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REFERENCE MATERIALS FOR THERMOGRAVIMETRY*

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The thermobalances available commercially have a wide range of heater-sample-temperature sensor relationships. Because of the differences, relating data from one apparatus to another has been imprecise. The International Confederation for Thermal Analysis has certified a set of magnetic reference materials for thermogravimetry. Analysis of the test data from eighteen instruments shows that, whereas data from several models of a single instrument show spans of measured temperatures from 3—15°, the spans for all instruments were 17—39°. The differences are systematic, not only between balance types but also for the same model of instrument in different laboratories. The use of these certified reference materials enables correlation between instruments.

The commercially available thermobalances 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 report.

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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.

The materials described herein have been certified by the International Confederation for Thermal Analysis as temperature standards for thermogravimetry. This paper describes the testing done by the ICTA Committee on Standardization and the data treatment and interpretation. The materials are four alloys and one metal that are magnetically permeable. In conjunction 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.

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.

The test program

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[1] 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.

After the initial trials by some of the Committee, a 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.

The several members of the Committee selected and contacted persons that were active in thermogravimetry and had a concern for data interpretation. 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; then after consideration of the larger set of data, the Committee decided to recommend to the ICTA Council that the materials be certified. The catalog number for the set is GM 761.

The preparation of the certificate was assigned to these authors. Upon approval by the ICTA Executive Committee, the certificate was printed and the materials and certificate forwarded to the United States National Bureau of Standards for distribution.

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 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 place from batch to batch; nickel is well known to be highly susceptible. The Committee emphasizes that these materials are not being certified; only these batches of materials are certified.

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.

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_1, T_2, T_3, 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 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 instrumenta 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 was a routine check for unusual behavior.

6. *All runs should be done in oxygen-free nitrogen, dried over* $Mg(ClO_4)_2$ *or its equivalent.* This was precautionary, to eliminate any differences in treatment which might obscure differences between balances.

7. *Results should be reported according to the recommendations for good practice defined by the Committee (Anal. Chem.* 39, (1967) 543). This was a reminder.

8. *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.

The need for reference standards was immediately evident from the scatter of the data, which was even 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 report. The treatment is thereby representative of the inter-laboratory comparisons that would be made using these reference materials.

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 opera-

tion of the furnace. These three data sets, two on Trafoperm and one of Permanorm 5, were deleted.

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.

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 were not even completely consistent in sign.

One of the considerations that led to the deletions of some data sets of 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 nor did the lower temperature materials in the same thermobalances.

An inference that the temperature distribution within the furnace assembly 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.

Table 1

Participant means and overall means, standard deviations and ranges for Permanorm 3

	T_1,°C	T_2,°C	T_3,°C
	255	267	265
	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	250–270	255–278
Mean temperature	253.3	259.1	266.4
Standard deviation	5.3	5.2	6.2

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 1 – 5. 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.

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

Table 2

Participant means and overall means standard deviations and ranges for Nickel

	T_1, °C	T_2, °C	T_3, °C
	344	345	346
	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	344 – 361	345 – 363
Mean temperature	351.4	352.9	354.4
Standard deviation	4.8	5.3	5.4

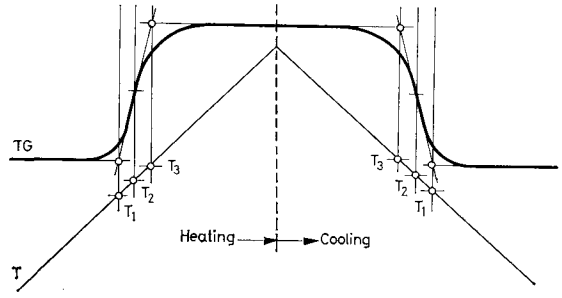

Fig. 1. The defined points of the thermogravimetric temperature calibration curve

Table 3

Participant means and overall means standard deviations and ranges for Mumetal

	T_1,°C	T_2,°C	T_3,°C
	376	378	380
	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	366–395	370–398
Mean temperature	377.4	381.6	385.9
Standard deviation	6.3	7.0	7.2

Table 4

Participant means and overall means, standard deviations and ranges for Permanorm 5

	T_1,°C	T_2,°C	T_3,°C
	458	465	470
	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	438–466	441–4 0
Mean temperature	451.1	455.0	459.3
Standard deviation	6.7	7.1	7.3

Table 5

Participant means and overall means, standard deviations and ranges for Trafoperm

	T_1,°C	T_2,°C	T_3,°C
	755	757	760
	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	731–769	733–770
Mean temperature	749.5	752.1	754.3
Standard deviation	10.9	10.9	11.0

Table 6

Averages of the differences of participants' means from overall means with the standard deviations of the differences

Participant		*Participant*	
Mean difference, °C	Standard deviation, °C	Mean difference, °C	Standard deviation, °C
−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 ± 1.12°C.

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.

Participants deviations from the mean – 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 6 shows the mean deviation

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

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 participant. 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.

Derivative thermogravimetric data – Two investigators reported DTG data. Of these, one reported computer-generated values very close to the TG values.

Table 7

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	Trafoperm	Sum
	7	1	4	4	2	21
	8	1	4	4	2	21 [1]
	9	1	5	5	2	22 [1]
	10	2	6	5	3	26 [2]
	10	2	6	6	4	28
	11	2	7	6	4	28
	12	2	7	8	5	31 [1]
	13	2	7	8	5	32 [1]
	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 [1]
	15	3	12	10		50
	17	5	13	12		42 [1]
	18	5	14	15		52
	18	5	15			73
	22	8	17			
Mean	13.3°C	3.0°C	9.2°C	8.0°C	4.5°C	35.5°C [3]
Standard deviation	3.9°C	1.8°C	4.1°C	3.0°C	2.3°C	13.2°C

[1] Four data points.
[2] Three data points.
[3] 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.

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 lags associated with the (resistance) setting in the circuit to enable a temperature correction.

Table 8

Investigator means and group means, standard deviations, and spans sorted by beam-sample relationship, for Permanorm 3

Loading	T_1 °C	T_2, °C	T_3, °C
Top	253	257	262
	263	266	273
	260	264	277
	251	259	266
	252	255	260
	260	270	278
	348	253	259
	242	255	264
	256	—	270
Mean	253.9	259.9	267.7
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	261.7	269.3
Standard deviation	2.5	3.8	5.9
Span	5	7	11
Bottom	246	250	257
	253	260	266
	253	260	268
	251	257	265
	257	260	265
	248	254	260
Mean	251.3	256.8	263.5
Standard deviation	3.9	4.1	4.1
Span	9	10	11

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.

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

Investigator means and group means, standard deviations, and spans sorted by beam-sample relationship, for Nickel

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

Table 7 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.

Table 10

Investigator means and group means, standard deviations, and spans sorted by beam-sample relationship, for Mumetal

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

Sample loading positi — Three general types of balances are readily identifiable — the top-loaded, the bottom-loaded, and the beam-loaded, in which the terms identify 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, a test of the data was indicated. The data are given, with means, standard deviations, and spans, in Tables 8–12, with assembly of the means in Table 13.

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

Table 11

Investigator means and group means, standard deviations, and spans sorted by beam-sample relationship, for Permanorm 5

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

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 different models. In comparing the balance type means with the overall means (Table 13), the weighting of the mean arising from the greater number of toploading balances should be taken into account.

Table 12

Investigator means and group means, standard deviations, and spans sorted by beam-sample relationship, for Trafoperm

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

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 5 are arranged in numerical order (to provide complete sets), the sequence of participants is precisely repeated for each of the five materials (Tables 1–5). Further, for the beam-loaded data of Tables 8–12, 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, of 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 14 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 uncertainties. The

Table 13

Summary of rounded means sorted by beam-sample relationship

Material		Overall mean	Top-loading	Beam-loading	Bottom-loading
Permanorm 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
Permanorm 5,	T_1	450.9	453	455	445
	T_2	454.7	457	459	449
	T_3	458.2	460	464	452
Trafoperm	T_1	748.5	754	751	739
	T_2	750.0	756	753	741
	T_3	751.0	754	756	743

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 important 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 standard 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.

Table 14

Investigator means and spans
for a single model of top-loading balance

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

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 out, 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.

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.

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.

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.

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 occurred 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.

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

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 an 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.

Reporting practices — This committee has previously recommended reporting details about the experiment and the experimental apparatus [2]. 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.

*

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RÉSUMÉ — Les thermobalances en vente ont une large gamme de dispositions respectives de l'ensemble chauffage — échantillon — détecteur de température. A cause de ces différences le rapprochement des données fournies d'un appareil à l'autre est imprécis. Le Confédération Internationale d'Analyse Thermique propose une série de substances de référence magnétiques certifiées pour la thermogravimétrie. L'analyse des données d'essais fournies par dixhuit instruments montre que le données fournies par les différents modèles d'un même instrument restent comprises dans un intervalle de températures mesurées de 3 – 15° tandis que l'intervalle peut être de 17 à 39° si les valeurs fournies par tous les instruments sont prises en compte. Les différences sont systématiques, non seulement entre les différents types de balances, mais aussi pour le même modèle d'instrument dans des laboratoires différents. L'utilisation de ces substances de référence certifiées permet de corréler les divers instruments.

ZUSAMMENFASSUNG — Die handelsüblichen Thermowaagen verfügen über eine breite Skala von Heizkörper-Probe-Temperaturfühler-Beziehungen. Wegen dieser Unterschiede waren die Angaben von einem Gerät zum anderen ungenau. Die Internationale Konföderation für Thermoanalyse hat eine Reihe magnetischer Referenzsubstanzen für die Thermogravimetrie bestätigt. Die Analyse der Prüfdaten von achtzehn Geräten zeigt, daß während die Angaben verschiedener Modelle in einem einzigen Instrument eine Spanne gemessener Temperaturen von 3 bis 15° zeigen, die Spannen für sämtliche Instrumente 17 bis 39° betragen. Die Differenzen sind systematisch, nicht nur zwischen Waagentypen, sondern auch für dasselbe Gerätemodell in verschiedenen Laboratorien. Der Gebrauch dieser geeichten Referenzsubstanzen gestattet die Korrelation zwischen Geräten.

Резюме — Для выпускаемых промышленностью термовесов характерным является наличие большого числа взаимовлияний в системе нагреватель — образец — температура. Вследствии имеющихся различий, относительные данные, полученные от разных приборов, были неточными. Международная федерация по термическому анализу вынесла решение об использовании в термогравиметрии магнитных материалов в качестве образцов сравнения. Анализ данных от восемнадцати приборов показал, что в то время как разброс данных от нескольких моделей одного и того же инструмента сосавил 3—15°, то разброс измеренных температур для всех приборов составил 17—39°. Различия являлись систематическими и не только между различными типами весов, но также для одной и той же модели прибора в различных лабораториях. Использование рекомендуемых материалов, как образцов сравнения, позволяет установить корреляции между приборами.