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An American National Standard

Designation: 369/(95)

Standard Test Method of Analysis of Oil-Soluble Petroleum Sulfonates by Liquid Chromatography[1]

This standard is issued under the fixed designation D 3712; 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.

This test method was adopted as a joint ASTM-IP standard.

ε[1] NOTE—Editorial corrections were made throughout in November 2000.

1. Scope*

1.1 This test method covers the analysis of refined and crude natural and synthetic oil-soluble sulfonate products. Resins, if present, are recovered with the oil phase and carboxylates are recovered as sulfonates.

1.2 This test method covers the determination of mineral oil, sodium sulfonate, inorganic salts, water, basicity or acidity, average molecular weight, and relative density of sodium sulfonate products.

1.3 This test method covers the determination of mineral oil, sulfonate, water, base number, average molecular weight, and relative density of calcium, barium, magnesium, and ammonium sulfonate products.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are provided for information only.

1.5 *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:*

D 95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation[2]

D 2896 Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration[2]

3. Terminology

3.1 *Symbols:*

3.1.1 Following are definitions of the symbols used in Section 17, and as noted in the sections in parentheses.

A	=	grams of sample of calcium, barium, magnesium, or ammonium sulfonate (8.1.1).
B	=	volume of chloroform solution, mL (10.1).
C	=	grams of sample of sodium sulfonate (10.1.1).
D	=	grams of oil recovered (10.4).
E	=	grams of sodium sulfonate recovered (10.5).
F	=	grams of residue from chloroform blank (10.6).
G	=	grams of residue from alcohol blank (10.6).
H	=	grams of sodium sulfonate (11.1).
I	=	grams of sodium sulfate ash from sodium sulfonate (11.2).
J	=	T/KS.
K	=	valence of cation.
S	=	average equivalent weight of sodium sulfonate (17.1.4).
T	=	average molecular weight of calcium, barium, magnesium, or ammonium sulfonate (17.1.5).
U	=	percentage of sodium sulfonate (17.1.2).
V	=	percentage of calcium, barium, magnesium, or ammonium sulfonate (17.1.3).
W_c	=	grams of water contained in pycnometer at 25°C (6.9).
W_s	=	grams of sample contained in pycnometer at 25°C (15.1).
X	=	grams of sodium sulfonate sample for basicity (12.1).
Y	=	volume of standard H_2SO_4 or NaOH solution used to determine basicity or acidity (12.1).
Z	=	normality of standard H_2SO_4 or NaOH solution to determine free basicity or acidity (12.1).
AA	=	grams of sodium sulfonate product ashed (13.1).
BB	=	grams of sodium sulfate from inorganic salt determination (13.1).
CC_A	=	percentage of free acidity of sodium sulfonate product as H_2SO_4(17.1.6).
CC_B	=	percentage of free basicity of sodium sulfonate product as NaOH (17.1.6).
DD	=	percentage of inorganic salts as sodium sulfate (17.1.7).

4. Summary of Test Method

4.1 The sample, except a sodium sulfonate product, is dissolved in ethyl ether and converted to sulfonic acid, using dilute hydrochloric acid. The sulfonic acid after extraction is converted to sodium sulfonate and the isolated sodium sulfonate and mineral oil are dissolved in chloroform. An aliquot of the chloroform solution, or a sample of a sodium sulfonate product, dissolved in chloroform, is placed on a silica gel column. The oil is eluted with chloroform, the sulfonate with

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

***A Summary of Changes section appears at the end of this standard.**

ethyl alcohol, and both are determined gravimetrically. Average molecular weight is calculated from the average equivalent weight of the sodium sulfonate, which is determined by ashing a portion of the isolated sodium sulfonate.

4.2 Water is determined by Test Method D 95. Base number is determined by Test Method D 2896. Relative density is determined by pycnometer.

5. Significance and Use

5.1 This test method provides a means of determining sulfonate content and of classifying and characterizing natural and synthetic petroleum sulfonate products by sulfonate content and average molecular weight. Purity of sodium sulfonate products is measured by basicity and inorganic salt contents and the reserve alkalinity of alkaline earth sulfonates by the total base number.

6. Apparatus

6.1 *Chromatographic column*, made of glass and consisting of a reservoir and separator section, and fitted with a TFE-fluorocarbon stopcock with a 2-mm bore, as shown in Fig. 1. A column with a detachable reservoir connected by a standard-taper joint can be used.

6.2 *Steam Bath*.

6.3 *Vacuum Desiccator*, shielded.

6.4 *Vacuum Oven*, capable of being maintained at 100°C (212°F) and connected to 559 to 635 mm (22 to 29 in.) Hg vacuum.

6.5 *Muffle Furnace*, capable of operating at 800 to 1000°C (1500 to 1800°F).

6.6 *Dish*, platinum, 100-mL capacity.

6.7 *Distillation Apparatus*, as described in Test Method D 95.

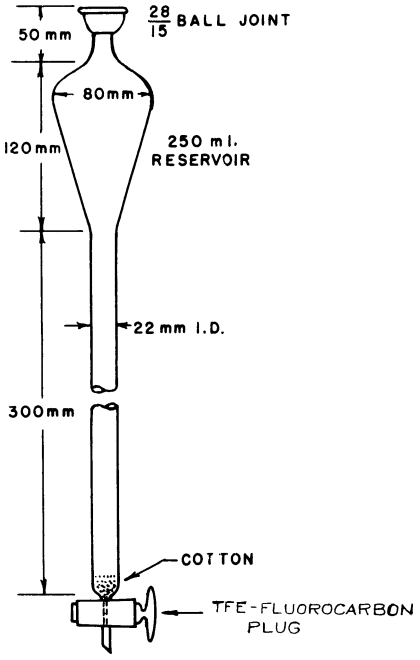

FIG. 1 Chromatographic Column

6.8 *Water Bath*, capable of being maintained at 25 ± 0.2°C (77 ± 0.3°F).

6.9 *Pycnometer*, as shown in Fig. 2. To calibrate, weigh to the nearest 1 mg with cap in place; then fill with distilled water at 15 to 20°C (60 to 68°F) and place in water bath at 25 ± 0.2°C (77 ± 0.3°F). After 30 min, adjust the water meniscus at the top of the neck so it is exactly level. To obtain a flat meniscus, add a minute amount of wetting agent to the water surface. Remove the pycnometer from the bath, and dry the outside. Replace the cap and weigh to the nearest 1 mg. Record the mass of water contained as W_c.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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 *Chloroform* (**Warning**—Flammable, Health Hazard.).

7.3 *Ethyl Alcohol* (95 %)—Either pure grain or denatured ethyl alcohol conforming to Formula 3A of the U.S. Bureau of Internal Revenue (**Warning**—Flammable. Denatured alcohol cannot be made nontoxic.).

7.4 *Ethyl Ether* (**Warning**—Extremely flammable. Harmful if inhaled. May cause eye injury. Effects may be delayed. May form explosive peroxides. Vapors may cause flash fire. Moderately toxic. Irritating to skin.).

[3] *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.

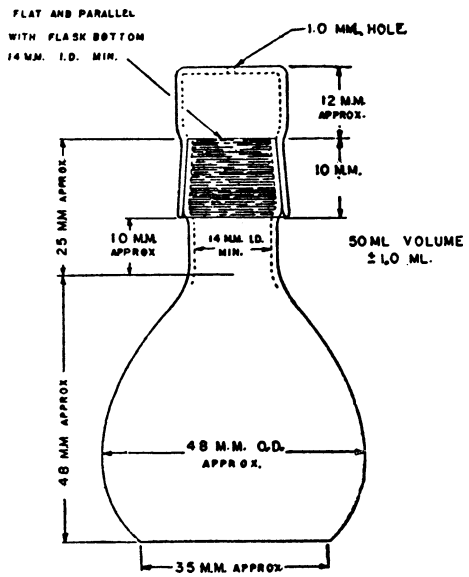

FIG. 2 Pycnometer for Determining Relative Density of Petroleum Sulfonates

7.5 *Filter Paper*, slow-filtering, ashless, gravimetric.

7.6 **Hydrochloric Acid (Concentrated)—(Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.).

7.6.1 **Hydrochloric Acid, Dilute (1 + 1)**—One volume of concentrated hydrochloric acid (HCl) is added to 1 volume of water.

7.6.2 **Hydrochloric Acid, Dilute (1 + 3)**—One volume of concentrated hydrochloric acid (HCl) is added to 3 volumes of water.

7.7 *Isopropyl Alcohol* (99 Mass %)—Water content shall be 0.9 mass % maximum. (**Warning**—Flammable.)

7.7.1 *Isopropyl Alcohol, Dilute* (1 + 1)—One volume of 99 mass % isopropyl alcohol is diluted with 1 volume of water.

7.8 *Methyl Orange Indicator Solution*—Dissolve 1.0 g of methyl orange in water and dilute to 1 L.

7.9 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of 50 mass % ethyl alcohol.

7.10 *Silica Gel*, 250 to 74 µm (60 to 200-mesh).[4]

7.11 *Sodium Hydroxide Solution, Standard* (0.1 mol/L) (**Warning**—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.)—Prepare and standardize a 0.1 mol/L aqueous, carbonate-free, NaOH solution.

7.12 *Sodium Sulfate, Anhydrous, Crystalline*.

7.13 *Sodium Sulfate Solution*—Dissolve 240 g of sodium sulfate (Na_2SO_4) in water and dilute to 1 L.

7.14 *Sulfuric Acid* (relative density 1.84)—Concentrated sulfuric acid (H_2SO_4), 36 mol/L. (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled. Contact with water liberates large amounts of heat. Spillage may cause fire.

7.14.1 *Sulfuric Acid Solution, Standard* (0.1 mol/L)—Prepare and standardize a 0.1 mol/L aqueous sulfuric acid (H_2SO_4).

8. Conversion of Calcium, Barium, Magnesium, or Ammonium Sulfonate to Sodium Sulfonate

8.1 *Conversion of Calcium, Barium, Magnesium or Ammonium Sulfonate to Sulfonic Acid*:

8.1.1 Transfer approximately 10 g of sample, weighed to the nearest 0.001 g into a 250-mL Erlenmeyer flask, designating this weight as *A*. Add 50 mL of ethyl ether and stir to dissolve the sample. Add 100 mL of dilute HCl (1 + 1) and swirl to mix thoroughly until reaction is complete. In analyzing barium sulfonate products if barium chloride crystallizes out, add sufficient water to redissolve.

8.1.2 Quantitatively transfer the mixture to a 500-mL separatory funnel. Shake well, let settle, and draw the aqueous acid layer into a 250-mL separatory funnel. Extract the aqueous acid layer in the 250-mL separatory funnel with three 50-mL portions of ethyl ether, using the ethyl ether washes to rinse the Erlenmeyer flask first. Combine all the ethyl ether extracts in the 500-mL separatory funnel and wash with 50 mL of dilute HCl (1 + 3). Combine all the aqueous acid layers and reextract them with 50 mL of ethyl ether.

8.2 *Conversion of Sulfonic Acid to Sodium Sulfonate*:

8.2.1 Collect all of the ether washes in the 500-mL separatory funnel and shake with successive 50-mL portions of Na_2SO_4 solution containing 2 to 3 drops of methyl orange indicator until a washing does not appear pink. Discard the salt washes.

8.2.2 Drain off as much of the aqueous layer as possible from the washed ether solution. Lay the separatory funnel on its side and introduce about 10 g of anhydrous Na_2SO_4. Stopper the funnel, making sure that the funnel mouth is free of Na_2SO_4 crystals and shake the mixture vigorously for 3 to 4 min, to remove the last traces of water, venting the funnel frequently. Place a 250-mL Erlenmeyer flask on a steam bath and filter the ether solution through a small plug of cotton, placed in the vortex of a filter funnel, into the Erlenmeyer flask, keeping approximately 50 mL of solution in the Erlenmeyer flask while evaporating. Rinse the funnel and filter with 50 mL of ethyl ether, adding the rinsing to the main ether solution. Evaporate the ethyl ether until approximately 10 mL of solution remains. Add 50 mL of 99 mass % isopropyl alcohol, several drops of phenolphthalein indicator solution, and titrate with 0.1 mol/L standard NaOH solution to the red color change. Place the flask on a steam bath and evaporate to dryness. Dissolve the sodium sulfonate and oil residue in chloroform; transfer quantitatively into a 100-mL volumetric flask, adjust to volume, and proceed directly with Section 10. The solution may turn acidic on standing in the laboratory. Should this occur, add sufficient 0.1 *N* NaOH solution to the aliquot taken until the solution is pink.

9. Preparation of the Column

9.1 With the stopcock closed, pour 80 to 100 mL of chloroform into the column, and push a wad of cotton to the bottom with a rod (Note 1). Compress the cotton enough to hold back the silica gel but not enough to impede the flow of solvent.

NOTE 1—A coarse-fritted disk made of borosilicate glass can be used in place of the cotton wad.

9.2 Pour 15 ± 1 g of silica gel into the column containing the chloroform. The column must be free of air bubbles to avoid channeling. Start the flow of chloroform by opening the stopcock. When the liquid level is within 13 mm (½ in.) of the surface of the gel, close the stopcock. Never allow the liquid level to fall below the surface of the silica gel.

10. Separation of Mineral Oil and Sodium Sulfonate

10.1 *Adsorption of the Sample*—Transfer a sufficient quantity of the chloroform solution of sodium sulfonate and mineral oil to provide approximately 1.25 g of Na_2SO_4(8.2.2) onto the column, being careful to prevent channeling. Designate the volume as *B*. Use the following information as a guide in selecting the appropriate volume of sample:

Approximate Sulfonate Content of Product	Volume of Aliquot
20 %	75 mL
30 %	50 mL
Above 40 %	25 mL

[4] Silica gel, Grade 62, obtainable from the W.R. Grace and Co., Davison Chemical Corp., Baltimore, MD 21203, has been found satisfactory for this purpose.

10.1.1 *For Sodium Sulfonate Products*—Transfer approximately 2 g of sample, weighed to the nearest 0.001 g, into a 100-mL beaker, designating this weight as *C*. Add 10 to 25 mL of chloroform and stir to dissolve the sample. Pour the solution onto the column, being careful to prevent channeling. Rinse the beaker several times with small portions of chloroform and add the rinses to the column.

10.2 *Elution of the Mineral Oil*—Tare a 250-mL beaker, to the nearest 0.0001 g and place it under the column. Open the stopcock and adjust the flow rate to between 1 and 5 drops per second. Maintain the flow rate throughout the elution of the oil and sulfonate.

10.2.1 When the liquid level is within 13 mm (½ in.) of the surface of the gel, rinse the sides of the column with 10 mL of chloroform. When the liquid level is again within 13 mm (½ in.) of the surface of the gel, add 200 mL of chloroform.

10.2.2 If a column with a detachable reservoir is used, attach the reservoir at this point.

10.2.3 When the receiving beaker is about half full, remove it and place a clean, untared 250-mL beaker under the column to continue the elution. Place the tared beaker on the steam bath and gently evaporate the chloroform by blowing filtered air over the liquid surface. When the liquid level in the column is within 13 mm (½ in.) of the surface of the gel, rinse the sides of the column with 10 mL of ethyl alcohol. When the liquid level is again within 13 mm (½ in.) of the surface of the gel, repeat the rinse. The adsorbed sulfonate is always clearly visible and is sufficiently high in the column to prevent elution of sulfonate at this stage. Close the stopcock and quantitatively transfer the contents of the untared beaker to the tared beaker on the steam bath, by the use of chloroform.

10.3 *Elution of Sulfonate*—Tare a second 250-mL beaker to the nearest 0.0001 g and place it under the column. Add 230 mL of ethyl alcohol to the reservoir, open the stopcock and adjust the flow rate as described in 10.2.1 (Note 2). When the receiving beaker is about half full, remove it and place a clean, untared 250-mL beaker under the column. Place the tared beaker on the steam bath and evaporate gently, blowing filtered air over the liquid surface. When the liquid level in the column is within 13 mm (½ in.) of the surface of the gel, close the stopcock and quantitatively transfer the contents of the untared beaker to the second tared beaker on the steam bath, by the use of ethyl alcohol.

NOTE 2—The flow rate may be maintained by applying compressed air if necessary.

10.4 *Determination of Oil*—Evaporate the chloroform solution from 10.2.2 until all but a few millilitres of chloroform have been evaporated. Remove the beaker from the steam bath and cool to room temperature. Place the beaker in a vacuum desiccator with a vacuum of 559 to 635 mm (22 to 25 in.) of mercury at room temperature. When the chloroform appears to have evaporated, remove the beaker and weigh. Return the beaker to the vacuum desiccator with a vacuum of 550 to 635 mm Hg (22 to 25 in.) for 30 min, remove, and weigh again. Repeat the drying and weighing until two successive weights are obtained that do not differ by more than 0.001 g. Designate the weight of the oil residue as *D*.

10.4.1 Some special petroleum sulfonate products may contain a light distillate as the diluent instead of mineral oil. In such cases, it is not possible to attain constant weight and the oil content determination must be disregarded.

10.5 *Determination of Sulfonate*—Evaporate the alcohol solution from 10.3 to dryness. Heat the beaker for 30 min in a vacuum oven at 100°C (212°F) and 550 to 635 mm Hg (22 to 25 in.) vacuum. Remove the beaker, cool, and weigh. Repeat the drying and weighing until two successive weights are obtained that do not differ by more than 0.001 g. Designate the mass of the sulfonate residue as *E*.

10.6 *Blank Determination*—Make a blank determination on a similar silica gel column, using the same lot of silica gel and reagents that are used in the analysis. Use the same procedure and quantities of reagents described in Section 9, but omit the sample. Determine the weights of the chloroform and alcohol residues as described in 10.4 and 10.5. Designate these weights as *F* and *G*, respectively. Repeat the blank determination whenever new lots of silica gel or reagents are used.

11. Average Equivalent Weight of Sodium Sulfonate

11.1 Dissolve the sulfonate residue (10.5) in 25 mL of chloroform, filter, if cloudy, through a slow-filtering, ashless, gravimetric paper and transfer the solution quantitatively into a tared, ignited, 100-mL platinum dish. Rinse the beaker, which contained the sulfonate residue with 25 mL of chloroform, adding the washings to the platinum dish, through the filter, if used. Evaporate to dryness on a steam bath. Dry to constant weight *H* in a vacuum oven at 100°C (212°F) and 559 to 635 mm Hg (22 to 25 in.) vacuum.

11.2 Carefully heat the dish over a small flame until the contents ignite and burn (Note 3). Place the dish on a hot plate and allow the contents to burn gently. Cool, add 3 or 4 drops of concentrated H_2SO_4(relative density 1.84) and heat gently over a small flame until fuming ceases, taking care not to heat strongly enough to cause spattering. Then ignite over a burner, never allowing the dish to become hotter than a dull red, until all carbon has disappeared. Cool, add 3 or 4 drops of concentrated H_2SO_4, and fume off the acid as before, taking care to avoid spattering. When fuming ceases, heat in a muffle furnace at 800 to 1000°C (1500 to 1800°F) to constant weight. Cool in a desiccator prior to weighing. Designate this weight as *I*.

NOTE 3—Ignition of sample and subsequent fuming with H_2SO_4 should be conducted in a suitable hood. Wear protective goggles during fuming of H_2SO_4.

12. Basicity or Acidity (Sodium Sulfonate Products)

12.1 The basicity of a sodium sulfonate product is determined by weighing 10 g of the sample (Note 4) to the nearest 0.01 g into a tared 250-mL beaker, designating the sample mass as *X*. Add 100 mL of isopropyl alcohol (50 %) and stir to dissolve the sodium sulfonate and disperse the oil; warm, if necessary, to hasten the process. Add a few drops of phenolphthalein indicator solution. If the solution is pink, titrate with 0.1 mol/L H_2SO_4 to the disappearance of the pink color. If the solution is colorless, titrate with 0.1 mol/L NaOH solution to the first persistent faint pink color (Note 5). Designate the volume of the reagent used as *Y* and its normality as *Z*.

NOTE 4—The weight of sample taken for analysis should contain approximately 5 g of pure sodium sulfonate.

NOTE 5—The basicity determined by the foregoing procedure includes that due to free NaOH and to the conversion of Na_2CO_3 to $NaHCO_3$. If the alkalinity is due to NaOH and Na_2CO_3 only, and a more accurate measure of free NaOH is required, the method of Treadwell and Hall[5] may be used.

13. Inorganic Salts (Sodium Sulfonate Products)

13.1 Weigh 3 g of sample to the nearest 0.5 mg in a tared ignited platinum crucible, designating the weight as *AA*. Carefully heat the dish over a small flame until the contents ignite and burn. Place the dish on a hot plate, and allow the contents to burn gently. Cool, add 3 or 4 drops of concentrated H_2SO_4, and heat gently over a flame until fuming ceases, taking care not to heat strongly enough to cause spattering (Note 3). Then ignite over a burner, never allowing the dish to become hotter than a dull red, until all carbon has disappeared. Cool, add 3 or 4 drops of concentrated H_2SO_4, and fume off the acid as before, taking care to avoid spattering. When fuming ceases, heat in a muffle furnace at 800 to 1000°F (1500 to 1800°F) to constant weight. Designate this weight at *BB*. Cool in a desiccator prior to each weighing.

14. Water

14.1 Determine the water content of the sample by Test Method D 95.

15. Relative Density

15.1 Fill the pycnometer with the sample, warming to 70 to 80°C (160 to 180°F). Hold the pycnometer at 70 to 80°C (160 to 180°F) until all air bubbles have risen to the top. Place in a bath at 25 ± 0.2°C (77 ± 0.3°F) for 2 h, adding more sample if necessary, so the pycnometer remains full. Remove excess product flush with top of the pycnometer by means of a spatula. Remove the pycnometer from the bath, wipe the sides of the neck with a cloth, moistened with alcohol; wipe thoroughly dry; put the cap into place; and weigh to the nearest 1 mg. Designate this mass as W_s.

16. Base Number

16.1 Determine the total base number by Test Method D 2896.

17. Calculations

17.1 Calculate the results as follows, using the symbols defined in 3.1.

17.1.1 *Mineral Oil*—Calculate the mass percentage of mineral oil as follows:

$$\text{Mineral oil, mass \%} = (D - F)100/(B/100)A \quad (1)$$

for calcium, barium, magnesium, or ammonium sulfonate or $(D - F)100/C$ for sodium sulfonate.

17.1.2 *Sodium Sulfonate*—Calculate the mass percentage of sodium sulfonate, *U*, as follows:

$$\text{Sodium sulfonate, mass \%} = (E - G)100/C \quad (2)$$

17.1.3 *Calcium, Barium, Magnesium, or Ammonium Sulfonate*—Calculate the mass percentage of calcium, barium, magnesium, or ammonium sulfonate, *V*, as follows:

$$V = (E - G)J100/(B/100)A \quad (3)$$

17.1.4 *Equivalent Weight of Sodium Sulfonate*—Calculate the average equivalent weight of sodium sulfonate, *S*, as follows:

$$S = 71\,H/I \quad (4)$$

17.1.5 *Average Molecular Weight of Calcium, Barium, Magnesium, or Ammonium Sulfonates*—Calculate the average molecular weight, *T*, of calcium, barium, magnesium, or ammonium sulfonate as follows:

$$T = 2S - 6 \text{ (for calcium sulfonate)} \quad (5)$$

$$T = 2S + 91 \text{ (for barium sulfonate)} \quad (6)$$

$$T = 2S - 22 \text{ (for magnesium sulfonate)} \quad (7)$$

$$T = S - 5 \text{ (for ammonium sulfonate)} \quad (8)$$

17.1.6 *Basicity or Acidity* (*Sodium Sulfonate Products*)—Calculate the basicity as percentage of NaOH (CC_B), or the acidity as percentage of H_2SO_4(CC_A) as follows:

$$CC_B = 40YZ/10X \quad (9)$$

$$CC_A = 40YZ/10X \quad (10)$$

17.1.7 *Inorganic Salts* (*Sodium Sulfonate Products*)—Calculate the percentage of inorganic salts, *DD*, as sodium sulfate.

$$DD = 100(BB/AA) - (71U/S) - (71CC_B/40) \quad (11)$$

17.1.8 *Relative Density*—Calculate the specific gravity as follows:

$$\text{Relative density, } 25/25°C = W_s/W_c \quad (12)$$

18. Precision and Bias

18.1 The precision of the method as determined by statistical examination of interlaboratory results is as follows:

18.1.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Constituent	Difference
Sulfonate, mass %	0.63
Mineral oil, mass %	0.92
Water, mass %	0.1
Average molecular weight	$0.000032S^2$ or $0.000032T^2$
Relative density	0.001

18.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

[5] Treadwell, F. P., and Hall, W. T., "*Analytical Chemistry*," John Wiley and Sons, Inc., New York, NY, Eighth Edition, Vol II, p. 512.

Constituent	Difference
Sulfonate, mass %	0.92
Mineral oil, mass %	1.74
Water, mass %	0.34
Average molecular weight	$0.000067S^2$ or $0.000067T^2$
Relative density	0.0075

18.2 *Bias*—Bias cannot be determined because there are no acceptable reference materials suitable for determining the bias in this test method.

19. Keywords

19.1 ammonium sulfonate; barium sulfonate; calcium sulfonate; inorganic salts; liquid chromatography; magnesium sulfonate; mineral oil; molecular weight; petroleum sulfonates

SUMMARY OF CHANGES

(1) Corrected the text to refer to 17.1.5 for Symbol *T* in the Terminology section.

(2) Corrected the text to refer to Note 1 in 9.1.
(3) Corrected the text to refer to Note 3 in 11.2..