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[54] METHOD FOR DETERMINING SULFATE CONCENTRATION

8 Claims, No Drawings

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[56] References Cited

OTHER REFERENCES

Sporek; K. F., Anal. Chem. 30, No. 6, June, 1958, 1,032–1,035.

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**ABSTRACT:** Method for determining the sulfate ion concentration of an aqueous solution. The mechanism of the method resides in the use of a chelate of a metal which under acidic conditions dissociates to release metal ions which will react with the sulfate ion present to produce a colloidal metal sulfate precipitate. In order to ensure that the free chelant does not precipitate or react to form a precipitate, there is also added to the solution a quantity of a metal compound, the metal of which will replace the original metal of the chelate to form a water soluble second chelate. The turbidity or color density of the aqueous solution is measured and compared to the color density values obtained for solutions containing known quantities of sulfate precipitate of the same metal.

# METHOD FOR DETERMINING SULFATE CONCENTRATION

## BACKGROUND OF THE INVENTION

In many situations there is the need to ascertain the sulfate ion concentration of an aqueous solution without utilizing the well-known techniques such as the gravimetric procedures which are time consuming and require delicate techniques and sophisticated equipment.

Oftentimes where sulfate determinations are required, the economics are such that manpower, time and equipment are prohibitive. Such situations are in the water treatment industry where tests are constantly being conducted in order to insure proper operational levels. In this field many control tests are constantly being conducted on a work shift basis in many cases and accordingly the time and equipment which can be devoted to each individual test is limited.

Sulfate ion concentrations and control thereof in waters of industrial boiler systems and cooling water systems are important since the sulfate ion concentration gives an indication as to the condition of the water. For example in cooling water sulfate ion determinations are conducted to insure that the concentrations of such do not exceed the solubility point under the particular operational conditions which if exceeded will produce scale due to precipitation and deposition of calcium sulfate. In boiler water, sulfate ion concentrations are important in order to establish in conjunction with conductivity the dissolved solids of the water are accordingly the rate of blowdown necessary to avoid saturation, concentration and finally precipitation and deposition of the original constituents which were previously in a dissolved form.

Since the goal of any test procedure is minimum time and manpower tieup and minimum equipment expenditure together with consistent accuracy, the industry is constantly looking for newer, faster and more accurate test methods and of course, not least of all simple tests which can be explained to an individual worker in a mater of minutes with the expectation that he will understand and be capable of conducting the test in a short precipitate Until the advent of the present invention a procedure was utilized which generally called for the precipitation of the sulfate ion of a solution by the addition thereto of 20 to 30 mesh barium chloride crystals. Since that system as with the present invention used turbidity or color density as the frame of reference for measuring the sulfate content, it was imperative that the barium chloride crystals dissolve slowly and uniformly to permit the formation of colloidal barium sulfate particles. The use of larger crystal sizes resulted in nonuniform dissolution and accordingly large flocs of precipitate which had the tendency to occlude the aqueous phase and settle. As can be appreciated the turbidity measurements in this case were not accurate and were not reproducible.

Because the procedure was completely dependent upon the particular mesh size to insure proper and uniform dissolution and consequently uniform precipitation, care need always be observed to assure that the individual crystal particles would not aggregate due to presence of a minor amount of moisture. The system was too delicate for an industry which requires simple, quick and accurate tests. Moreover barium chloride crystals of the size required are no longer commercially available. Accordingly it was applicants goal to devise a quantitative test for sulfate which although simple, quick and accurate did not suffer from the peculiarities and the sensitivities of the method described above.

## GENERAL DESCRIPTION OF THE INVENTION

The method of the present invention generally comprises adding to a sample of a sulfate containing aqueous solution, a water soluble metal chelate which possesses the property of dissociating under acid conditions to release ions of the metal and free chelant. With proper pH control i.e. adjusting from generally the neutral state to the acidic state slowly, and preferably to a pH of from about 2.5 to 5.5, the metal ions are released slowly and uniformly so as to permit reaction of the metal ion with the sulfate ions present to produce the colloidal precipitate. Generally there is some idea as to the relative range of the sulfate concentration present in the solution, therefore it is necessary of course that sufficient metal chelate be added to insure that total reaction of the sulfate ions occurs.



In order to assure that the free chelant does not react in such a way as to produce a competitive or obscuring precipitate, a water soluble compound of second metal is added to the sample solution. This compound in solution of course yields ions of the metal. The metal ions, however, must be of such a nature that reaction with the free chelant is preferential and the resultant chelate is water-soluble. In this manner it is assured that the colloidal precipitate formed is only the metal sulfate.

Although it is not necessary a stabilizing material can be added either before, during or after the pH adjustment. The primary function of the stabilizing material is to maintain the colloidal metal sulfate precipitate dispersed in the aqueous solution to thereby provide an accurate turbidity or color density reading.

As is evident from the foregoing since the test is based upon turbidity or color density readings, the volume of sample and the volume of the addition of the particular reagent should be controlled in order to assure a proper relationship with a control. In this regard it is advisable to utilize a smaller volume sample of the solution to be tested that the reference solution, since distilled water can be added to increase the volume of test sample to conform with that of the reference solution. At this point it should perhaps be explained that the reference solution is prepared with a known quantity of sulfate ion and the solution is treated in accordance with the present invention to thereby permit the obtention of photometric readings for turbidity or color density.

Standard sulfate solutions are prepared in accordance with "ASTM STANDARDS" Part 23, 1968 pp. 54–62. These standard solutions are prepared so as to obtain in accordance with the above method readings for the inspection of turbidities or color densities for solutions containing 0, 5, 10, 15, 20, 25, etc. parts by weight of sulfate ion per million parts of weight of solution, Accordingly when turbidity or color density readings for a sample solution are taken, these reading may be compared with the reference solutions to thereby accurately determine the concentration of the sulfate ion. Although the method has been proven to be accurate by testing under many circumstances, there are certain precautions that should be observed. For example since the test is predicated upon a measurement of light transmission, any turbid sample of solution should be filtered and refiltered if necessary, to obviate any increase in the ultimate readings. As can be appreciated the presence of undesirable colloidal matter will ultimately result in higher and inaccurate reading.

In addition, care must be taken and the procedure should be modified in the determination of sulfate concentrations below5 p.p.m. This problem arises because the solubility of barium sulfate which although low will at these levels provide a sizable percentage error in the ultimate readings. This problem however can be overcome by either concentrating the sample or by adding, for example 5 milliliters of a standard sulfate solution (1 ml.=0.100 mg. sulfate) to a 50 ml. sample. This will add 0.5 mg. of sulfate to the sample which must be subtracted from the final result.

Having thus described the invention broadly, a specific embodiment is set forth as illustrative of the invention and is not to be considered limitative thereof.

## PREPARATION OF REAGENTS

Reagent No. 1

Weigh on a torsion balance 50.0 grams of sodium chloride and 26.5 grams of aluminum chloride. Dissolve the salts in approximately 500 ml. of distilled water. By means of the gradu-

ated cylinder transfer 20 ml. of the concentrated hydrochloric acid to the solution. Dilute the solution with distilled water to 750 ml. Pour 250 ml. of the glycerine reagent into the solution and mix well.

Reagent No. 2

50.0 grams of the barium chloride and 80.0 grams of the ethylene diamine tetraacetic acid-di-sodium salt into approximately 900 ml. of distilled water. Adjust the pH of the solution to 7.0 using solutions of hydrochloric acid and/or sodium hydroxide. Dilute the solution to 1 liter with distilled water.

## PROCEDURE

Filter the sample if turbid and adjust the sample to near room temperature (15° to 30° C.). Pipet into the 100 ml. beaker 50 ml. of the clear sample and add by pipet 10 ml. of Reagent No. 1. Stir the solution until mixed and pour it into the optical cell. Set the instrument to zero absorbance. Pour the sample solution back into the beaker and add by pipet 5 ml. of Reagent No. 2. Set the timer immediately and stir the solution for 5 seconds. Let stand for 4 minutes and pour the solution into the optical cell. Measure the turbidity at the 5 minute mark.

Using the above described procedure and reagents: test solutions containing known quantities of sulfate ions were produced according to the "ASTM STANDARDS," Part 23, 1968, pp. 54–62.

The test solution contained the parts per million of sulfate as set forth in the following table. Duplicate solutions for each concentration were produced. One set of the test solutions were subjected to the procedure outlined above to obtain electrically a reading for the turbidity. These results were recorded. The duplicate samples were then treated in accordance with the procedure to establish whether the absorbance values obtained closely approximated those of the initial test series. From the data recorded in the following table, it was apparent that the values obtained coincided within reasonable limits with those recorded for the initial test series and that the procedure is in fact accurate for the purpose claimed.

TABLE

| Initial sample Solutions with the specified sulfate concentrations | Absorbence readings × 1,000 for— | | Duplicate sample solutions with the specified sulfate concentration |
|---|---|---|---|
| | Initial samples | Duplicate samples | |
| 0 | 2 | 2 | 0 |
| 5 | 8 | 8 | 5 |
| 10 | 45 | 44 | 10 |
| 25 | 170 | 165 | 25 |
| 50 | 360 | 360 | 50 |

Although the foregoing explanation has a dealt exclusively with the use of barium-ethylene diamine tetraacetic acid as the barium chelate compound it is obvious that other chelating agents such as barium-nitrilotriacetic acid (or salt) chelate compound or a barium diethylenetriamine pentaacetic acid chelate compound can be used. Likewise, although aluminum chloride has been specified as the water soluble compound of the second metal, various water salts of copper, iron, trivalent chromium, zinc, etc., can also serve the same purpose. It should be appreciated that since sulfate is being measured the sulfate of the metal of course will not be used. Such salts as copper chloride, iron chloride (ferric), chromous chloride and zinc chloride have been used successfully. The general prerequisites for the metal compound is that the metal at one which will readily react with the free chelant of the barium chelate and which will not react with the sulfate present to form a precipitate.

In addition hydrochloric acid has been named as the acid used to adjust the pH, however as is obvious, other acids other than sulfuric, of course, can be used for this purpose so long as the acid does not interfere with the mechanism of the procedure. Similarly glycerin has been stated as the stabilizing agent. However any compound or material can be used which performs the same function with the prerequisite, of course that it does not possess an appreciable adsorbence value of its own so as to add to the turbidity readings.

In order to ascertain whether in fact other ions or components in a water sample would interfere with the test, various samples of water were taken from different locations within the United States and from various installations where water was being used industrially for the purpose set forth in table 2. The samples as received were tested for sulfate concentration according to the procedure outline above. After the sulfate concentration for was determined for of the samples, 20 parts per million were added to additional portions of the respective samples and each sample was again subjected to the procedure outlined above. The sequence of course was utilized to ascertain the sulfate concentration of the sample as received. This known value then permits an accurate assay when the samples bearing the added sulfate ion were subjected to the test procedure. The results of the evaluation were as follows.

TABLE 2

| Location from which sample taken | Use of water in the facility | P.p.m. sulfate ion added | P.p.m. sulfate found |
|---|---|---|---|
| Louisiana | Make-up water to a boiler | 20 | 19 |
| Ohio | Raw water fed to softeners for boiler. | 20 | 22 |
| California | do | 20 | 20 |
| Texas | Sump or bottom of cooling water tower. | 10 | 8.8 |
| North Carolina | Sump of cooling water tower | 20 | 20 |
| Do | Sump of cooling tower | 20 | 20 |

The results of the test recorded in the above table confirmed conclusively that the test method operated effectively with water from many sources and that no interference by additional ions and components in the water was observed. It should also be noted, of course, that the water used in both cooling water towers and as boiler feed has generally been treated not only with corrosion inhibitors such as phosphates, chromates and zinc but also dispersants such as natural and synthetic polymers, organic phosphonates, etc. Accordingly the present method operated effectively even with these materials or ions present.

Having thus described my invention, what is claimed is:

1. A method for determining the sulfate ion concentration of an aqueous solution which comprises mixing said solution with (i) a quantity of water-soluble metal chelate compound which under acidic conditions will dissociate to release the quantity of metals ions necessary to react with all of the sulfate ions in said solution to form colloidal precipitate, (ii) a water soluble compound of a second metal which under acidic conditions will provide metal ions which will react to replace the metal of the metal chelate compound to form a second water-soluble chelate; adjusting the aqueous solution to an acid pH whereby said metals ion from said metal chelate compound are released and react with said sulfate ions of said solution to produce the colloidal precipitate and said ions of said second metal reacts so as to replace said metal of the metal chelate to thereby produce the water-soluble chelate of said second metal and measuring the sulfate concentration by comparing the turbidity or color density of said solution with those of standard solutions containing known quantities of colloidal metal sulfate precipitate.

2. A method according to claim 1 wherein a material capable of stabilizing the precipitate formed upon adjustment of the solution to an acid pH is added to said solution.

3. A method according to claim 1 wherein said metal chelate compound is a barium-ethylenediaminetetraacetic acid chelate and said water-soluble compound of said second metal is aluminum chloride.

4. A method according to claim 3 wherein the pH of said solution is adjusted to a pH of from about 2.5 to about 5.5 by the addition of hydrochloric acid.

5. A method according to claim 4 wherein a material capable of stabilizing the precipitate formed upon adjustment of the solution to an acidic pH is added to said solution.

6. A method according to claim 5 wherein said pH is adjusted by adding a solution containing hydrochloric acid, sodium chloride and glycerine.

7. A method according to claim 3 wherein said aqueous solution containing said sulfate is filtered prior to the addition of said chelate compound and said second metal compound.

8. A method according to claim 1 wherein the metal chelate compound is selected from the group consisting of barium-ethylenediaminetetraacetic acid chelate, barium-nitrilotriacetic acid chelate and barium-diethylene-triamine pentaacetic acid chelate, and said water-soluble compound of a second metal is selected from the group consisting of copper chloride, ferric chloride, chromous chloride and zinc chloride.

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