

VIII. CONCLUSIONS

A. General

The reproducibility demonstrated by the several participants indicates that the materials are suitable temperature reference standards. The variability between participants is largely due to instrument design, particularly with regard to the geometric relation between the sample and the temperature measuring point. In some instruments, variation of this relationship is possible from investigator to investigator or even from day to day in the same laboratory.

These variations, avoidable or not, make the use of temperature reference standards necessary for correlation of data.

B. Magnet Position

The development of thermobalances has taken many directions; the commercial products do not have a general enough form to enable specification of a single or even a small number of magnet positions. The committee, in its preparation of the protocol, assumed that each participant was familiar with the general properties of magnets and magnetism. As a precaution, however, it illustrated some already-tested positions that might be used in case the optimum position could not be used. (This occured in several cases because there was no access to a position close above or below the sample position.)

Because a thermobalance is designed to measure changes in mass, it is obvious that the most useful effect can be obtained by a force operating either in support of or in opposition to gravity. It is better that the force should pull away from the balance beam rather than toward it; that is, if a sample is supported above the beam, the upward pull of a magnet will not cause any horizontal deflection; the same is true of a downward pull on a sample below the beam. Even so, a small axial force toward the beam should cause little difficulty.

The magnet force needs to be only large enough to cause an unmistakable balance deflection, so a small magnetic flux is adequate when a magnet can be mounted directly above or below.

If a magnet must be mounted to the side, a horizontal force is introduced which is almost certain to be larger than the vertical component of flux. Whether or not a measurable mechanical deflection occurs depends not only upon the relative strength, position, and distance of the magnet but also upon the mass and moment arm of the sample support.

There is no reason to believe a horseshoe magnet is superior to a bar magnet or a disc magnet. Any magnet that can produce a detectable deviation is satisfactory.

C. Kind of Magnet

The basis for choice of the kind of magnet for this study was the convenience in mounting in an effective position. Horseshoe and bar alloy magnets are commonly available; ceramic based magnets are still rare; electromagnets are generally too large for convenient mounting. This lack of convenience may have discouraged some participants.

The magnetic flux could most easily be generated by a direct current flowing through a vertical-axis coil. It is reasonable to expect that use of magnetic reference materials will lead manufacturers to include a well-placed coil in future thermobalance assemblies. Such a coil could even be used intermittent

to monitor an actual experiment. Further, the field strength could be changed for use with different sensitivities.

D. Recommended Procedures

1. Position of Magnet

The optimum position of the magnet is directly above or below the sample holder so that the magnet flux is aligned with the gravitational field. Another possible arrangement is the use of a small magnet well out of the heated zone with the flux concentrated by a permeable rod leading closer to the sample.

2. Strength of Magnet Field

No a priori values can be established. The magnetic flux for a given magnet decreases with the second power of the distance.

The magnet need not be large because it needs to produce only an identifiable deflection, not a half- or quarter-scale deflection.

A variable field would be useful to enable calibration during the ordinary use of the thermobalance. This can be done by:

(a) using a electromagnet;

(b) varying the position (proximity) of the magnet; or

(c) if permeable rods are used, changing the length of the rod.

3. Multiple Calibrations

There is no reason why more than one reference material cannot be used in a single run. Difficulty in recording may arise from using an excessive portion of the range for calibration but re-zeroing can be used to enable full use of the balance range for the real weight loss.

E. Reporting Practices

This committee has previously recommended reporting details about the experiment and the experimental apparatus[3]. This information enables the reader to judge whether or not some or all of any apparent disagreement is due to apparatus or procedure differences.

In reporting data from experiments in which the temperature calibration was done using magnetic transition, this additional information should be included:

1. The physical relation between the sample and the magnet; and
2. the position of the temperature sensor with respect to the sample, specifying whether or not it is in contact with the sample holder.

IX. THE CERTIFIED REFERENCE MATERIALS

Each of these Certified Reference Materials is supplied in the form of a thin metal strip or strips that can be cut to whatever size provides a suitable response with the magnet an sensitivity range used. In principle, the pieces should be re-usable but the experiences of the participants were varied. The committee does not recommend re-use.

Most participants have been able to place a magnet close enough that 10-20 mg provided an easily detectable signal with commercial apparatus. Generally, quite sensitive ranges were used for the test program. In case a greater range is used routinely and inclusion of the reference material with the worki run is to be practiced, a larger piece may be useful. However, if the heating conditions are to be duplicated for a calibration run, a more sensitive range and small piece of reference materia will provide equally valid calibration data.

X. ACKNOWLEDGEMENTS

The material contained in this report represents the labors of eighteen different laboratories, all of whom voluntarily contributed time and effort to participate in the Sixth International Test Program. The authors are grateful to them and their supporting organizations.

The protocol was developed from experience with an earlier test program, the Fifth ITP. The authors are grateful to those participants, who are G. Hentze, J. Klingner, and V. Kramer from the Federal Republic of Germany; M. Dechamps and M. Escoubes from France; J. Paulik from Hungary; H. Kambe, T. Kaneko, T. Ozawa, H. Tasui, and R. Yokota from Japan; and H. Oswald from Switzerland.

For the special support of these authors in carrying out the test program and the computations, these authors are grateful to The University of Akron, the United States National Bureau of Standards, and to Mettler Instrumente A. G.

The authors also acknowledge the assistance of Messrs. J. P. Cali, R. K. Kirby and G. Uriano of the NBS Office of Standard Reference Materials in preparing for the marketing of these materials and Mrs. Grace Musyt in preparation of the manuscript.

XI. REFERENCES

1. McAdie, H. G.; Garn, P. D.; Menis, O.; NBS Special Publication 260-40. U. S. Government Printing Office, Washington, D. C. 20402

2. S. D. Norem, M. J. O'Neill, A. P. Gray, Proc. Third Toronto Symp. Thermal Analysis, 1969, pp221-32. Edited by H. G. McAdie. Chem. Inst. Canada, Ottawa, Can.

3. H. G. McAdie, Anal. Chem. 39, 543 (1967).

APPENDIX A

PROCEDURES

Sixth International Test Programme

Temperature Standards for TG

Magnetic Reference Temperature Standard Method

1. The operating conditions of each instrument should be those normally employed for thermogravimetric measurements.

2. The accuracy of the temperature sensor should be known. The Committee prefers use of recognized temperature standards.

3. All temperature data T_i, T_{max} and T_e defined in the accompanying figure, should be reported to nearest 1°C.

4. Each material should be examined at heating rates of 1-2°C. min^{-1}.

5. A time-temperature curve from the temperature sensor should be included. Apparatus with DTG should also include the DTG curve.

6. One curve of the balance with emply sample holder exposed to the magnet should be supplied, using the same sensitivity employed with the test material.

7. The test material should be used as supplied. Use whatever number of piéces is needed. If there is need, ask the Chairman for instructions.

8. With the measurements a sketch or photograph of the magnet-furnace-sample arrangement should be added. (See attached sketch.)

9. Platinum or its alloys should not be in direct mechanical contact with the metal sample. The thermocouple may be in direct contact with the sample holder if the design permits. If the thermocouple is not in contact with the sample support assembly, the separation should be stated.

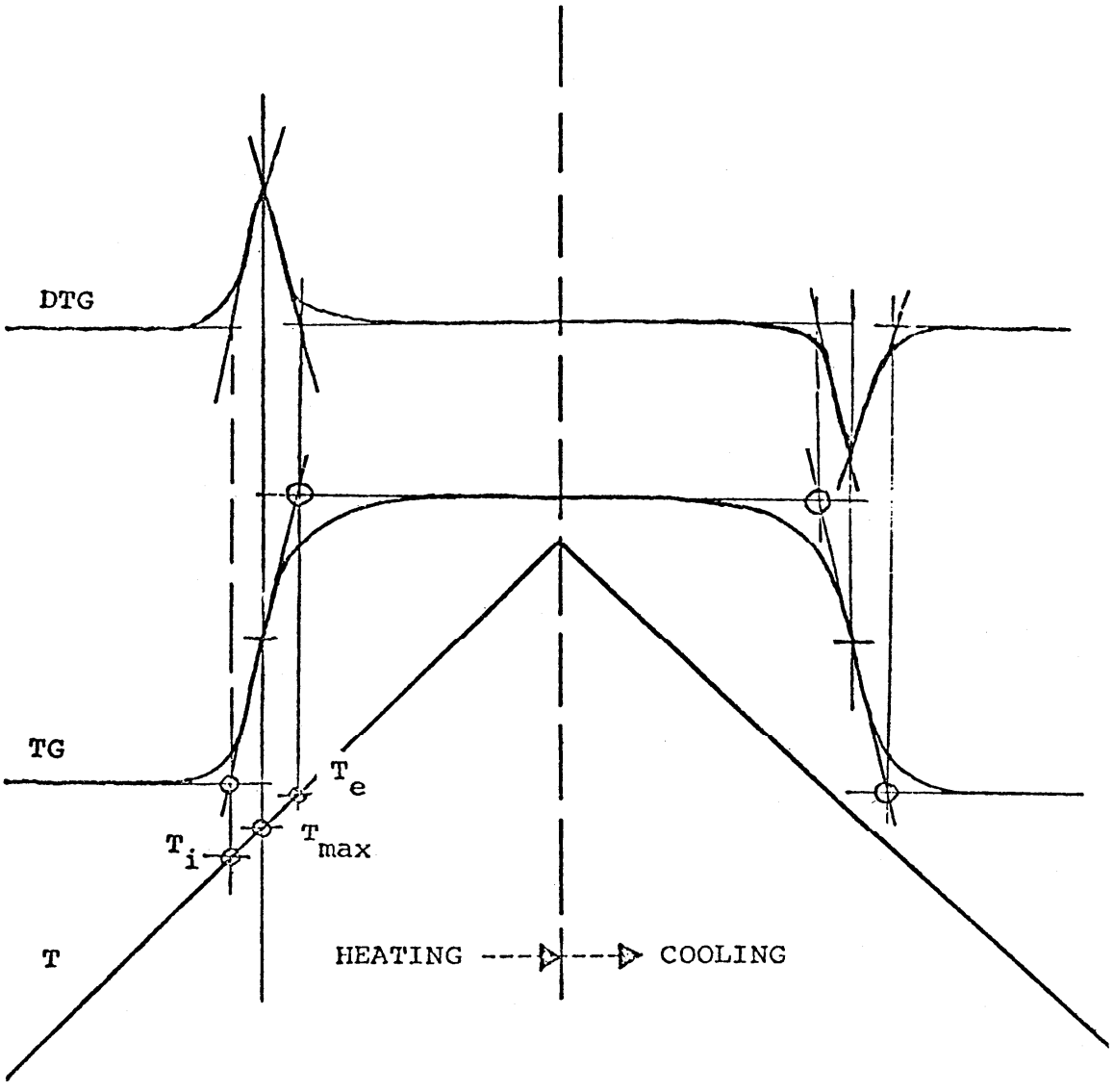
10. A minimum of 2 runs of two cycles each on separate samples should be made at each heating rate.

11. For the investigations a low sensitivity of the balance should be used in order that effects of buoyancy, oxidation, etc., may be reduced vs. ferro-paramagnetic effect.

12. All runs should be one in oxygen-free nitrogen, dried over $Mg(ClO_4)_2$ or its equivalent.

13. Results should be reported according to the recommendations for good practice defined by the Committee [Anal. Chem. 39, 543 (1969)].

14. Send curves and data to Dr. Hans-Georg Wiedemann, Mettler Instruments AG, CH-8606 Greifensee, Zürich, Switzerland.



INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

COMMITTEE ON STANDARDIZATION

INSTRUMENT DESCRIPTION

Sixth International Test Program

Temperature Standards for TG

Investigator _____

Mailing Address _____

Instrument ManufacturerQ _____

Instrument Model No. _____

T Thermocouple* Material _____

T Thermocouple* Reference Temp. (°C) _____

Was T Thermocouple* Calibrated: Yes___No___ If yes, How?_____

_____

Method of T Measurment (Strip chart, X-Y recorder, other) _____

Sample Holder Material _____

Description of Sample Holder Size and Shape _____

Sample Atmosphere Flow Pattern _____

Sample Atmosphere Flow Rate ($cc.min.^{-1}$) _____

The temperature sensor

- ◯ is in the sample
- ◯ is in the sample holder
- ◯ is _____mm above the sample
- ◯ is_____mm below the sample
- ◯ supports the sample holder
- ◯ is_____ other

Please supply a small drawing or photograph of the sample holder or enclosure.

*If another temperature sensor was used please describe.

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

COMMITTEE ON STANDARDIZATION

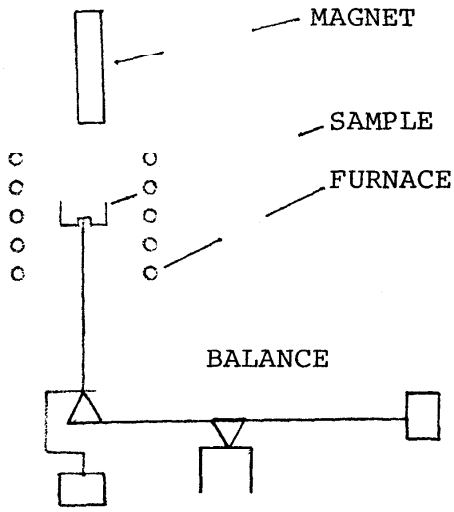
DATA REPORT

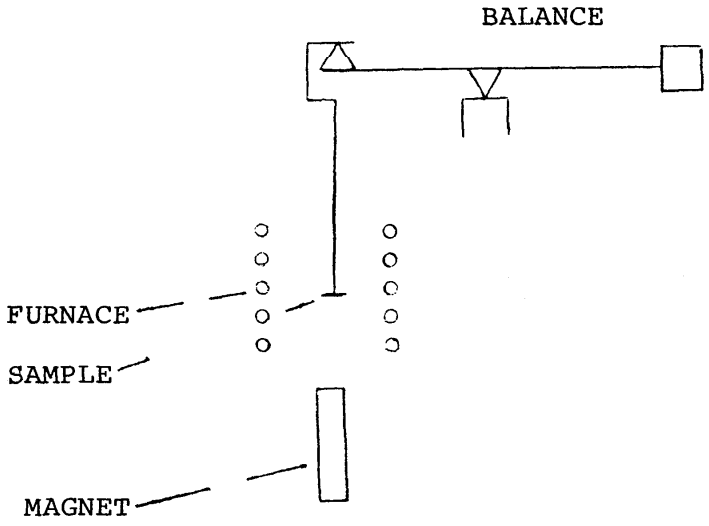
Sixth International Test Programme

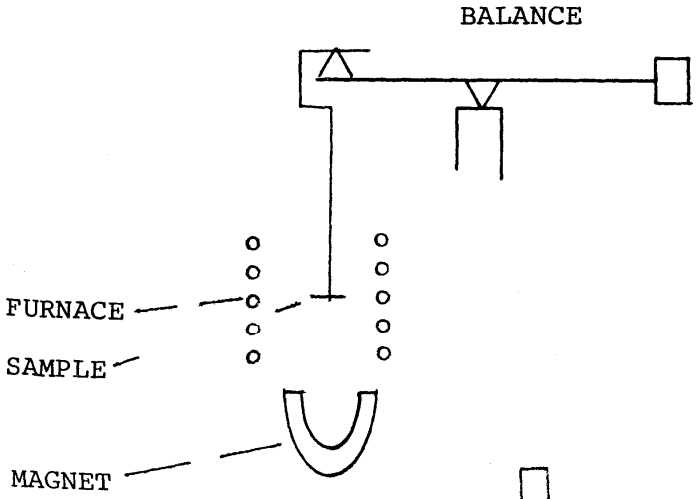
Temperature Standards for TG

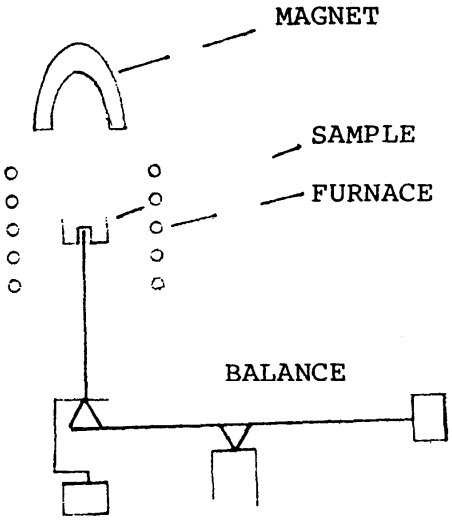
Magnetic Reference Point Method

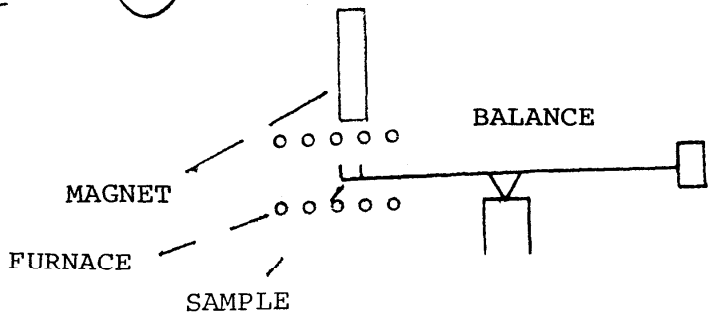
Chart or Run No.	Sample Weight (mg)	TG Sensitivity $mg.cm^{-1}$	DTG Sensitivity $mg.\ cm^{-1}.min^{-1}$	Chart Speed $cm.\ min^{-1}$	Heating	Temperature (°C) T_i T_{max} T_e (See Attached Sketch)


MAGNET
SAMPLE
FURNACE
BALANCE


BALANCE
FURNACE
SAMPLE
MAGNET


BALANCE
FURNACE
SAMPLE
MAGNET


MAGNET
SAMPLE
FURNACE
BALANCE


BALANCE
MAGNET
FURNACE
SAMPLE

APPENDIX B

WORK SHEETS

Material	Point	Date	Date	Date	Date	Date	Date	Date
Permanorm 3	T_1	____	____	____	____	____	____	____
	T_2	____	____	____	____	____	____	____
	T_3	____	____	____	____	____	____	____
Nickel	T_1	____	____	____	____	____	____	____
	T_2	____	____	____	____	____	____	____
	T_3	____	____	____	____	____	____	____
Numetal	T_1	____	____	____	____	____	____	____
	T_2	____	____	____	____	____	____	____
	T_3	____	____	____	____	____	____	____
Permanorm 5	T_1	____	____	____	____	____	____	____
	T_2	____	____	____	____	____	____	____
	T_3	____	____	____	____	____	____	____
Trafoperm	T_1	____	____	____	____	____	____	____
	T_2	____	____	____	____	____	____	____
	T_3	____	____	____	____	____	____	____

APPENDIX B

WORK SHEETS

Material	Point	Date	Date	Date	Date	Date	Date
Permanorm 3	T_1						
	T_2						
	T_3						
Nickel	T_1						
	T_2						
	T_3						
Numetal	T_1						
	T_2						
	T_3						
Permanorm 5	T_1						
	T_2						
	T_3						
Trafoperm	T_1						
	T_2						
	T_3						

APPENDIX B

WORK SHEETS

Material	Point	Date	Date	Date	Date	Date	Date	Date
Permanorm 3	T_1							
	T_2							
	T_3							
Nickel	T_1							
	T_2							
	T_3							
Numetal	T_1							
	T_2							
	T_3							
Permanorm 5	T_1							
	T_2							
	T_3							
Trafoperm	T_1							
	T_2							
	T_3							

APPENDIX B

WORK SHEETS

Material	Point	Date	Date	Date	Date	Date	Date
Permanorm 3	T_1						
	T_2						
	T_3						
Nickel	T_1						
	T_2						
	T_3						
Numetal	T_1						
	T_2						
	T_3						
Permanorm 5	T_1						
	T_2						
	T_3						
Trafoperm	T_1						
	T_2						
	T_3						

APPENDIX B

WORK SHEETS

Material	Point	Date	Date	Date	Date	Date	Date	Date
Permanorm 3	T_1							
	T_2							
	T_3							
Nickel	T_1							
	T_2							
	T_3							
Numetal	T_1							
	T_2							
	T_3							
Permanorm 5	T_1							
	T_2							
	T_3							
Trafoperm	T_1							
	T_2							
	T_3							

Figure 1. The defined points on the thermogravimetric temperature calibration curve.

A best-straight-line is drawn through the weight-gaining or weight-losing portion of the curve. The intersections of the base lines with this line are defined as the initial temperature, T_1, and the end temperature, T_3. The mid-point of the line if T_2.

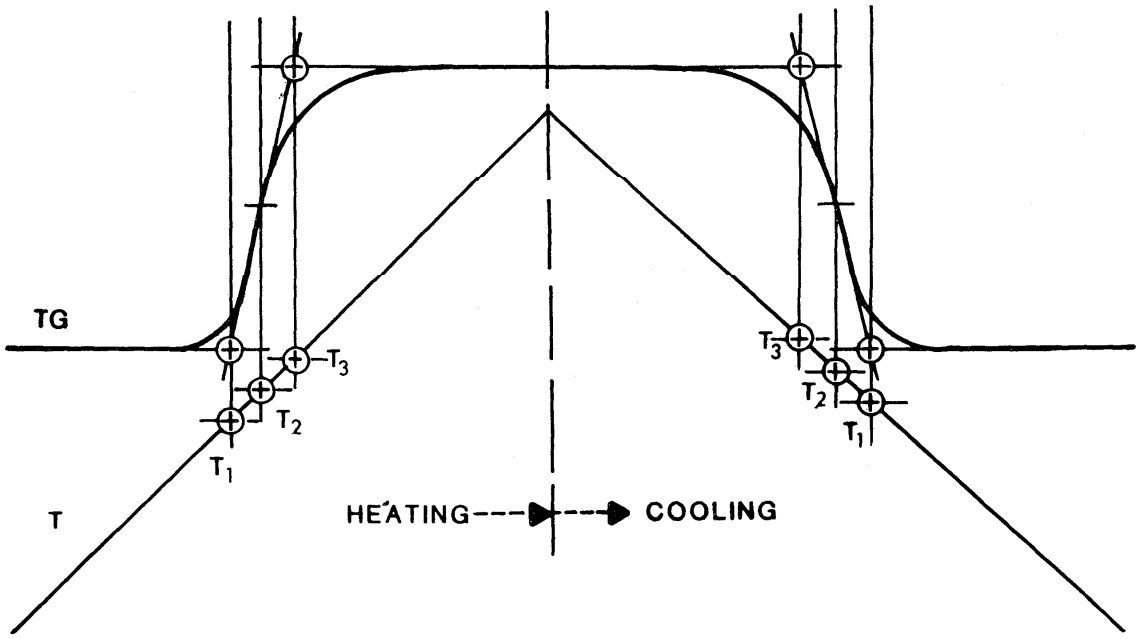


Figure 2. Magnet-Sample relations reported in the Sixth International Test Program.

The magnets were either a "horseshoe" or bar. The representations a to d show the relationships in the top-loaded balances; c and d differ in that in d the magnet poles were on opposite sides of the furnace tube, whereas in c the magnet poles did not extend around the furnace. Sketches e and f are horseshoe and bar magnets above a beam-loaded-balance pane. Sketches g and j show horseshoe and bar magnet relations to bottom-loaded samples; only in the arrangement shown in j was the magnet physically inside the furnace assembly.

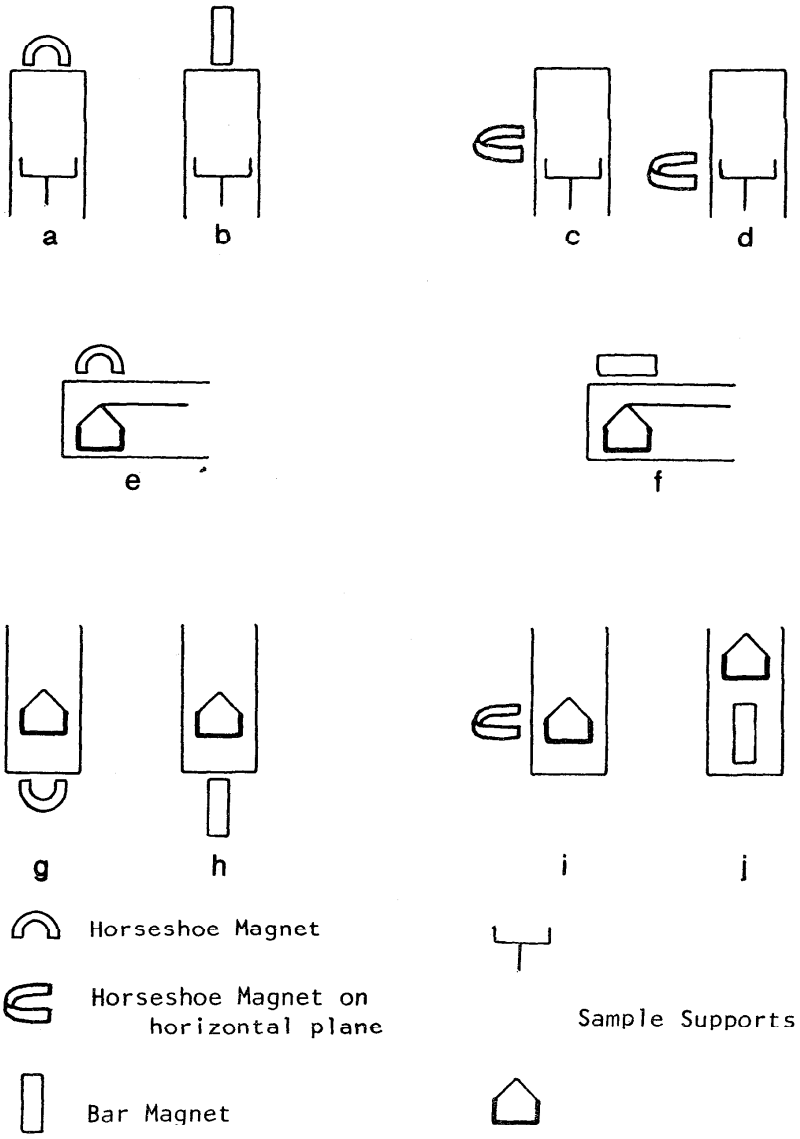


TABLE 2

Participant Means and Overall Means, Standard Deviations and Ranges for Permanorm 3

	T_1	T_2	T_3
	255°C	260°C	265°C
	253	260	266
	242	255	264
	258	266	276
	251	257	265
	253	260	266
	256	-	270
	260	264	277
	251	259	266
	263	266	273
	253	257	262
	257	260	265
	246	250	257
	248	253	259
	248	254	260
	253	259	267
	260	270	278
	252	255	260
Range	242-263°C	250-270°C	255-278°C
Mean Temperature	253.3°C	259.1°C	266.4°C
Standard Deviation	5.3°	5.2°	6.2°

TABLE 3

Participant Means and Overall Means
Standard Deviations and
Ranges for Nickel

	T_1	T_2	T_3
	344°C	345°C	346°C
	355	357	358
	354	357	359
	346	347	348
	353	357	358
	352	353	355
	350	350	351
	354	-	357
	360	360	363
	360	361	362
	350	352	352
	350	-	351
	343	344	345
	348	349	350
	351	355	359
	357	359	360
	348	350	353
	350	351	353
Range	343-360°C	344-361°C	345-363°C
Mean Temperature	351.4°C	352.9°C	354.4°C
Standard Deviation	4.8°	5.3°C	5.4°C

TABLE 4

Participant Means and Overall Means
Standard Deviations and
Ranges for Mumetal

	T_1	T_2	T_3
	376°C	378°C	380°C
	380	382	389
	373	382	390
	383	385	388
	376	384	391
	375	376	377
	381	-	387
	392	395	398
	377	380	387
	377	380	387
	376	381	385
	363	366	370
	380	383	387
	380	391	393
	376	385	390
	378	380	380
	386	389	393
	365	370	375
Range	363-392°C	366-395°C	370-398°C
Mean Temperature	377.4°C	381.6°C	385.9°C
Standard Deviation	6.3°	7.0°	7.2°

TABLE 5

Participant Means and Overall Means, Standard Deviations and Ranges for Permanorm 5

	T_1	T_2	T_3
	458°C	465°C	470°C
	450	454	458
	455	-	460
	450	454	458
	447	458	462
	448	450	452
	435	438	441
	450	452	456
	451	454	461
	448	450	455
	457	460	465
	454	458	464
	452	458	461
	442	448	452
	463	466	471
	458	460	463
Range	435-463°C	438-466°C	441-470°C
Mean Temperature	451.1°C	455.0°C	459.3°
Standard Deviation	6.7°	7.1°	7.3°

TABLE 6

Participant Means and Overall Means, Standard Deviations and Ranges for Trafoperm

	T_1	T_2	T_3
	755°C	757°C	760°C
	760	763	766
	755	756	757
	736	737	740
	747	749	752
	744	748	750
	748	750	751
	728	731	733
	767	769	771
	752	759	762
	753	754	755
Range	728-767°C	731-769°C	733-771°C
Mean Temperature	749.5°C	752.1°C	754.3°C
Standard Deviation	10.9°	10.9°	11.0°

TABLE 7

Arithmetic Means of Standard Deviations (in Degrees) Calculated from Each Participant's Data

	Permanorm 3	Nickel	MuMetal	Permanorm 5	Trafoperm
T_1	2.1 (1.8)*	1.6	2.2	2.9 (2.3)*	1.8
T_2	2.3 (2.4)*	1.3	2.2	2.9 (2.2)*	1.6
T_1	2.6	1.6	2.9	3.5 (2.6)*	1.8

*Recalculated mean of participants' standard deviations after deleting five outlying data.

TABLE 8

Averages of the Differences of Participants' Means from Overall Means with the Standard Deviations of the Differences

Participant		Participant	
Mean Difference	Standard Deviation	Mean Difference	Standard Deviation
-10.4°	4.7°	1.5°	3.8°
3.3	5.3	-8.1	3.9
-0.9	3.8	-0.7	2.8
-3.4	4.3	6.2	3.0
-2.6	2.6	-13.7	5.5
0.3	4.4	3.0	1.8
10.9	4.1	7.2	2.0
-0.2	2.6	-0.5	2.8
4.6	4.9		

Mean Standard Deviation = 3.59 $\pm$ 1.12°

TABLE 9

Breadth of Deflection, T_3-T_1, for all Participants and Each Material and the Sum of T_3-T_1 for Each Participant.

(Data are arranged in numerical order.)

	Perma-norm 3	Nickel	Mumetal	Perma-norm 5	Trafo-perm	Sum
	7	1	4	4	2	21
	8	1	4	4	2	21*
	9	1	5	5	2	22*
	10	2	6	5	3	26#
	10	2	6	6	4	28
	11	2	7	6	4	28
	12	2	7	8	5	31*
	13	2	7	8	5	32*
	13	3	9	8	5	34
	14	3	9	8	6	34
	14	3	10	9	6	35
	14	3	10	10	10	37
	15	3	10	10		38*
	15	3	12	10		50
	17	5	13	12		42*
	18	5	14	15		52
	18	5	15			73
	22	8	17			
Mean	13.3°	3.0°	9.2°	8.0°	4.5°	35.5°@
Standard Deviation	3.9°	1.8	4.1°	3.0°	2.3°	13.2°

*Four data points

#Three data points

@Calculated from the ten complete sets of data. In addition to the data dropped, there were in some cases missing data because the participant was unable to measure T_3 satisfactory.

TABLE 10

Investigator Means and Group Means, Standard Deviations, and Spans Sorted By Beam-Sample Relationship, for Permanorm 3

Loading	T_1	T_2	T_3
Top	253°C	257°C	262°C
	263	266	273
	260	264	277
	251	259	266
	252	255	260
	260	270	278
	248	253	259
	242	255	264
	256	---	270
Mean	253.9°C	259.9°C	267.7°C
Standard Deviation	6.6°	6.1°	7.2°
Span	21°	20°	23°
Beam	258°	266°	276°
	255	260	265
	253	259	267
Mean	255.3°C	261.7°C	269.3°C
Standard Deviation	2.5°	3.8°	5.9°
Span	5°	7°	11°
Bottom	246°C	250°C	257°C
	253	260	266
	253	260	268
	251	257	265
	257	260	265
	248	254	260
Mean	251.3°C	256.8°C	263.5°C
Standard Deviation	3.9°	4.1°	4.1°
Span	9°	10°	11°

TABLE 11

Investigator Means and Group Means, Standard Deviations, and Spans Sorted By Beam-Sample Relationship, for Nickel

Loading	T_1	T_2	T_3
Top	352°C	353°C	355°C
	351	355	359
	350	352	352
	360	361	362
	360	360	363
	353	357	358
	350	350	351
	354	357	359
	354	---	357
Mean	353.8°C	355.6°C	357.3°C
Standard Deviation	3.8°	3.8°	4.1°
Span	10°	11°	12°
Beam	357°C	359°C	360°C
	350	351	353
	355	357	358
Mean	354.0°C	355.7°C	357.0°C
Standard Deviation	3.6°	4.2°	3.6°
Span	7°	8°	7°
Bottom	343°C	344°C	345°C
	348	350	353
	346	347	348
	344	345	346
	348	349	350
	350	---	351
Mean	346.5°C	347.0°C	348.8°C
Standard Deviation	2.7°	2.5°	3.1°
Span	7°	6°	8°

TABLE 12

Investigator Means and Group Means, Standard Deviations, and Spans Sorted By Beam-Sample Relationship, for Mumetal

Loading	T_1	T_2	T_3
Top	376°C	381°C	385°C
	392	395	398
	378	380	380
	380	390	392
	386	389	393
	376	385	390
	373	382	390
	377	380	387
	381	---	387
Mean	379.9°C	385.2°C	389.1°C
Standard Deviation	5.9°	5.6°	5.2°
Span	22°	23°	24°
Beam	380°C	383°C	387°C
	383	385	388
	376	378	380
Mean	379.7°C	382.0°C	385.0°C
Standard Deviation	3.5°	3.6°	4.4°
Span	7°	7°	8°
Bottom	380°C	382°C	389°C
	375	376	377
	377	380	387
	363	366	370
	365	370	375
	376	384	391
Mean	372.7°C	376.3°C	381.5°C
Standard Deviation	6.9°	7.1°	8.6°
Span	17°	18°	21°

TABLE 13

Investigator Means and Group Means, Standard Deviations, and Spans Sorted by Beam-Sample Relationship, for Permanorm 5

Loading	T_1	T_2	T_3
Top	451°C	454°C	461°C
	458	460	463
	452	458	461
	442	442	446
	447	458	462
	454	458	464
	463	466	471
	455	---	460
Mean	452.8°C	456.6°C	461.0°C
Standard Deviation	6.4°	7.4°	7.0°
Span	21°	24°	25°
Beam	457°C	460°C	465°C
	450	452	456
	458	465	470
Mean	455.0°C	459.0°C	463.7°C
Standard Deviation	4.4°	6.6	7.1°
Span	8°	13°	14°
Bottom	450°C	454°C	458°C
	435	438	441
	450	455	458
	448	450	452
	442	448	452
Mean	445.0°C	449.0°C	452.2°C
Standard Deviation	6.5°	6.8°	6.9°
Span	15°	17°	17°

TABLE 14

Investigator Means and Group Means, Standard Deviations, and Spans Sorted By Beam-Sample Relationship, for Trafoperm

Loading	T_1	T_2	T_3
Top	743°C	746°C	749°C
	744	745	746
	755	756	757
	760	763	766
	767	769	771
	752	759	762
Mean	753.5°C	756.3°C	758.5°C
Standard Deviation	9.3°	9.5°	9.7°
Span	24°	24°	25°
Beam	755°C	757°C	760°C
	747	749	752
Mean	751.0°C	753.0°C	756.0°C
Standard Deviation	5.7°	5.7°	5.7°
Span	8°	8°	8°
Bottom	728°C	731°C	733°C
	736	737	740
	753	754	755
Mean	739.0°C	740.7°C	742.7°C
Standard Deviation	12.8°	11.9°	11.2°
Span	25°	23°	22°

TABLE 15

Summary of Rounded Means Sorted By Beam-Sample Relationship

Material		Overall Mean	Top-Loading	Beam-Loading	Bottom-Loading
Perma-norm 3,	T_1	253.4°C	253°C	255°C	251°C
	T_2	259.2	259	262	257
	T_3	266.9	267	269	264
Nickel	T_1	351.4	354	354	346
	T_2	352.9	355	356	347
	T_3	354.9	357	357	349
Mumetal	T_1	377.8	379	380	373
	T_2	381.7	384	382	376
	T_3	385.8	388	385	382
Perma-norm 5,	T_1	450.9	453	455	445
	T_2	454.7	457	459	449
	T_3	458.2	460	464	452
Trafo-perm	T_1	748.5	754	751	739
	T_2	750.0	756	753	741
	T_3	751.0	754	756	743

TABLE 16

Investigator Means and Spans For a
Single Model of Top-Loading Balance

Permanorm 3	T_1	T_2	T_3
	251°C	258°C	266°C
	248	253	259
	252	255	260
	242	255	264
Span	9°	5°	7°
Nickel	353°C	357°C	358°C
	351	355	359
	352	353	355
	350	352	352
Span	3°C	5°C	7°C
Mumetal	378°C	380°C	380°C
	373	382	390
	376	385	390
	376	381	385
Span	5°	5	10
Permanorm 5	448°C	450°C	455°C
	447	458	462
	451	454	461
	454	458	464
Span	7°	8°	9°
Trafoperm	760°C	763°C	766°C
	748	750	751
	755	756	757
	752	759	762
Span	12	13	15