Rapid, Accurate Method for the Determination of Sulfur Trioxide in Hydraulic Cement

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A method for determining sulfur trioxide (SO_3) content of hydraulic cement is described. The method depends on heating the sample with the least possible amount of nitric acid. After filtration, the filtrate is diluted to a given volume and an aliquot passed through a cation exchange resin (hydrogen form) to separate all cations present. The eluant is diluted to volume, and an aliquot titrated against standard barium perchlorate solution using dimethylsulfonazo III (DMSA III) as visual indicator. Acetone helps detection of the equivalence point that is characterized by a color change from purple to sky blue. Seven Standard Reference Material portland cements and three commercially available cements were analyzed. Each cement sample was analyzed six times. The average absolute error for 60 determinations amounted to ±0.041 percent, and the pooled standard deviation, s_p, for the 10 samples is 0.031 percent, for 50 degrees of freedom. All of the samples analyzed passed the t test at the 99 percent level. One sample determination consumes about 2 hr. The method requires no equipment other than a pH meter and ordinary glassware.

The significance of the sulfur trioxide (SO_3) content of cement cannot be overemphasized. The amount of SO_3 present in portland cement affects the creep as well as other physical properties of concrete (*1*). The behavior of portland cement mortars (*2*) is also influenced by the SO_3 content.

A sulfate environment, as well, can be detrimental. Sodium sulfate in the ground moisture subjects concrete to corrosion and destruction (*3*). Asbestos cement pipes are vulnerable to sulfate attack if sulfate salts exist in the vicinity (*4*). Ouyang et al. (*5*) discussed the sulfate attack resistance of portland cement mixtures containing phosphogypsum.

The ASTM C114-85 describes a gravimetric method for determination of the SO_3 content in hydraulic cement (*6*). In that method, sulfate is precipitated as barium sulfate ($BaSO_4$); after digestion for 12 to 24 hr, the precipitate is ignited at 800°C to 900°C for several hours. After cooling to room temperature, the weight of $BaSO_4$ is used to calculate the SO_3 equivalent. For rapid determinations, the digestion time may be cut to 3 hr, but rejection of a cement for violation of the specification requirement must be based only on the 12- to 24-hr digestion period.

A visual titrimetric finish can offer both the high degree of accuracy and the level of precision usually associated with gravimetry, but in a much shorter time, provided a suitable indicator is available. Sulfate ion (either as inorganic sulfate, or as obtained after oxidative combustion of organic sulfur) can be determined titrimetrically against barium ion solution using thorin (*7,8*), tetrahydroxyquinone (*9*), carboxyarsenazo (*10*), sulfonazo III (*11*), arsenazo III (*12*), or chlorphosphonazo III (*13*) as visual indicator. But there seems to be some difficulty in detecting the equivalence point with most of these indicators (*11,14,15*). Budesinsky and Krumlova (*16*) carried out a comparative study on the titrimetric determination of sulfur and sulfate, against barium ion solution using six different indicators: thorin, carboxyarsenazo, sulfonazo III, dinitrosulfonazo III (*17*), dimethylsulfonazo III (DMSA III) (*18*), and dibromosulfonazo III (*18*). The authors (*16*) noted that DMSA III is the best indicator, and that this is true both for the visual and the photometric titrations. Reijnders et al. (*19*) reported the superiority of DMSA III to other indicators, e.g., thorin, for determination of sulfate in real environmental water samples. Not surprisingly, a titrimetric procedure (*20*) applying DMSA III as the indicator has been recommended by the Association of Official Analytical Chemists (AOAC), for titration of sulfate against barium perchlorate solution.

In the present method, DMSA III is used as visual indicator of the equivalence point for the sulfate versus barium titration. The amount of sulfate involved and the cement matrix, however, did introduce difficulties, and pretreatment of the sample is deemed necessary.

EXPERIMENTAL

Apparatus

Orion pH meter, model 601A, digital Ionalyzer, capable of reading the pH value to 0.01 of a pH unit.

Reagents and Materials

- Potassium sulfate (ACS), powdered and dried;
- Dowex 50W, cation exchange resin, hydrogen form, 8 percent cross-linked, dry-mesh 50–100;
- Barium perchlorate standard solution, 0.01 M. Dissolve about 3.4 g of the anhydrous salt in 1 L of distilled water and adjust the pH value of the solution to 3.0 with 0.5 N HCl. Standardize as follows. Weigh, by difference, 5 to 10 mg (weighed to the nearest 0.01 mg) of freshly dried potassium sulfate.

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Introduce the sample into a 200-ml tall-form graduated beaker. Add 50 ml of distilled water, and stir to dissolve. Adjust the pH value of the solution to 3.0 ± 0.2 by addition of 0.5 N HCl. Add 50 ml of acetone, followed by 0.3 ml of DMSA III indicator solution. Titrate as described later under procedure. Correct the titration by making a blank determination under the same conditions but without sulfate. Calculate the exact molarity of the barium perchlorate solution.

- Dimethylsulfonazo III indicator solution, 0.1 percent. Dissolve 100 mg of DMSA III in 30 ml of distilled water. Elute the solution through a column of Dowex 50 ion exchange resin (pretreated with HCl). Dilute the eluent to 100 ml with distilled water.
- Ammonium hydroxide, 1:1, and 0.5 N solutions.
- Acetone, reagent grade.
- Nitric acid, 70 percent solution.

Procedure

Weigh, by difference, 0.5 g of cement to the nearest 0.01 mg. Introduce the sample into a 250-ml beaker. Add 25 ml of distilled water, then 1.2 ml of concentrated nitric acid solution. Grind the material with a glass rod, and add 25 ml more of distilled water. Digest for 10 min on a hot plate at a temperature just below boiling, then boil gently for 5 min. Filter to separate undissolved matter, and transfer the filtrate quantitatively to a 100-ml volumetric flask. Complete to volume with distilled water. Pipet 50 ml of the solution into a separatory funnel mounted at the top of a 100-ml buret filled with the ion-exchange resin. Elute the sample solution through the column at a flow rate of 3 to 4 ml/min. Rinse the column with three 50-ml portions of distilled water. Collect the eluant and washings in a 250-ml volumetric flask, and add distilled water up to the mark.

Pipet 50 ml in a 200-ml tall-form graduated beaker. Immerse a combined glass electrode in solution and introduce a few drops of 1:1 ammonium hydroxide solution until the pH value of solution is about 2.0. Adjust the pH value to 3.0 ± 0.2 with 0.5 N ammonium hydroxide solution. Add 50 ml of acetone, then 0.3 ml of DMSA III solution. Stirring vigorously, titrate slowly with 0.01 M barium perchlorate solution to a sky-blue color that persists while stirring for at least 30 sec.

Carry out a reagent blank under exactly the same conditions except for the cement sample.

The ion exchange resin (*21*) is regenerated as follows. At a high flow rate, elute 1 L of 1 N HCl solution through the column. Rinse the regenerant with 100 ml of distilled water. After every three or four sample runs, backwash the resin bed to eliminate resin compaction and to wash off insoluble contaminants.

Calculate the SO_3 percentage as follows:

$$SO_3, \% = \frac{80.06 \times [\text{ml } Ba(ClO_4)_2 - \text{Reagent Blank}] \times F \times 100}{V \times W} \quad (1)$$

where

80.06 = atomic weight of SO_3, mg;
F = dilution factor (F = 10 for the given volumes);
V = volume of barium perchlorate solution that contains 1 mM of barium ion, ml; and
W = sample weight, mg.

RESULTS AND DISCUSSION

In the present method, sulfate is removed from solution as barium sulfate; complete removal is manifested by appearance of the blue color of the stable barium-DMSA III complex. The use of barium as titrant offers the advantage that its sulfate salt has the lowest solubility product (1.1×10^{-10}) among the insoluble sulfates (*22*).

Pretreatment of Sample

For DMSA III to detect the equivalence point of the precipitation titration of sulfate versus barium, the reaction medium has to have a pH value of 3.0 ± 0.2. Under this condition, metal ions such as iron, aluminum, and calcium known to be present in cement will precipitate and render detection of the end point difficult. Elimination of iron and aluminum through precipitation as hydroxides by addition of 1:1 ammonium hydroxide solution, and removal of calcium as calcium oxalate by addition of solid ammonium oxalate, then removing the excessive oxalate (which would otherwise precipitate barium) by boiling with HCl solution was tried, but, the color change of the indicator was not very sharp, and the repeated steps of boiling, precipitation, filtration, and washing render the procedure more susceptible to error.

To eliminate metal ions from sample solution, at the same time avoiding the introduction of foreign ions in the reaction medium, an alternative approach is to use a cation exchange resin in the H^+ form.

The color change of DMSA III proved to be much sharper in dilute solutions. In order to have a minimum ionic concentration in the reaction medium, 1.2 ml of nitric acid solution is used to dissolve the cement sample, instead of the 5 ml of hydrochloric acid solution used in the reference method (*6*). To effect dissolution, a 10-min digestion period is necessary. Subsequent boiling of the acidic sample solution for 5 min ensures decomposition of any carbonate present to avoid formation of barium carbonate precipitate (*22*) during the subsequent titration.

After eluting the sample solution through the resin bed, the eluant volume is increased to 250 ml. For each titration, 50 ml is used. Such a design has two advantages: (a) it keeps the ionic concentration at a low level, and (b) it allows three or four titrations from each sample solution. The volume of titrant consumed per titration is not too small and is in the vicinity of 2 ml for most of the samples analyzed.

In order to test the effect of time on the treated sample solution, a part of an eluant was titrated 24 hr after elution. Comparing the results with those obtained immediately after elution reveals practically no variation in the volume of titrant consumed. Thus, the treated sample solution may be left to stand overnight before titration, if necessary.

Barium-DMSA III Complex

In the precipitation titration of sulfate against barium, the poorest reversibility of the indicator color change occurs at the beginning of the titration, because of the precipitation mechanisn of the titration; the proper course of the titration requires the formation of precipitation centers in solution (*16*). Therefore, the first three or four drops of titrant should be added slowly. The reversibility of the color change improves rapidly as the titration continues and is satisfactory at the equivalence point. Budesinsky et al. (*23*) reported an experimental value of 3.8×10^4 for the effective stability constant of the barium-DMSA III complex.

Accuracy, Precision, and *t*-Test for Sample Averages

Analysis of seven Standard Reference Material (SRM) portland cements, obtained from the National Institute for Standard Technology, and three commercially available cements reveals high accuracy of the proposed method (Table 1). For 60 sample runs, the average absolute error amounted to ± 0.041 percent. The precision, as calculated by the sample standard deviation, s, ranged between 0.009 and 0.043 percent for the 10 samples analyzed; for each estimate of s, the degrees of freedom (df) was equal to 5. However, the pooled standard deviation, s_p, would be based on the sum of the df values for each of the standard deviation estimates, in this case $(n - 1)$

TABLE 1 ANALYSIS OF STANDARD AND COMMERCIAL CEMENT SAMPLES FOR THEIR SO_3 CONTENT

Sample	Sample Weight (mg)	SO_3 (%) Expected	Found	Error	Standard Deviation, s
SRM 633	–	2.20	–	–	0.043
	452.23		2.19	−0.01	
			2.17	−0.03	
			2.15	−0.05	
	532.46		2.11	−0.09	
			2.09	−0.11	
			2.09	−0.11	
SRM 634	–	2.21	–	–	0.036
	480.45		2.22	+0.01	
			2.20	−0.01	
			2.14	−0.07	
	487.82		2.24	+0.03	
			2.18	−0.03	
			2.17	−0.04	
SRM 635	–	7.07	–	–	0.036
	481.34		6.96	−0.11	
			7.01	−0.06	
			6.99	−0.08	
	483.59		7.03	−0.04	
			7.06	−0.01	
			7.04	−0.03	
SRM 636	–	2.31	–	–	0.009
	482.86		2.36	+0.05	
			2.36	+0.05	
			2.34	+0.03	
	503.16		2.28	−0.03	
			2.27	−0.04	
			2.27	−0.04	
SRM 637	–	2.38	–	–	0.036
	506.32		2.45	+0.07	
			2.43	+0.05	
			2.38	0.00	
	456.90		2.41	+0.03	
			2.41	+0.03	
			2.35	−0.03	
SRM 638	–	2.34	–	–	0.018
	529.38		2.33	−0.01	
			2.36	+0.02	
			2.36	+0.02	
	482.56		2.40	+0.06	
			2.38	+0.04	
			2.31	−0.03	
SRM 1880	–	3.37	–	–	0.033
	463.36		3.27	−0.10	
			3.29	−0.08	
			3.36	−0.01	
	458.06		3.33	−0.04	
			3.34	−0.03	
			3.31	−0.06	

(*continued on next page*)

TABLE 1 (*continued*)

Sample	Sample Weight (mg)	SO_3 (%) Expected	Found	Error	Standard Deviation, *s*
Missouri Portland Type III	–	2.95	–	–	0.027
	556.82		3.02	+0.07	
			3.02	+0.07	
			2.99	+0.04	
	455.00		2.95	0.00	
			2.98	+0.03	
			3.00	+0.05	
Monarch Type II	–	2.45	–	–	0.014
	498.13		2.42	−0.03	
			2.46	+0.01	
			2.46	+0.01	
	553.06		2.42	−0.03	
			2.41	−0.04	
			2.41	−0.04	
Monarch Type III	–	2.85	–	–	0.042
	464.61		2.89	+0.04	
			2.87	+0.02	
			2.83	−0.02	
	485.45		2.77	−0.08	
			2.83	−0.02	
			2.86	+0.01	

(0.10) = 50, where n is the number of determinations carried out for each sample, and 10 is the number of standard deviations involved. The pooled standard deviation is calculated from the following expression (*24*):

$$s_p = \left[\frac{(s_1^2 \times df_1) + (s_2^2 \times df_2) + \ldots (s_n^2 \times df_n)}{df_1 + df_2 + \ldots df_n}\right]^{1/2} \quad (2)$$

where s_1^2, s_2^2, s_n^2 = variance for first, second, and nth sample data, respectively, and df_1, df_2, df_n = degrees of freedom for first, second, and nth sample, respectively. The pooled standard deviation = 0.031 percent, for 50 df.

Because the population standard deviation, σ, is not known, a test of significance should use the t statistic (*25*).

$$t = \frac{\bar{x} - \mu}{s/(n)^{1/2}} \quad (3)$$

where $\bar{x}$ is the average SO_3 percentage found, and μ is the expected value.

The t test was first used to find out whether the calculated statistic of sample average, $\bar{x}$, found for each of the seven SRM cement samples agrees with the expected value (the population average, μ). The t test was then applied to judge whether the calculated sample average, $\bar{x}$, found for each of the commercially available cement samples agrees with the value reported by the Materials Unit Laboratories of the Kansas Department of Transportation (KDOT) using ASTM C114 (*6*) for the SO_3 content. Table 2 indicates that the null hypothesis (H_0: $\mu = \mu_0$) is correct for all of the samples analyzed. That is, for the seven SRM cements, the sample average, $\bar{x}$, found practically agrees with the population average, μ, reported by the SRM certificate; for the commercial cements, $\bar{x}$ agrees with the SO_3 content reported by the Materials Unit, KDOT.

For SRM 634, the t statistic is

$$t = \frac{2.19 - 2.21}{0.036/(6)^{1/2}} = -1.333$$

From the t distribution critical values table, across from df = 5, a t value equal to 1.333 (the sign is not significant) has a P-value between 0.10 and 0.15. Because the alternate hypothesis, H_a is double-sided, the P-value should be doubled and is between 0.20 and 0.30. At the 99 percent level, α equals 0.01, and $p = \alpha/2$ or 0.005. A comparison between the value of p (0.005) and the P-value of 0.20 to 0.30 indicates that the standardized difference between the sample average obtained (2.19 percent) and the SRM certificate value of 2.21 percent is not statistically significant, and is caused by the expected sampling distribution. For a commercial cement, t is calculated similarly except that the SO_3 content reported by the Materials Unit Laboratories is substituted for μ in the previous equation.

Under the specified experimental conditions, the proposed method can detect as little as 0.1 percent of SO_3 in cement.

SO_3 Content of Fly Ash

As for cement, the SO_3 content of fly ash is of interest. The present method has been tested, without modification, on fly ash. The results of testing a limited number of samples agree favorably with those obtained by the ASTM C311-77 (*26*),

TABLE 2 APPLICATION OF THE *t* TEST FOR THE AVERAGE SO_3 CONTENT OF THE CEMENT SAMPLES ANALYZED

Sample	Average SO_3 %, $\bar{x}$	Null Hypothesis	Alternate Hypothesis*	t**	P-Value (range)	Decision §
SRM 633	2.13	H_o:μ=2.20	H_a:$\mu\neq$2.20	-3.889	0.010-0.020	a
SRM 634	2.19	H_o:μ=2.21	H_a:$\mu\neq$2.21	-1.333	0.200-0.300	a
SRM 635	7.01	H_o:μ=7.07	H_a:$\mu\neq$7.07	-4.000	0.010-0.020	a
SRM 636	2.31	H_o:μ=2.31	H_a:$\mu\neq$2.31	0.0	>0.50	a
SRM 637	2.41	H_o:μ=2.38	H_a:$\mu\neq$2.38	2.000	0.100-0.200	a
SRM 638	2.36	H_o:μ=2.34	H_a:$\mu\neq$2.34	2.857	0.020-0.040	a
SRM 1880	3.32	H_o:μ=3.37	H_a:$\mu\neq$3.37	-3.846	0.010-0.020	a
Missouri Portland Type II	2.99	H_o:μ=2.95	H_a:$\mu\neq$2.95	3.636	0.010-0.020	a
Monarch Type II	2.43	H_o:μ=2.45	H_a:$\mu\neq$2.45	-3.333	0.020-0.040	a
Monarch Type III	2.84	H_o:μ=2.85	H_a:$\mu\neq$2.85	-0.588	>0.50	a

* Double-sided test.
** df = 5 for each estimate.
§ At the 99% confidence level, with p equal to 0.005.
a = H_o is correct.

but the time required for analysis is much shorter than for the reference method. Details from testing an adequate set of standard and samples will be published in the future.

CONCLUSIONS

The proposed method is characterized by having high precision and accuracy. The maximum difference between replicates, as well as the maximum difference of the average of replicates from seven SRM certificate values, are within the limits specified by the ASTM C114-85 method (*6*). Furthermore, the time required for one determination is about 2 hr. This time compares favorably with the ASTM C114-85 method (*6*) used at KDOT, which requires a period of 9 hr, as a minimum for routine testing, and 18 hr for check testing. The present method is recommended as a reference method for determination of the SO_3 content of hydraulic cement.

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