

[54] **DETERMINATION OF SULFATE USING
FERRIC ION-SELECTIVE ELECTRODE**

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[58] Field of Search **204/1 T, 195 G, 195 M**

[56] **References Cited**

UNITED STATES PATENTS

3,709,811 1/1973 Saunders..... 204/195 M

3,709,813 1/1973 Johnson et al..... 204/195 G

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National Bureau of Standards Special Publication 314,

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Primary Examiner—T. Tung

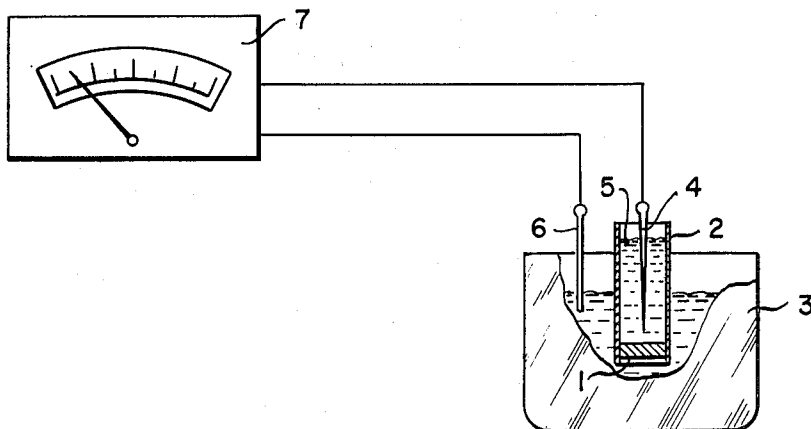
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[57]

ABSTRACT

Sulfate ion concentration in aqueous solution is determined by initially adding a known concentration of ferric ion to the solution, and adjusting the pH of the solution to a suitable value, whereby ferric ion is complexed by the sulfate ion. The activity of the remaining, uncomplexed ferric ion is then measured by means of a ferric ion-selective electrode comprising a glass of the formula $\text{Fe}_x\text{Ge}_y\text{Sb}_z\text{Se}_n$, where n is about 1.5 to 3.0, x is about 27 to 29, y is about 11 to 13 and z is about 59 to 61.

5 Claims, 2 Drawing Figures



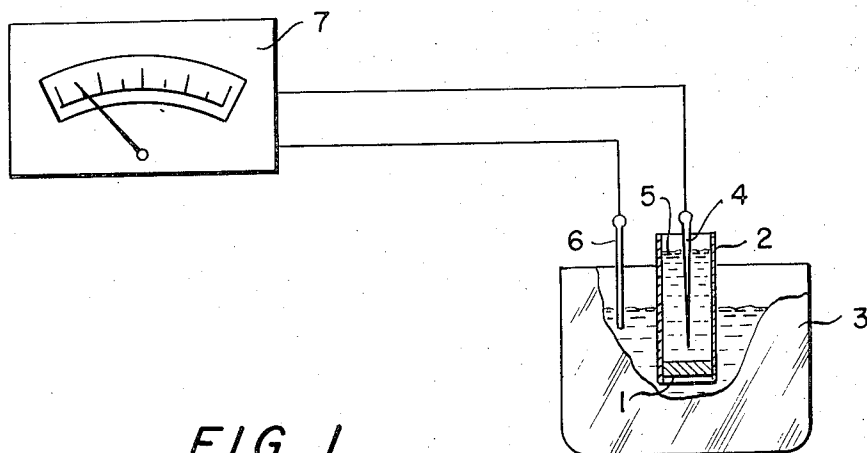


FIG. 1.

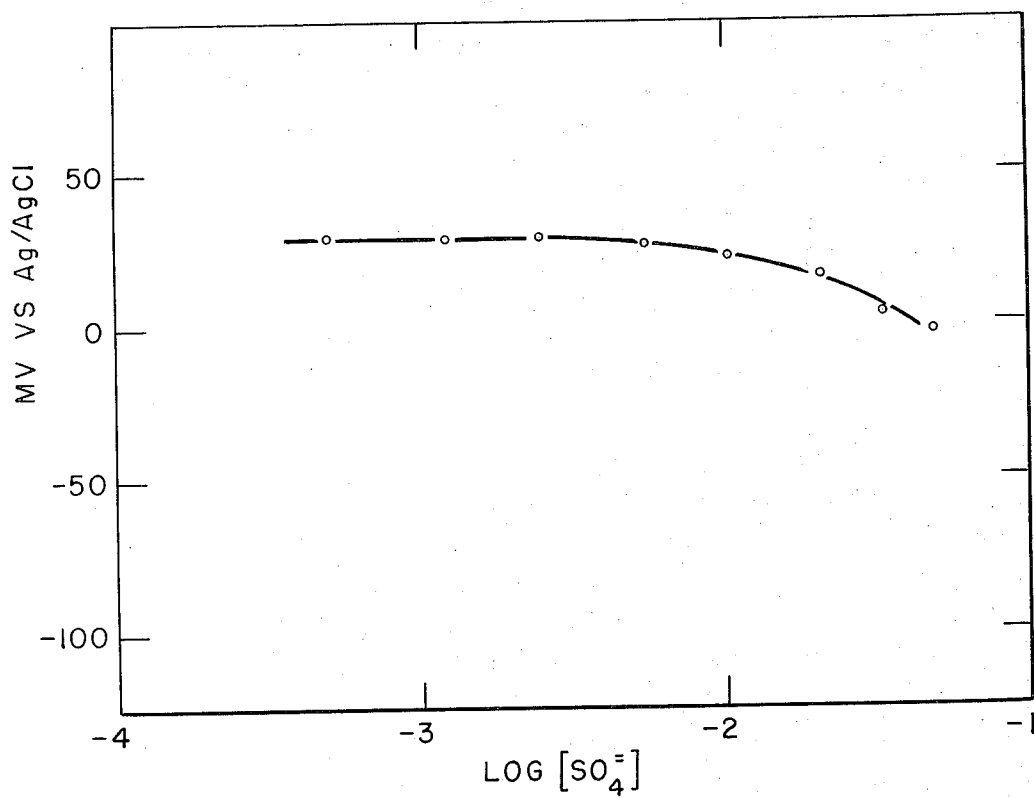


FIG. 2.

DETERMINATION OF SULFATE USING FERRIC ION-SELECTIVE ELECTRODE

Detection and measurement of the concentration of various ions in aqueous solution by means of ion selective electrodes finds utility in a variety of environmental and industrial applications. Analytical potentiometry, and ion selective electrodes or sensors therefor, can be employed for control of water quality, to obtain optimum yields in chemical processes, etc. Prior art sensors for copper, iron and sulfate ions are disclosed in copending application Ser. No. 335,397, filed Feb. 23, 1973, in U.S. Pat. No. 3,709,813 and in U.S. Pat. No. 3,709,811, respectively. In the latter, a variety of prior art process for measurement of sulfate ion concentration are disclosed. However, these processes have generally been deficient in various properties such as sensitivity, selectivity and reliability.

It has now been found, according to the process of the invention, that sulfate ion may be detected or measured in aqueous solution by means of an indirect process that is free of most of the prior art limitations. This process involves (1) addition to the test solution, i.e., the solution whose sulfate ion content is to be measured, of a known concentration of ferric ion, (2) adjustment of the pH of the test solution to a value of about 1.5 to 3, preferably about 2, and (3) measurement of the resulting activity of the ferric ion in the solution by means of a ferric ion-selective sensor, as described below.

The principle of operation on which the process of the invention is based depends on (1) the response of the ferric ion-selective sensor to hydrated ferric ion only and (2) the complex-ion forming reactions of sulfate ion with ferric ion. The ferric ion selective sensor will respond only to ferric ion in the hydrated form (hereafter referred to as Fe^{+3}). It will not respond to ferric ion in the sulfate-complexed state, even though the valence of the iron itself is still trivalent.

The chemical environment of the test solution is so chosen that the ferric iron-sulfate complexes are sufficiently strong to remove some of the ferric iron from the hydrated form, but not so strong as to purge the solution entirely of the hydrated form. The quantity of Fe^{+3} present, and thus sensed by the ferric ion-selective sensor, is a function of the total ferric iron present in the test solution, pH of the test solution and total sulfate ion concentration in the test solution. Therefore, fixing two of these variables, i.e., pH and total ferric iron, and measuring Fe^{+3} defines the total sulfate ion concentration.

The process of the invention may be used to measure sulfate ion concentrations in solutions containing sulfate in concentrations of about 0.005 moles per liter to saturation. Suitable concentrations of ferric iron in the test solution will generally range from about 10^{-5} to 0.1 moles per liter. Optimum values of the concentration of ferric iron, as well as pH, may vary considerably depending on the range of sulfate ion concentration, other ionic species in the test solution, specific ferric ion-selective sensor employed, etc., and are best determined empirically. Other ionic species that may be present in the test solution without interfering with the measurement of sulfate ion include Cl^- , NO_3^- , ClO_4^- , Br^- , I^- , Zn^{++} , Pb^{++} and Na^+ .

If the test solution initially contains a known concentration of ferric ion within the above limitations, addition of further ferric iron may not be necessary. If, how-

ever, addition of further ferric iron is necessary, it may be added in the form of a soluble inorganic ferric salt such as ferric chloride or ferric nitrate. Addition may be in the form of the salt or an aqueous solution thereof, provided only that the final concentration of ferric iron (combined Fe^{+3} and sulfate-complexed ferric ion) in the test solution is known, and is within the above-mentioned range.

Adjustment of the pH of the test solution, if necessary, may be made by addition of conventional reagents such as hydrochloric or nitric acids, or bases such as sodium hydroxide or ammonia.

The ferric ion-selective sensor used in the process of the invention is disclosed in above-mentioned U.S. Pat. No. 3,709,813. It consists essentially of a glass membrane of a particular composition, one side of which contacts a reference solution and the other side of which contacts the test solution. The glass membrane consists of an iron-doped glass composition having the formula $\text{Fe}_n\text{Ge}_x\text{Sb}_y\text{Se}_z$ where n is about 1.5 to 3.0, x is about 27 to 29, y is about 11 to 13 and z is about 59 to 61. This composition is prepared by a conventional glass making technique, such as that described in Pat. No. 3,709,813. This consists of compounding a mixture of the components of the composition in the proportions desired in the glass product. This mixture is placed in a quartz ampule, which is then evacuated to about 10^{-5} to 10^{-3} mm of Hg, sealed and placed in a rocking furnace. The mixture is then slowly heated to a temperature sufficient to ensure that the reactants are in a liquid state. A temperature of about 900° to 1000°C is usually sufficient. A gentle rocking motion is imparted to the furnace to mix and react the constituents for a period of about 16 to 24 hours. The resulting molten mass is slowly cooled to about 700°C , and rapidly air-quenched to the solid state. It is then annealed at a temperature of about 275°C for about 2 to 3 hours to remove any strains that may have developed during the cooling cycle.

The Fe, Ge, Sb and Se are preferably employed in essentially pure form and in the form of powders of mesh size of about 40 to 200. The iron may, however, be employed in the form of fine wire or mesh, of a diameter of about 0.007 to 0.012 inch. It may also be added in the form of a compound such as FeSe . As also discussed in Pat. No. 3,709,813, the glass composition may be prepared either by reacting a mixture of all the ingredients, or by doping the prereacted chalcogenide glass, i.e., the $\text{Ge}_x\text{Sb}_y\text{Se}_z$ glass, by addition of the appropriate amount of iron, with a subsequent reaction under the above-described conditions to take the iron into solution.

The method of the invention will now be described with reference to FIG. 1. The $\text{Fe}_n\text{Ge}_x\text{Sb}_y\text{Se}_z$ glass composition is employed in the form of a membrane (reference 1 in FIG. 1) consisting of a disc having a thickness of about 1.0 to 2.5 mm and a diameter of about 5 to 10 mm. Optimum thickness and size of the disc may, however, vary considerably depending on the specific size and type of apparatus employed, the type of solution to be monitored, the reference electrode, etc., and are best determined empirically.

Membrane 1 is sealed in the bottom of tube 2, which may be of any suitable inert material, such as Plexiglass (poly-methylmethacrylate polymer), and is immersed in solution 3, the test solution, i.e., the solution to be measured or monitored. Reference electrode 4 is

mounted within tube 2 which is filled with a reference solution 5. A second reference electrode 6 is immersed in the test solution and reference electrodes 4 and 6 are connected to high-impedance voltmeter 7.

Reference electrodes 4 and 6 may be any conventional reference electrodes, such as a saturated calomel electrode or a silver-silver chloride electrode, provided only that they are compatible with the test and reference solutions. Reference solution 5 consists of an aqueous solution of a fixed concentration of ferric ion and an electrolyte. This solution suitably consists of a solution of ferric chloride or ferric nitrate in a concentration of about 10^{-3} to 10^{-2} mole per liter, and an electrolyte consisting of sodium chloride, sodium nitrate, potassium chloride or potassium nitrate in a concentration of about 0.1 to 1.0 mole per liter. Preferably, the reference solution consists of an aqueous solution of about 10^{-3} M ferric chloride or nitrate and about 0.1 M sodium or potassium chloride or nitrate.

According to one embodiment of the method of the invention, potential responses of the ferric ion-selective electrode, i.e., the electrode comprising the $\text{Fe}_n\text{Ge}_x\text{Sb}_y\text{Se}_z$ glass membrane, the ferric ion-containing reference solution and the reference electrode immersed therein, versus the reference electrode immersed in the test solution are plotted as a function of sulfate content of the test solution. Thus, a definite relationship between potential and sulfate concentration is determined, and this relationship may be used for measuring sulfate concentration in unknown solutions.

A second possible embodiment of the invention involves chemical titration for sulfate ion. Ferric ion concentration and pH of the test solution are again adjusted as described above. The test solution is then titrated with an aqueous solution of a known concentration of a chemical that will remove sulfate ion from solution. Changes in electrical potential of the test solution are sensed throughout the titration by means of the ferric ion-selective sensor. The titrant continuously removes complexed and uncomplexed sulfate from solution, and in the process ferric iron is released from the sulfate complex to form the hydrated ferric ion (Fe^{+3}) which is sensed by the ferric ion-selective electrode. When the sulfate ion is completely removed, the formation of Fe^{+3} ceases and the solution potential ceases to change. This onset of a constant potential defines the end point of the titration.

The preferred titrant is barium chloride, which removes sulfate as a barium sulfate precipitate. Other titrants may, however, be employed, e.g., lead chloride, lead perchlorate and barium perchlorate.

The ferric iron-selective electrode, prepared as described above, may be employed directly in the method of the invention. However, the sensitivity and selectivity of the electrode is generally improved by polishing and by conventional activation treatment. Furthermore, reactivation of the electrode may be necessary where sensitivity has declined over a period of use. Activation is conveniently accomplished by initially etching in caustic, e.g., by rinsing or immersing in a solution of alkali such as a 2.0 to 3.0 molar solution of NaOH or KOH, followed by rinsing with an aqueous solution of 0.1 M NaCl containing sufficient HCl to adjust the

pH to about 2 and, finally, equilibration with a solution of ferric ion at a pH of about 1.5 to 3.0 for a period of about 12 to 24 hours. For this purpose, the electrode may be simply immersed in a solution of ferric nitrate or chloride of about 0.0008 to 0.005 molar concentration for the required time.

The method of the invention is ordinarily practiced at ambient conditions of temperature and pressure and is capable of detecting 100 ppm sulfate ion in aqueous solution. Furthermore, it may be used for measuring sulfate concentration in media having a high chloride ion concentration, e.g., sea water, brackish water and industrial waste water.

The following example will more specifically illustrate the invention.

EXAMPLE

A disc 8.0 mm in diameter and 1.5 mm in thickness, and consisting of $\text{Fe}_2\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$, was prepared by the procedure described above. This disc was sealed in a Plexiglas tube 13 cm long and of O.D. of 1.5 cm and I.D. of 1.3 cm, and was then mechanically polished and activated by etching with 2.5 molar NaOH solution and rinsing with aqueous 0.1 M NaCl-HCl solution (pH = 2), and finally exposing it to 0.1 M ferric nitrate solution at a pH of 1.6 for 30 minutes. The tube was filled with a reference solution consisting of 10^{-3} M $\text{Fe}(\text{NO}_3)_3$ in 0.1 M KNO_3 , and was then immersed in the test solution, as shown in FIG. 1. The test solution consisted of an aqueous solution of 10^{-3} M $\text{Fe}(\text{NO}_3)_3$ and sulfuric acid in an amount sufficient to provide varying concentrations of sulfate ion. The pH of the test solution was maintained at 1.6 by addition of nitric acid or sodium hydroxide as required. Ag/AgCl reference electrodes were immersed in the test solution and in the reference solution, and both were connected to a high impedance voltmeter.

Results are shown in FIG. 2, which is a plot of the logarithm of the concentration of sulfate ion in the test solution against the potential developed between the reference electrodes.

We claim:

1. A method for measuring sulfate ion concentration in an aqueous solution comprising adding to said solution a known concentration of ferric ion sufficient to provide a concentration of about 10^{-5} to 10^{-1} moles per liter in the solution, adjusting the pH of the solution to about 1.5 to 3, and measuring the potential of the resulting solution by means of a ferric ion-selective electrode comprising an iron-containing glass of the formula $\text{Fe}_n\text{Ge}_x\text{Sb}_y\text{Se}_z$, where n is about 1.5 to 3.0, x is about 27 to 29, y is about 11 to 13 and z is about 59 to 61.

2. The method of claim 1 in which the ferric iron is initially added in an amount sufficient to provide a concentration of about 10^{-3} moles per liter of solution.

3. The method of claim 1 in which the pH of the solution is initially adjusted to about 2.

4. The method of claim 1 in which the glass has the formula $\text{Fe}_n\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$, where n is about 1.5 to 3.0.

5. The method of claim 4 in which n is 2.0.

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