Automated Determination of Silicate and Carbonates in Detergents[1]

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ABSTRACT

The analysis of silicate and carbonate builders in detergents is time consuming by standard gravimetric procedures (1,2). By modifying established Technicon AutoAnalyzer methods, rapid and simple methods of analyzing these detergent builders have been achieved. Standard AutoAnalyzer modules, arranged for colorimetric analysis, are used, and 10-15 samples per hour can be handled. In the silicate analysis, an aqueous solution of the sample is reacted with ammonium molybdate in an acid medium to form silicomolybdic acid. This acid is partially reduced by ascrobic acid forming the pentavalent molybdenum blue complex. The carbonate method is based upon the evolution of carbon dioxide gas, which is reacted with a buffered phenolpthalein solution. The color intensity of the system is inversely proportional to the carbon dioxide concentration. When a blend of carbonate and bicarbonate is present in the sample, analysis before and after heating is required.

INTRODUCTION

The analysis of soluble silicate was adopted from an automated system used by the cement industry (3). Their procedure entails a fusion step in the sample preparation and the use of hydrofluoric acid to eliminate iron interferences. Since the amount of insoluble silicate present in detergents is generally less than 1.0% and no iron is present, eliminating the fusion step and the hydrofluoric acid provided a simple and rapid analysis of soluble silicate in detergents.

The carbonate method is based on Technicon's AutoAnalyzer Methodology N-22 (4) and has been adopted for use in detergent samples.

ANALYSIS OF SOLUBLE SILICATE IN DETERGENTS

Apparatus

Technicon AutoAnalyzer system: Sampler II with cam 20 1:1, proportioning pump, one 40 ft glass coil, colorimeter with 8 mm flow cell and 660 nm filter, and recorder.

Materials

1.0% Ammonium molybdate: 5.0 g reagent grade ammonium molybdate and 3 ml concentrated sulfuric acid are dissolved in distilled water, and diluted to 500 ml. 1.0% Ascorbic acid: 5.0 g ascorbic acid USP are dissolved in distilled water and diluted to 500 ml. Detergent solution: 0.5 ml Brij 35 is diluted to 1 liter. Silicate standard: Metso anhydrous silicate 2048 from Philadelphia Quartz Co. (assay-47.0% as SiO_2) or equivalent.

TABLE I

Effect of Sample Size on Per Cent SiO_2

Sample no.	1 g/100 ml	2.5 g/500 ml	5 g/500 ml
1	5.21	5.48	5.60
2	5.41	5.68	5.55
3	5.02	5.29	5.60
4	5.18	5.48	5.47
5	5.55	5.36	5.55
6	5.55	5.53	5.80
$\bar{x}$	5.32	5.47	5.60
s	0.22	0.14	0.11
Coefficient of variation	4.1%	2.6%	2.0%

Preparation of Standards

An anhydrous silicate, such as Metso anhydrous silicate powder (Philadelphia Quartz Co.), is prepared as a stock solution using distilled water containing 10.0 mg SiO_2 per milliliter. From this stock solution, various aliquots are diluted to 200 ml. These solutions are further diluted, 5 ml to 100 ml. When a 2.5 g sample is diluted as described below, the final concentrations of the standards will be equivalent to direct per cent as SiO_2. For example, for an expected 10% SiO_2 sample, it is recommended that 8, 9, 10 and 11 ml aliquots of the stock solution be taken and diluted to 200 ml. The solutions are then diluted, 5 ml to 100 ml. The solutions will then correspond to 8, 9, 10 and 11% SiO_2, respectively.

Sample Preparation

Our experience shows that detergent samples approach homogeneity when ground in an Osterizer. Particular care must be taken when grinding samples, since heat generated causes lumping of the sample and eventually jamming of the blade. The following procedure has been adopted: all samples are ground intermittently for a total period of 1 min; for example, 100 g of sample are ground 10-15 sec; the mason jar is removed, inverted, and turned a few times; then the sample is ground again 10-15 sec and so on.

A 2.500 ∓ 0.005 g sample is weighed and diluted to 500 ml distilled water. This solution is heated on a steam bath for 15 min to ensure that the silicate is completely dissolved; the mixture is cooled to room temperature and 5 ml/100 ml distilled water aliquoted.

Analysis

Figure 1 shows the various Technicon modules arranged for the analysis of silicate as SiO_2. Solutions of standard silicate and sample solutions are placed on a sample tray and aspirated into the system at a rate of 20 cups per hour by the sampler. The aspirated solution is diluted with water and simultaneously segmented with air in order to eliminate cross-contamination of one solution by another. After the diluted solution has been mixed by passing through a glass coil, an acidified 1.0% ammonium molybdate solution is introduced, which forms a silicomolybdic acid complex (5). The next step is the partial reduction of the silicomolybdic acid complex by a 1.0% solution of ascorbic acid, which forms the pentavalent molybdenum blue complex. To ensure color development of the complex, the solution flows through a 40 ft glass time-delay coil. The solution flows from the coil into a colorimeter, and the color intensity is measured at a wavelength of 660 nm. The observed intensity of the molybdenum blue complex is directly proportional to the concentration of silicate.

Calculation

The maximum peak heights of the standards and samples are read in optical density. A calibration curve is drawn using per cent SiO_2 vs. optical density. From this calibra-

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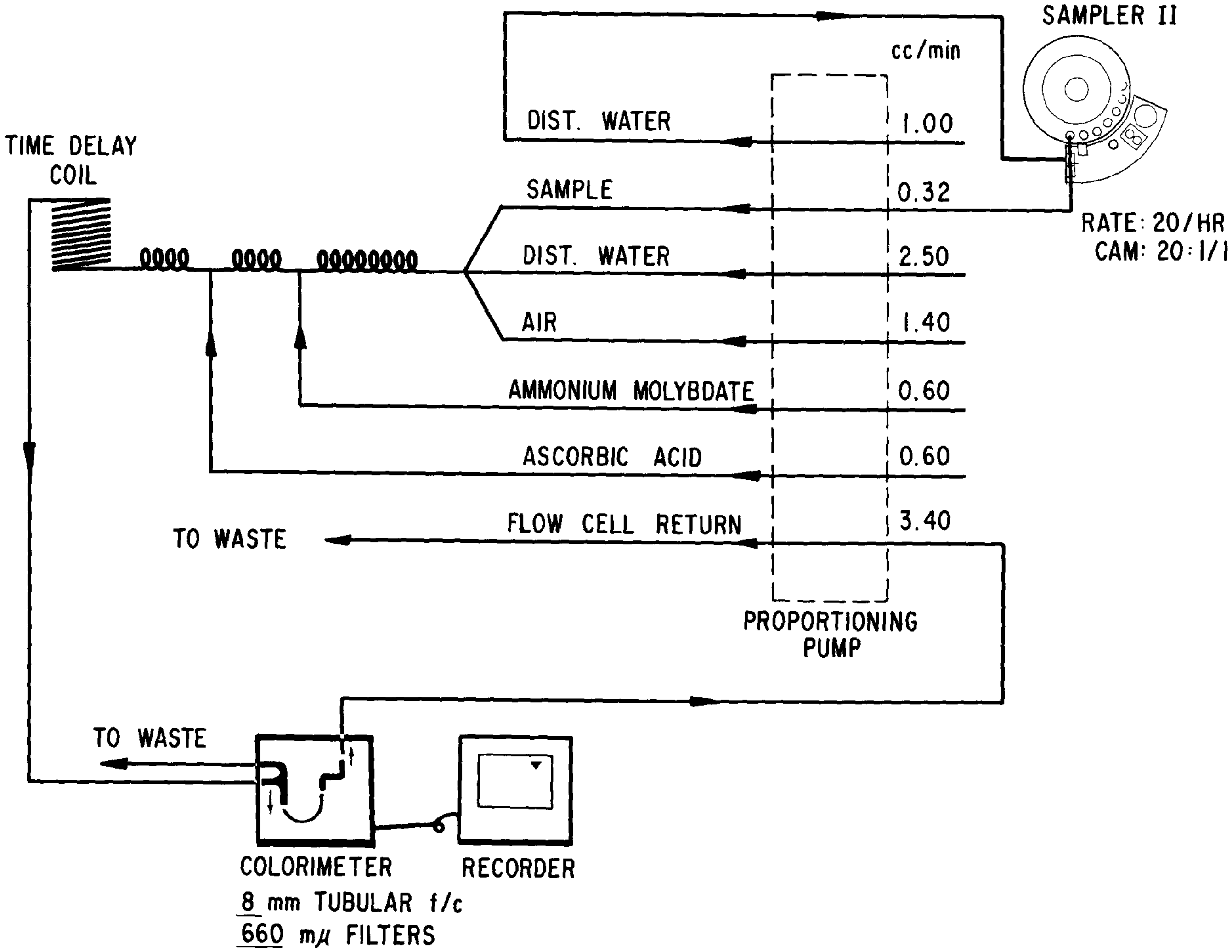

FIG. 1. Flow diagram for analysis of soluble silicate.

tion curve, direct per cent SiO_2 is obtained from the respective optical density. Correction for any instrumental drifting is accomplished by using standards between sample series. The per cent SiO_2 can easily be converted to sodium silicate, provided the ratio of Na_2O to SiO_2 is known.

Results and Discussion

To check the precision of the manifold, a single-weighed detergent sample was aliquoted six times. From the data, a coefficient of variation was calculated and found to be 0.6%, indicating a stable manifold.

When a 1.0 g sample was taken for analysis, poor precision was obtained. Thus an experiment was devised to see the effect of sample size. A commercial detergent sample was ground for 1 min. Six 1.0 g samples, six 2.5 g samples and six 5.0 g samples were weighed and diluted as shown in Table I. These solutions were further diluted so that the final concentrations were equivalent.

The same detergent analyzed three times by a standard gravimetric method gave a mean 5.54% SiO_2. The increase in coefficient of variation as the sample size decreases may be due to heterogeneity of the sample itself. As the sample weight, 2.5 g of sample was chosen based on two considerations. First, the data indicates that large sample weights should be taken because of sample nonuniformity. Secondly, since detergent formulations differ widely, having different solubilities, the samples should be initially dissolved in the greatest convenient volume.

To ensure the dissolution of the silicate, the sample solution should be heated. The amount of heating will be dependent upon the sample's other components and left to the discretion of the analyst. The solution must be cooled to room temperature and an aliquot taken as soon as possible. The reason for aliquoting the sample immediately is that these solutions, on standing, can begin to precipitate and even gel. To illustrate the effect of heating, a detergent was sampled 10 times and diluted; five samples were heated before analysis and the others were not. The mean of the SiO_2 values for the heated samples was 5.0%, while the mean of the nonheated samples was 4.3%. A gravimetric analysis gave a value of 4.7% SiO_2; therefore the practice of heating the sample solutions is encouraged. A number of commercial detergent samples containing silicate were analyzed both by the automated and gravimetric methods. Table II compares the results of both methods. The data indicate good agreement between the automated and

TABLE II

Comparison of Silicate Analysis by Automated and Gravimetric Methods

Sample	Automated	Gravimetric
1	16.9	17.4
2	17.7	18.0
3	18.8	18.6
4	9.5	8.8
5	5.8	5.7
6	6.2	6.3
7	22.4	21.4
8	9.7	9.2

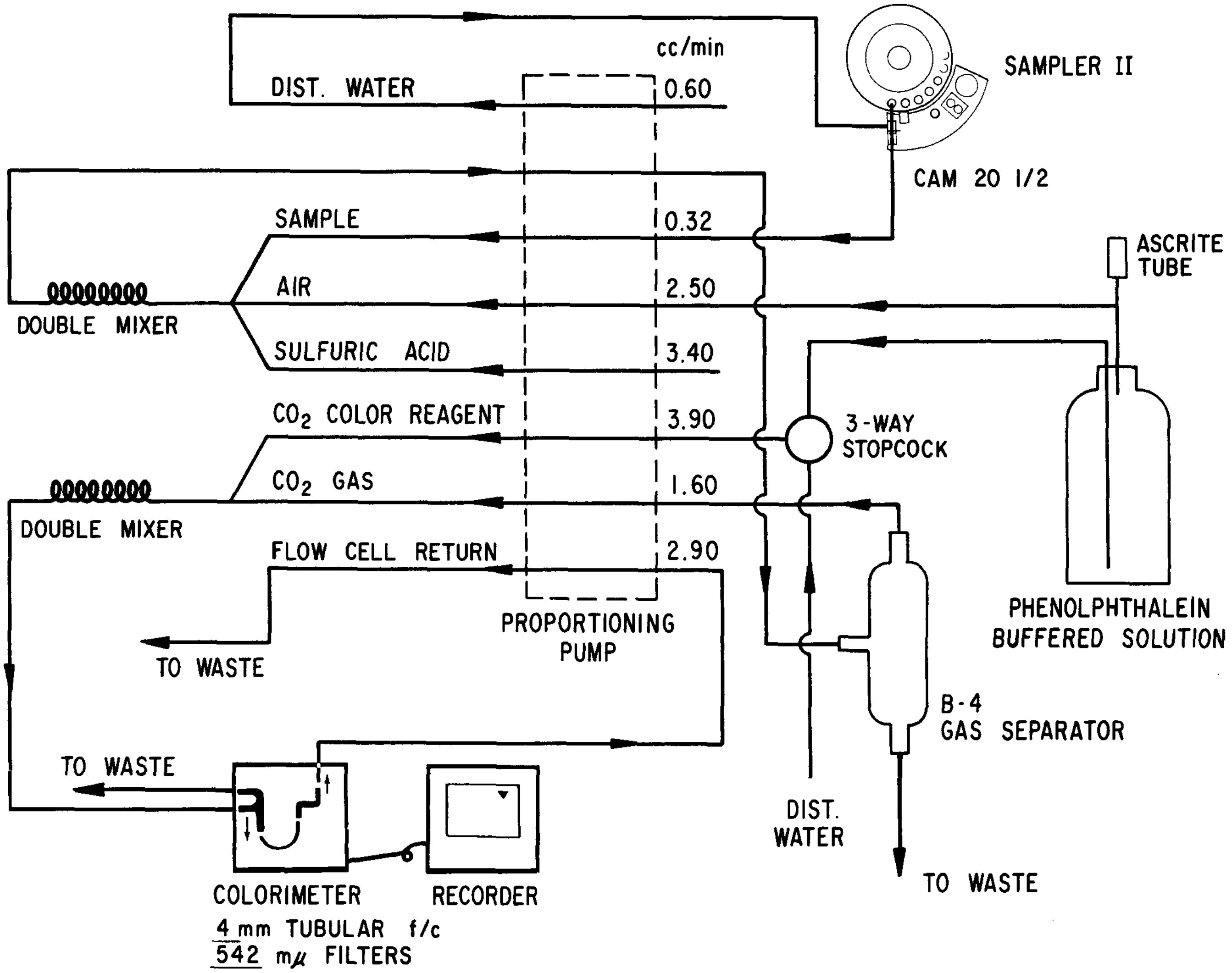

FIG. 2. Flow diagram for analysis of carbonates.

gravimetric techniques used in the analysis of silicate.

Interference

Phosphate is considered an interference in silicate analysis that uses the molybdenum blue complex technique. To evaluate the extent of the interference, a blend of 40% sodium tripolyphosphate with 30% sodium sulfate and 30% metasilicate was analyzed. The mean of eight samplings of this blend was 29.6% sodium silicate, indicating no interference by sodium tripolyphosphate. Ortho- and pyrophosphate were also checked for interference, and it was found that pyrophosphate did not interfere but orthophosphate did.

In general, the average detergent contains only negligible amounts of orthophosphate, insufficient to affect the analytical results. When there is doubt as to the presence of orthophosphate, a phosphate breakdown analysis should be done; if orthophosphate is found, a correction factor can easily be inserted into the calculation.

When the pH of the initial solution of a detergent sample is above 10, our results indicate complete recovery. However, at a lower pH, recovery is incomplete. A detergent formulation containing 8.5% silicate was dissolved in water and had a pH of 7.5. The resulting SiO_2 analysis was 4.1%. When the same sample was dissolved in 0.2% Na_2CO_3, the result was 8.4%. The strength of the carbonate must be kept at the 0.2% level; otherwise it will attack the glass volumetric flasks and the glass coil in the manifold. Further work is presently in progress in this area.

ANALYSIS OF CARBONATES IN DETERGENTS

Apparatus

Technicon AutoAnalyzer system: Sampler II with cam 20 1:2; proportioning pump; colorimeter with 4 mm flow cell and 542 nm filter; recorder; extraction gas separator B-4.

Ascarite drying tube: A 6 in. drying tube with a small

TABLE III

Buffered Phenolphthalein Reagent

% Carbonate	ml Buffer	+	ml Phenolphthalein
0-10	2		10
5-20	4		7
15-25	5		7
10-40	7		6

TABLE IV

Comparison of Carbonate Analysis between Automated and Gravimetric Methods

Detergent sample	Automated	Gravimetric
1	41.6	41.4
2	41.0	41.1
3	29.0	27.5
4	59.6	62.0
5	11.4	11.0
6	42.0	41.6

wad of cotton or glass wool is used. An inch of Drierite, then 3 in. Ascarite, followed by another inch of Drierite are added. The air drawn through this Ascarite tube is split by the use of a glass T. One portion leads into the manifold for air segmentation, and the other part is fitted to the top of the CO_2 color reagent bottle for venting.

Materials

Sodium carbonate, 1.0 M: 106.0 g reagent grade sodium carbonate is dissolved in distilled water and diluted to 1 liter. Sodium bicarbonate, 1.0 M: 84.0 g reagent grade sodium bicarbonate is dissolved in distilled water and diluted to 1 liter. Phenolpthalein reagent, 1.0%: 1.0 g phenolpthalein is dissolved in methyl alcohol and diluted to 100 ml; then Brij 35 is added. Antifoam reagent: 5 ml General Electric Antifoam 60 is diluted to 500 ml in distilled water. Sulfuric acid reagent: 15 ml concentrated sulfuric acid and 5 ml antifoam reagent are diluted to 2 liters in distilled water. Detergent solution: 0.5 ml Technicon Brij 35 is diluted in distilled water to 1 liter. Buffer solution (used to prepared CO_2 color reagent): 1 part sodium carbonate solution is mixed with 2 parts sodium bicarbonate solution. This solution is very stable and can be stored for several weeks in a plastic bottle. Buffered phenolphthalein reagent: The buffer and phenolphthalein solutions needed to prepare this reagent are diluted in distilled water to 2 liters. The amounts of these solutions added depends upon the concentration range of carbonate expected. The aliquots of buffer and phenolphthalein reagents for various carbonate concentration ranges are listed in Table III.

Preparation of Standards

Whenever possible, the same carbonate that is present in the sample should be used, but a reagent grade Na_2CO_3 is also acceptable. A stock solution of Na_2CO_3 is prepared by weighing 5.000 g Na_2CO_3 to the nearest milligram and diluting to 250 ml with distilled water. Aliquots of the stock solution are taken so that these standards are within concentration range of the samples being analyzed. For example, 2 ml, 4 ml, 6 ml, 8 ml, diluted to 100 ml, are equivalent to 4.0%, 8.0%, 12%, 16%, respectively, of Na_2CO_3 in the original product when a 1.00 g sample is diluted to 100 ml.

Sample Preparation

The detergent samples are ground for 1 min intermittently in an Osterizer. A 1 g sample is weighed and diluted to 100 ml with distilled water. If the sample contains a higher concentration than 35.0% Na_2CO_3, it should be diluted to 200 ml. Mix solution with a magnetic stirrer until dissolved or for at least 5 min.

Analysis

Diagram 2 shows the various Technicon modules arranged for the analysis of Na_2CO_3.

Standard and sample solutions are aspirated into the system at a rate of 20 cups per hour by the sampler. The aspirated solution is mixed with sulfuric acid solution and segmented with air in order to eliminate cross-contamination of samples. When the solution reaches the gas separator, all of the aqueous phase goes to the waste. The air and evolved carbon dioxide is pumped back into the system and reacted with a buffered phenolphthalein solution. After mixing, the solution passes through the colorimeter. The color intensity is inversely proportional to the concentration of carbonate and is measured at a wavelength of 542 nm using a 4 mm flow cell.

Calculation

The peak heights (optical density) of the standards and samples are subtracted from the base line optical density. A calibration curve is drawn—per cent carbonate vs. optical density. From this calibration curve, direct percentage of Na_2CO_3 is obtained for the samples. The standards between the samples are used for correction if there is drifting.

Results and Discussion

Solid standards were prepared at different sodium carbonate concentrations and analyzed using the automated method. The results show the analysis at different levels, viz., 10%, 20%, 40% and 70% of sodium carbonate, to be within 1.0% of the given concentration level with a coefficient of variation of from 0.3 to 1.1%.

A variety of differently formulated detergent products containing sodium carbonate were analyzed using this automated method and a gravimetric method. It should be noted that these samples contained soap, perborate, free chlorine, silicate, sulfate, phosphate and organic compounds in varying combinations. The data obtained from the two methods of analysis agree with one another as shown in Table IV.

Interferences

This comparison leads one into the question of interference. So far, no interferences have been found except for sodium bicarbonate. Equations 1 and 2 show the reactions when carbonate and bicarbonate mixes with the sulfuric acid in the system. Equation 3 shows what happens when bicarbonate is heated in an oven at 260 C.

$$Na_2CO_3 + H_2SO_4 \longrightarrow CO_2 + Na_2SO_4 + H_2O \qquad [1]$$

$$2NaHCO_3 + H_2SO_4 \longrightarrow 2CO_2 + Na_2SO_4 + 2H_2O \qquad [2]$$

$$2NaHCO_3 \xrightarrow[\text{Heat}]{\text{260 C}} CO_2 + Na_2CO_3 + H_2O \qquad [3]$$

By analyzing a sample before and after heating, a loss in total CO_2 can be related to the amount of bicarbonate present in the sample. The percentages of carbonate and bicarbonate in a sample are calculated using the following equations:

$$(A\text{-}B) \times \frac{2\ (\text{mol wt. } NaHCO_3) = \%\ NaHCO_3}{\text{mol wt. } Na_2CO_3}$$

$$(B\text{-}[A\text{-}B]) = \%\ Na_2CO_3$$

where A = apparent % Na_2CO_3 befoe heating and B = apparent % Na_2CO_3 after heating. A manual method, based on the same principle currently used in our labs, gave comparable results. This automated method has the advantage of being faster and simpler to run.

ACKNOWLEDGMENT

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