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Standard Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Fired Ceramic Whiteware Products by the Dilatometer Method[1]

This standard is issued under the fixed designation C 372; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the linear thermal expansion of premelted frit (porcelain enamel and glaze) and ceramic whiteware products by the thermal dilatometer method. This test method is applicable to apparatus meeting the reproducibility and accuracy requirements of this test method, which are to produce percent linear expansion accuracy of ±3 % or better and coefficient of linear expansion accuracy of ±5 % or better.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 220 Method for Calibration of Thermocouples by Comparison Techniques[2]

E 228 Test Method for Linear Thermal Expansion of Solid Materials with a Vitreous Silica Dilatometer[3]

E 230 Temperature-Electromotive Force (EMF) Tables for Standardized Thermocouples[2]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *mean coefficient of linear thermal expansion*—from temperature T_1 to temperature T_2 ($T_1 < T_2$):

$$\alpha,\ \text{mm/mm}\cdot\text{°C or in./in.}\cdot\text{°C} = \frac{0.01\,P}{T_2 - T_1}$$

where:

α = mean coefficient of linear thermal expansion from temperature T_1 to T_2, and

P = percent linear thermal expansion as defined in 3.1.2.

3.1.2 *percent linear thermal expansion*—from temperature T_1 to temperature T_2 ($T_1 < T_2$):

$$P = \frac{L_2 - L_1}{L_0} \times 100 + A$$

$$= \frac{\Delta L}{L_0} \times 100 + A$$

where:

P = percent linear thermal expansion from temperature T_1 to T_2,

L_0 = sample length at T_0 (T_0 between 20 and 30°C),

L_1 = sample length at T_1,

L_2 = sample length at T_2, and

A = instrument correction.

4. Significance and Use

4.1 Measurement of thermal expansion is useful for predicting stress within joined materials or single materials under conditions of changing or nonuniform temperature. It can also serve as an indicator of phase composition or changes in structure.

5. Apparatus

5.1 *Thermal Dilatometer*:

5.1.1 *General Description*—A thermal dilatometer is an apparatus that provides means for varying the temperature of a test specimen in a controlled manner, measuring the specimen length, and measuring the temperature of the specimen for each reading of specimen length. There are several different types as follows:

5.1.1.1 *Manual*—A manual dilatometer is one in which any or all of the above are done by manual means and the corrected percent linear thermal expansion curve is plotted by hand.

5.1.1.2 *Recording*—A recording dilatometer is an apparatus by which the above are recorded by instrumental means but the

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[2] *Annual Book of ASTM Standards*, Vol 14.03.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

final corrected percent linear thermal expansion curve is plotted by hand.

5.1.1.3 *Automatic Recording*—An automatic recording dilatometer is a recording dilatometer with provision for automatically plotting the corrected percent linear thermal expansion curve.

5.1.2 Any generally accepted apparatus that is capable of measuring the length changes produced by thermal expansion may be used in this method. The accuracy of the expansion-measuring apparatus including transducer, electronic, mechanical or optical amplification and readout device must be ±0.0001 in. (±0.003 mm) and should be reproducible to ±0.00005 in. (±0.0013 mm). A dilatometer may use a direct method of sighting on either of the two ends of the test specimen or suitable markings at the ends, by means of two telescopes mounted on a measuring bank. Another method transmits the change in length of the specimen to a sensitive dial gage or transducer by means of members that are chemically inert and free of phase transformations, having ground and polished surfaces at points of contact with the test specimens.

5.2 *Scale or Caliper*, capable of measuring the length of the specimen with an accuracy of ±0.0005 in. (±0.010 mm) must be used.

5.3 *Furnace* that is electrically heated and designed so that the thermal gradient over the length of the test specimen shall be less than 3°C. This may be accomplished by electrical shuntings, individually controlled zones, or other methods.

5.4 *Temperature-Measuring Device*—Temperature measurements shall be made by means of a thermocouple placed in contact with the test specimen approximately at its mid-length. The thermocouple shall have the accuracy specified in Table 15 of Standard E 230. Type S or Type K thermocouples are recommended for this method.

5.5 *Temperature-Indicating Device*—The temperature-indicating device may be a millivolt potentiometer, a calibrated meter or recorder, or other apparatus with a precision of ±5°C and an accuracy specification equivalent to the precision.

6. Test Specimens

6.1 For frit or dried slip samples, specimens shall be prepared as follows:

6.1.1 Frit should be crushed and screened through a 10-mesh sieve to remove large lumps. Then, a refractory boat crucible shall be filled with the sample material. If it is desired to reuse the crucible, it should be first lined with powdered alumina as a parting agent. The crucible can be of any suitable refractory material such as porcelain or alumina, but shall be unglazed. For frits that will be fired at less than 800°C, a metal mold may be used, if desired.

6.1.2 The test specimen shall be subjected to the same firing cycle used commercially in order to give a smooth surface on a bulk sample.

NOTE 1—The sample must be cooled slowly over several hours to preserve structural integrity.

6.2 For all samples, test specimens may be of any convenient length, provided the uniformity of the furnace has been determined over that length. The minimum thickness of the specimen shall be 0.2 in. (5.1 mm) and the maximum cross-sectional area shall be 0.45 in.^{2} (2.9 cm^2). The ends of the specimen shall be ground flat and perpendicular to the axis of the specimen.

6.3 Test specimens shall be conditioned in accordance with the history of the specimen. Conditioning shall include drying, annealing, or protection against moisture expansion, as may be necessary.

6.4 The length of the specimen shall be measured to within an accuracy of 0.1 %.

7. Calibration

7.1 Periodic calibration of the thermal dilatometer is recommended to assure the accuracy required by this method. Procedures for calibrating the component parts of the dilatometer are given below. A less time-consuming method for standardizing a complete apparatus, especially the recording type, is also given. A calibration check of the components of the apparatus should be done on an annual basis and calibration of the complete instrument using a standard sample should be done within 90 days preceding a report prepared under this method. The date of last calibration by either method should be included on the report.

7.2 *Calibration Procedures*:

7.2.1 *Dilatometer*:

7.2.1.1 If a direct sighting method is used, the dilatometer can be calibrated with a standard sample with a known length that has been measured by a micrometer with an accuracy of ±0.0001 in. (0.003 mm). The reference sample should be made from a material that has a very low thermal expansion, such as fused silica or invar. The dilatometer system can be calibrated by measuring the length of the sample using a movable telescope and comparing it with the known value.

7.2.1.2 If a dial gage transducer system is used, the dilatometer can be calibrated with a micrometer or thickness gage. Fix the dial gage transducer and micrometer in position on the instrument itself or in a special fixture during calibration. The system can be calibrated by displacing the probe of the transducer a known amount with the micrometer or thickness gage and adjusting the instrument to give that value. Whichever technique is used, the micrometer or thickness gage shall be accurate to ±0.0001 in. (0.003 mm).

7.2.2 *Furnace*—The thermal gradient that occurs over the sample length within the furnace should be determined by simultaneously measuring the temperature at the center, and at the ends of an alumina sample ⅜ to ½ in. (10 to 13 mm) in diameter and equal in length to the standard size sample for which the apparatus is intended. The thermocouples shall be Type S or Type K. Thermocouple wire of 0.010-in. (0.25-mm) diameter or less should be used. The thermocouple beads should be in contact with the test sample surface. Bring thermocouple wires out of the furnace for termination. A common negative wire may be used for all three thermocouples to reduce the number of leads brought from the furnace. Reference the center thermocouple to 0°C and use for the temperature reading in degrees Celsius. Connect the thermocouples in differential as shown in Fig. 1 so as to indicate the temperature difference between the center and each end. With the specimen, sample tubes, and readout thermocouple in their

normal measuring configuration mounted in the furnace, the furnace should be heated as specified in 8.2. The temperature differentials can be measured with a microvoltmeter at intervals of 50°C or less during heating. The microvoltmeter should have an accuracy of ±1 μV. The maximum thermal gradient shall be 3°C.

7.2.3 *Temperature-Measuring Device*—Any one of the techniques described in Method E 220 may be used to calibrate the thermocouple to the accuracy given in Table 15 of Standard E 230. The temperature readout device can be calibrated with a potentiometer or other source of known millivoltage that has an accuracy of ±0.01 mV. This testing device shall have an accuracy of ±0.5 % and shall be capable of being read to ±0.25 % of full scale.

7.2.4 *Determination of Instrument Correction*—A correction, *A*, must be added algebraically to the measured values of percent expansion to compensate for the percent linear thermal expansion of the material comprising the supporting members of the dilatometer and other parameters of the apparatus that cause a reproducible deviation from the correct values. While line-of-sight apparatus have no deviation caused by the supporting members, there will be reproducible deviations introduced by other parts of the apparatus for which corrections must be made. Determine the correction by the following method:

7.2.4.1 Prepare a sample of chemically pure (0.999 %) platinum in accordance with the requirements of this method. A reference standard as described in 7.2.6 may also be used.

7.2.4.2 Measure by the method given in Section 8 the expansion of the selected standard over the complete temperature range for which the apparatus is intended. Plot the percent linear thermal expansion measured. In automatic recording dilatometers the automatic correction should not be connected. Plot on the same graph the curve for the accepted values of the standard material or reference standard (see Test Method E 228, Table A2).

7.2.4.3 The difference between the two curves is the correction for the apparatus. This amount must be added algebraically to all observed percent expansion measurements to produce the corrected percent expansion curve required for this method. The addition can be done either manually or by automatic recording means.

7.2.5 *Calibration Using Platinum or Reference Standard*—Periodic calibration of the complete apparatus can be accomplished as follows. The reference standard must meet the requirements of 7.2.6.

7.2.5.1 Run the platinum or reference standard in accordance with the requirements of this method.

7.2.5.2 Plot the percent expansion obtained for the platinum or reference standard with the correction factor added as shown in 9.1.

7.2.5.3 Plot the accepted values of the platinum or reference standard on the same graph plotted in 7.2.5.2 at no more than 100°C intervals. The results plotted in 7.2.5.2 must agree with the accepted values for the platinum or reference standard within ±1% of the expansion value of platinum over the full-scale temperature range. If the values do not agree within that amount, the values of the correction at those points should be adjusted to produce results within tolerance. These new values of correction, either manual or automatic, should be used until the next calibration. If corrected measured values differ from the accepted values by more than ±2.5 % of full scale at any reading, it is recommended that the complete calibration of the component parts of the apparatus as required by this method be done. In dilatometers using fused silica support members it is recommended that the tubes be checked visually for devitrification effects before complete calibration is undertaken. Devitrification becomes evident as haze in the tube. Tube devitrification will result in the formation of recrystallized quartz and produce additive or subtractive effects depending upon which member is devitrified. Moreover, when devitrification occurs, breakage can be expected shortly.

7.2.6 *Reference Standard*—A reference standard of relatively stable nature can be used. The reference standard should be of size and shape consistent with the requirements of this method. For this method a reference standard should be similar in composition to a typical whiteware body with quartz as a major component. Prepare and treat the reference standard in such a manner that it is stable up to 1200°C. Determine the corrected (accepted values) percentage expansion of the reference standard in a thermal dilatometer that has been calibrated against platinum to within± 0.5 % of full scale at every 100°C interval in the temperature range. The calibration against platinum must immediately precede the determination of the values for the reference standard with a time lapse of no more than one day.

8. Procedure

8.1 Insert the test specimen into the furnace at room temperature. Allow it to stand until specimen temperature and furnace temperature are equal. At this time, record the reading of the dial indicator or other device that indicates the expansion of the specimen, together with the temperature.

8.2 Apply power to the furnace and make adjustments from time to time to give a heating rate of not more than 3°C/min.

8.3 Take temperature and expansion readings as frequently as necessary but at no greater interval than 25°C. The linear thermal expansion of some ceramic materials changes rather abruptly over certain temperature ranges due to crystal transformation and this temperature range may be found by measuring at narrower temperature intervals.

8.4 With frit or dried slip samples, immediately either turn off the furnace or remove the sample from the furnace when the incipient fusion point is reached, as shown by a decrease in expansion with further temperature increase, to avoid reaction of the sample with the apparatus.

9. Calculation

9.1 Percentage expansion can be plotted directly with automatic recording apparatus or calculated and plotted manually as follows:

$$P = \frac{\Delta L}{L_0} \times 100 + A$$

Percentage expansion shall always include the apparatus correction *A*, as defined in 7.2.4.

9.2 Plot a curve showing each temperature reading, *T*, on

the horizontal axis versus the corresponding percentage expansion along the vertical axis.

9.3 The coefficient of thermal expansion, α, can be calculated for any temperature range, T_1 to T_2, within the limits of the test, as follows:

$$\alpha = \frac{0.01P}{T_2 - T_1}$$

as defined in Section 3.

10. Report

10.1 Report the following information:

10.1.1 Designation of material,

10.1.2 Method of preparation of test specimen,

10.1.3 Identification of type of apparatus used, with date of last calibration,

10.1.4 Data sheet including:

10.1.4.1 Form and dimensions of test specimen,

10.1.4.2 Starting temperature,

10.1.4.3 Temperature at each reading, percentage expansion, *P*, for each reading, or automatic recording dilatometer chart, and

10.1.4.4 Heating rate,

10.1.5 The temperature-percentage expansion curve, and

10.1.6 Mean coefficient of linear thermal expansion per degree Celsius over the desired temperature ranges.

11. Precision and Bias

11.1 *Interlaboratory Test Data*:

11.1.1 An interlaboratory study was carried out between 14 laboratories using dilatometers of the push rod type from 3 different manufacturers.

11.1.2 Samples of borosilicate glass (NBS/NIST SRM 731), whiteware, and C. P. platinum were selected in 1 and 2 in. lengths.

11.1.3 Percent linear thermal expansion and mean coefficient of linear thermal expansion were obtained at 25–350°C (glass), 25–650°C (whiteware), and 25–1000°C (platinum).

11.1.4 Analysis of data was done statistically following Practice E 691.

11.2 *Precision*:

11.2.1 The results of the interlaboratory study indicate that the relative repeatability limit (within laboratory) is 4.75 % (3.61 to 7.39 %) of test value for percent linear thermal expansion and mean coefficient of thermal expansion. A test result for a given sample should be considered significantly different at the 95 % confidence level if this repeatability interval is exceeded. The repeatability coefficient of variation may be obtained by dividing the relative repeatability limit by 2.8.

11.2.2 The interlaboratory results indicate that the relative reproducibility limit (between laboratory) is 10.73 % (6.55 to 13.53 %) of test value for percent linear thermal expansion and mean coefficient of thermal expansion. A test result for a given sample should be considered significantly different at the 95 % confidence level if this reproducibility interval is exceeded. The reproducibility coefficient of variation may be obtained by dividing the relative reproducibility limit by 2.8.

11.3 *Bias*—The indicated basis of the test method relative to NIST thermal expansion values per Hahn and Kirby is 0.0066 % (0.0059 to 0.0074 %) for percent linear thermal expansion or 4.45 % (4.40 to 4.50 %) of reported value for linear thermal expansion and mean coefficient for borosilicate glass ($\alpha = 5.4 \times 10^{-6}$ mm/mm°C) from 25–350°C and 0.55 % (0.52 to 0.59 %) of reported value for linear thermal expansion and mean coefficient of platinum ($\alpha = 10.3 \times 10^{-6}$ mm/mm°C) from 25–1000°C.