Designation: D 5547 – 95 (Reapproved 2003)

Standard Test Method for Clay and Zeolite in Powdered Laundry Detergents by Atomic Absorption[1]

This standard is issued under the fixed designation D 5547; 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 atomic absorption tests applicable to powdered laundry detergents containing clay and zeolite.[2]

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

3. Summary of Test Method

3.1 The test sample is fused with lithium metaborate, dissolved in acid, its silicon and aluminum content measured by atomic absorption, and the silicon/aluminum (Si/Al) ratio calculated. The clay and zeolite content of the test sample is calculated from the Si/Al ratio of the test sample and the Si/Al ratio of the clay and zeolite expected in the test sample.

4. Interferences

4.1 Materials other than clay and zeolite that contain silicon or aluminum, or both, will interfere.

5. Principle

5.1 Clay and zeolite contain silicon and aluminum at different relative levels.[4] The silicon/aluminum ratio is then a measure of the relative level of clay and zeolite in detergent powders. That is, detergent powders with a Si/Al ratio matching clay or zeolite contain only clay or zeolite, respectively. Detergent powders with Si/Al ratio falling between the Si/Al ratio of clay and zeolite contain both clay and zeolite.

5.2 This test method is based on the linear relationship between the relative composition (or ratio) of clay/zeolite in detergent powders and the Si/Al ratio of such detergents.

5.3 A calibration equation is derivable, therefore, from just two experimental points: the Si/Al ratio of the zeolite standard (100 zeolite, 0 % clay) and the Si/Al ratio of the clay standard (0 % zeolite, 100 % clay).

6. Apparatus

6.1 *Suitable Atomic Absorption Spectrophotometers*, fitted with a nitrous oxide-acetylene burner and aluminum and silicon hollow cathode source lamps.

6.2 *Nitrous Oxide and Acetylene Tanks*, with suitable regulators.

6.3 *Muffle Furnace*, capable of reaching 1000°C.

6.4 *Analytical Balance*.

6.5 *Fisher Burner or Equivalent*.

6.6 *20-mL or Larger Platinum Crucibles*.

6.7 *Platinum-tip Tongs*.

6.8 *25-mL Buret*.

6.9 *100-mL and 200-mL Polypropylene Volumetric Flasks*.

6.10 *10-mL and 25-mL Graduated Cylinders*.

6.11 *150-mL Plastic Beakers*.

6.12 *Magnetic Stirrer and Magnetic Stirring Bars*.

6.13 *Blender*, such as Waring[5] or Osterizer[6] or an industrial lab model, or a mortar and pestle, if a blender is not available.

7. Reagents

7.1 *Purity of Reagents*—Reagents grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

[1] This test method is under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and is the direct responsibility of Subcommittee D12.12 on Analysis of Soaps and Synthetic Detergents.

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[2] Silicon and aluminum measurements are by atomic absorption in this test method. ICP can be used to make such measurements as well.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] The Si/Al ratio is usually about 1 in zeolites and about 3 in clays.

[5] Waring blenders are available commercially.

[6] Osterizer blenders are widely available commercially.

such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equal purity.

7.3 *Aluminum Standard*, 1000 µg Al/mL[8] or equivalent.

7.4 *Silicon Standard*, 1000 µg Si/mL.[8]

7.5 *Potassium Chloride*, Baker-analyzed reagent or equivalent.

7.6 *Potassium Chloride Solution (1 %)*—Dissolve 1 g of potassium chloride in 100 mL of distilled water. Mix well and store in plastic container.

7.7 *Concentrated Hydrochloric Acid*, Baker-analyzed reagent or equivalent.

7.8 *Hydrochloric Acid Solution (1 + 1)*—Mix equal parts of concentrated HCl and distilled water by volume. Mix well and store in plastic container.

7.9 *Potassium Iodide*, Baker-analyzed reagent or equivalent.

7.10 *Lithium Metaborate SPEX Grade, Special for Fusions*[9].

7.11 *Zeolite Standard*—The same material expected in the test sample, to be used as standard.

7.12 *Clay Standard*—The same material expected in the test sample, to be used as standard.

8. Instrumental Conditions

8.1 Following the instrument manufacturer's instructions, set up the atomic absorption instrument as follows:

	To measure Aluminum	To measure Silicon
Wavelength, nm	309.3	251.6
Range	UV	UV
Slit, nm	0.2	0.2
Flame	Nitrous oxide-acetylene. Rich, red.	Nitrous oxide-acetylene. Strongly reducing red cone 2–3 cm high with yellow outer edge.

9. Procedure

9.1 *Determination of Aluminum*:

9.1.1 Accurately weigh 0.1 g (to the nearest 0.1 mg) of zeolite standard (the same material expected in the test sample) into a clean, dry, platinum crucible. Also accurately weigh 0.2 g of clay standard (the same material expected in the test sample) into another clean, dry, platinum crucible.

9.1.2 Grind a representative powdered detergent test sample in a blender to a fine, homogenous powder. (If a blender is not available, use a mortar and pestle).

9.1.3 Accurately weigh 0.3 g (to the nearest 0.1 mg) of the ground test sample(s) into still another clean, dry, platinum crucible.

9.1.4 Add 2 g (±0.1 g) of lithium metaborate to each platinum crucible, and mix the contents with a plastic rod.

9.1.5 Place the crucibles containing the mixtures in a cool muffle furnace and turn on the heat. When the temperature reaches 1000°C, maintain heat for at least 5 additional min.

NOTE 1—The sample will ignite and splatter if placed in a hot furnace. If it is not possible to start with a cool furnace, gently char the sample with a Fisher burner first, avoiding ignition, then place in the furnace.

9.1.6 Place 90 mL of distilled water into 150-mL plastic beakers. (Use as many beakers as there are standards and samples).

9.1.7 Add a magnetic stirring bar to each beaker, and place on a magnetic stirrer. Mix rapidly to make the water swirl in the beaker, but do not allow anything to splash out. This apparatus should be near the furnace containing the ashed standards and sample(s).

9.1.8 Using platinum-tip tongs, remove one crucible at a time from the furnace, and immediately place over a Fisher burner flame without allowing the melted sample to solidify.

9.1.9 Add about 2 mg (a pinch on the end of a spatula) of potassium iodide (KI) to the melted sample. A molten ball will form. Roll the ball around the inside of the dish to pick up any droplets or particles. The KI releasing agent is volatile, and it is necessary to carry out this step rather quickly (about 2 min). If the ball collapses and flows into the dish, start again by adding fresh KI.

9.1.10 Drop each molten ball quickly into the swirling water of each plastic beaker.

NOTE 2—**Precaution:** Use face shield and protective clothing.

9.1.11 Add 20 mL of 1 + 1 HCl and 20 mL of 1 % potassium chloride solution and mix until completely dissolved. Quantitatively transfer to a 200-mL plastic volumetric flask with distilled water. Dilute to volume and mix well.

9.1.12 Using a buret, add 5, 7.5, and 10 mL of 1000-ppm aluminum standard into 3 separate 100-mL plastic volumetric flasks. These standards contain 50, 75, and 100 µg Al/mL respectively. (Make these standards fresh each day).

9.1.13 Add 10 mL 1 + 1 HCl, 10 mL 1 % KCl, and 1 g of lithium metaborate to each flask. Dilute to volume with distilled water and mix until completely dissolved.

9.1.14 Prepare a reagents blank.

9.1.15 Set up the atomic absorption instrument as described in 8.1.

9.1.16 Zero the instrument with the reagents blank. Measure the absorbance of the aluminum standards, the zeolite standard, the clay standard and the test sample at 309.3 nm. Repeat the measurement three more times for each flask and calculate the average absorbance. *Save the solutions, except the aluminum standards, for silicon determination in 9.2.*

9.1.17 Prepare a standard curve by plotting the average absorbance versus concentration in µg/mL of each aluminum standard.

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[8] Available from Fisher Scientific Co., Fairlawn, NJ 07410.

[9] Available from SPEX Industries, Box 798, Metuchen, NJ 08840.

9.1.18 Determine the concentration of aluminum in the test sample(s) by comparing the average absorbance to the standard curve and reading aluminum concentration in µg/mL directly.

NOTE 3—This test method describes manual data gathering and calculation from a calibration curve so that the technique can be carried out using all atomic absorption units. It is acceptable to use the automatic concentration modes in modern atomic absorption units if so equipped.

9.1.19 *Calculation*:

$$\frac{C \times 200}{\text{wt.} \times 10\,000} = \%\ \text{aluminum} \quad (1)$$

where:
C = aluminum concentration (µg/mL),
200 = final dilution in mL,
wt. = weight of zeolite and clay standards, and test sample(s), in g, and
10 000 = conversion factor, µg/g to percent.

9.2 *Determination of Silicon*:

9.2.1 Pipet 5, 10, and 15 mL of 1000-ppm silicon standard into three separate 100 mL plastic volumetric flasks.

9.2.2 Add 10 mL 1 + 1 HCl, 10 mL 1 % KCl, and 1 g of lithium metaborate to each flask. Dilute to volume with distilled water and mix until completely dissolved. These standards contain 50, 100, and 150 µg Si/mL respectively. (Make these standards fresh each day.)

9.2.3 Prepare a reagents blank and dilute with distilled water 50.0 mL of the clay standards from 9.1 to 100.0 mL in a 100-mL plastic volumetric flask.

9.2.4 Set up the atomic absorption instrument as described in 8.1.

9.2.5 Zero the instrument with the reagents blank. Measure the absorbance of the silicon standards at 251.6 nm. Measure, also at 251.6 nm, the absorbance of the zeolite standard, the clay standard, and the test sample(s) from 9.1. Repeat the measurement three more times for each flask and calculate the average absorbance.

9.2.6 Prepare a standard curve by plotting the average absorbance versus concentration in µg/mL of each silicon standard.

9.2.7 Determine the concentration of silicon in the test sample(s), the zeolite standard, and the clay standard by comparing the average absorbance to the standard curve and reading the silicon concentration in µg/mL directly.

NOTE 4—This test method describes manual data gathering and calculation from a calibration curve so that the technique can be carried out using all atomic absorption units. It is acceptable to use the automatic concentration modes in modern atomic absorption units if so equipped.

9.2.8 *Calculation*:

$$\frac{C \times 200}{\text{wt.} \times 10\,000} = \%\ \text{silicon} \quad (2)$$

where:
C = silicon concentration from curve (µg/µL),
200 = final dilution in mL,
wt. = weight of zeolite and clay standards and test sample(s), in g, and
10 *000* = conversion factor, µg/g to percent.

10. Calculation of Percent Clay and Percent Zeolite in Test Samples

10.1 Calculate the Si/Al ratio for the clay standard, the zeolite standard, and the test sample(s) from percent aluminum and percent silicon obtained in 9.1 and 9.2, respectively.

10.2 Derive the equation of the straight line, $y = mx + c$, connecting the points:

$$x_1, y_1 = \text{Si/Al}\ (C),\ 0 \quad (3)$$
$$x_2, y_2 = \text{Si/Al}\ (Z),\ 100$$

where:
Si/Al(C) = Si/Al ratio of clay standard,
Si/Al(Z) = Si/Al ratio of zeolite standard,
0 = concentration of zeolite in clay standard, and
100 = concentration of zeolite in zeolite standard.

10.3 Calculate the relative level of zeolite in the test sample(s) using the equation from 10.2 and the Si/Al ratio of the test sample(s) from 10.1:

$$y(RLZ) = mx + c \quad (4)$$

where:
$y(RLZ)$ = relative level of zeolite in the test sample,
m = slope of the line (10.2),
x = Si/Al ratio of test sample, and
c = intercept of the line (10.2).

10.4 *Percent Zeolite in Test Sample*:

$$\frac{(ATS)(RLZ)}{(AZ)} = \%\ \text{zeolite} \quad (5)$$

where:
ATS = percent aluminum in test sample (9.1),
RLZ = relative level of zeolite in test sample (10.3), and
AZ = percent aluminum in zeolite standard.

10.5 *Percent Clay in Test Sample*:

$$\frac{(ATS)(100 - RLZ)}{(AC)} = \%\ \text{clay} \quad (6)$$

where:
ATS = percent aluminum in test sample (9.1),
RLZ = relative level of zeolite in test sample (10.3), and
AC = percent aluminum in clay standard.

10.6 *Sample Calculation for a Typical Clay, Zeolite, and Powdered Detergent*:

10.6.1 *Experimental Results*:

	Clay standard	Zeolite standard	Powder detergent
% Aluminum	8.8	16	3.3
% Silicon	27.3	17.6	5.4
Si/Al ratio	3.1	1.1	1.64

10.6.1.1 Using the points x_1, $y_1 = 3.1$, 0; x_2, $y_2 = 1.1$, 100, the equation of the line is:

$$y = -50x + 155 \quad (7)$$

10.6.1.2 *Relative Level of Zeolite (RLZ) in Detergent Powder*:

$$y = -(50)(1.64) + 155 = 73 \quad (8)$$

10.6.1.3 *Percent Zeolite in Detergent Powder*:

$$\frac{(ATS)(RLZ)}{(AZ)} = \frac{(3.3)(73)}{(16)} = 15.1 \quad (9)$$

10.6.1.4 *Percent Clay in Detergent Powder*:

$$\frac{(ATS)(100 - RLZ)}{(AC)} = \frac{(3.3)(100 - 73)}{(8.8)} = 10.1 \quad (10)$$

11. Precision and Bias

11.1 Six laboratories collaborated in analyzing two powder detergents (A and B). See Table 1.

11.2 The standard deviations for clay, covering the 5.2 to 9.9 % clay range, and the standard deviations for zeolite, covering the 19.6 to 28.9 % zeolite range, were pooled. See Table 1.

11.3 The following criteria should be used to judge the acceptability of the results.[10,11]

11.3.1 *Repeatability (Single Analyst) of Clay*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.7 % weight absolute, at 12° of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 2.2 % weight absolute.

11.3.2 *Repeatability (Single Analyst) of Zeolite*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 1.0 % weight absolute, at 12° of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 3.1 % weight absolute.

11.3.3 *Reproducibility (Multi-laboratory) of Clay*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 1.3 % weight absolute, at 10° of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 4.1 % weight absolute.

11.3.4 *Reproducibility (Multi-laboratory) of Zeolite*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 2.3 % weight absolute, at 10° of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 7.2 % weight absolute.

11.3.5 *Checking Limits for Duplicates for Clay*—Report percent clay to the nearest percent. Duplicate runs that agree within 3.2 % weight absolute are acceptable for averaging (95 % confidence level).

11.3.6 *Checking Limits for Duplicates for Zeolite*—Report percent zeolite to the nearest percent. Duplicate runs that agree within 3.8 % weight absolute are acceptable for averaging (95 % confidence level).

11.3.7 *Bias*—For clay the bias was about 2 % high, relative, and for zeolite it was about 3 % low, relative (11.1).

[10] Supporting data are available from ASTM Headquarters. Request RR: D12-1005.

[11] This statistical analysis follows Practice E 180 for developing precision estimates.

TABLE 1 Analysis of Two Powder Detergents by Six Laboratories[A]

Sample	Clay, %		Zeolite, %	
	Added	Found (n = 24)	Added	Found (n = 24)
A	5.20	5.2	29.79	28.9
B	9.74	9.9	19.95	19.6

[A] Data from all six laboratories are included, even though one of the six laboratories was an outlier between runs for Day 2 for each analyte and product.

12. Keywords

12.1 aluminum; atomic absorption; clay; ICP; powdered laundry detergents; silicon; zeolite