Chemical and Biological Engineering Publications   Chemical and Biological Engineering

1964

Rapid Titrimetric Determination of Sulfate in Mixtures of Gypsum, Anhydrite, Calcium Oxide, and Calcium Sulfide Using Ion Exchange

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Rapid Titrimetric Determination of Sulfate in Mixtures of Gypsum, Anhydrite, Calcium Oxide, and Calcium Sulfide Using Ion Exchange

Abstract

The conventicnal sulfate determination by gravimetrically precipitating barium sulfate is very tedious and time consuming. The present technique uses an ion exchanger so the sulfate can be titrimetrically determined as sulfuric acid. An analysis can be completed in 30 minutes. This method is being used for the routine analysis of sulfate in mixtures of gypsum, anhydrite, calcium oxide, and calcium sulfide. The mixturrs are produced from laboratory and pilot plant investigations on the i

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This secondary oxidation places a lower limit of about 1% on the level of certain isomers which can be accurately determined. However, for relatively pure isomers, recovery of all the cleavage fragments eliminates the doubt caused by the secondary oxidation, since each dicarboxylic acid must have a matching monocarboxylic acid fragment and vice versa. Identification of the fragments from methyl linoleate in sample A, methyl oleate in sample B, and methyl petroselaidate in sample E shows that small amounts of isomers or closely related compounds can easily be detected.

Figures 1 through 3 illustrate typical gas chromatograms of mono- and/or dicarboxylic acid ester cleavage products. Figure 1 shows the monocarboxylic acid esters obtained upon oxidation of a mixture of dodecene isomers. Figure 2 shows the oxidation products given by the monoenoic esters isolated from a partially hydrogenated fat by chromatography of the mercury derivatives (5). Methyl octadecenoates having double bonds in the 6- through 13-position are indicated by the cleavage pattern. The chromatogram of Figure 3 was obtained upon oxidation of sample E in Table II. The fragments from the added methyl petroselaidate as well as those from the 11-octadecenoate isomer are easily detected and measured.

LITERATURE CITED

(1) Cason, J., Tavs, P., J. Biol. Chem. **234**, 1401 (1959).
(2) Chang, T. C. L., Sweeley, C. C., J. Lipid Res. **3**, 170 (1962).
(3) Chisholm, M. J., Hopkins, C. Y., Can. J. Chem. **38**, 805 (1960).
(4) Craig, B. M., et al., J. Am. Oil Chemists' Soc. **40**, 61 (1963).
(5) Kuemmel, D. F., ANAL. CHEM. **34**, 1003 (1962).
(6) Oette, K., Ahrens, E. H., Ibid., **33**, 1847 (1961).
(7) Rudloff, E. v., Can. J. Chem. **34**, 1413 (1956).

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Rapid Titrimetric Determination of Sulfate in Mixtures of Gypsum, Anhydrite, Calcium Oxide, and Calcium Sulfide Using Ion Exchange

SIR: The conventional sulfate determination by gravimetrically precipitating barium sulfate is very tedious and time consuming. The present technique uses an ion exchanger so the sulfate can be titrimetrically determined as sulfuric acid. An analysis can be completed in 30 minutes. This method is being used for the routine analysis of sulfate in mixtures of gypsum, anhydrite, calcium oxide, and calcium sulfide. The mixtures are produced from laboratory and pilot plant investigations on the reductive decomposition of gypsum.

Ion exchangers have been used to some extent for analysis of solutions (3), but the present technique uses an ion exchanger for the analysis of a slightly soluble solid. The method is similar to procedures developed by Kniestedt and Wahle (1) for determining sulfate in naturally occurring anhydrite and by Perry (2) for determining the sulfate content of gypsum, anhydrite, and hemihydrate. The main step uses a cation exchange resin in the hydrogen form so that all the cations in solution will be replaced by hydrogen ions. The resin used can be either Dowex 50 or Amberlite IR 120. Both resins have a high capacity and high thermal stability.

The sulfate exists in the solid samples mostly as calcium sulfate. When the solids are suspended with an excess of exchange resin in hot water, all of the calcium sulfate will eventually dissolve (1). The main reactions that occur are as follows:

$$CaSO_{4(s)} = Ca^{+2} + SO_4^{-2} \quad (1)$$

$$2\,HR + Ca^{-2} = CaR_2 + 2H^{+1} \quad (2)$$
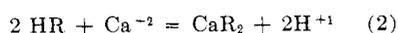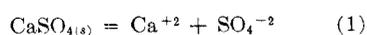
where HR = hydrogen-form cation exchange resin.

With a mixture of solids the overall reactions are as follows:

$$2HR + CaSO_4 = CaR_2 + H_2SO_4 \quad (3)$$

$$2HR + CaO = CaR_2 + H_2O \quad (4)$$

$$2HR + CaS = CaR_2 + H_2S \quad (5)$$

All of the calcium is replaced by hydrogen ions. Calcium oxide gives no net change of hydrogen ions in solution and calcium sulfide gives hydrogen sulfide which can be liberated by heating. The calcium sulfate equivalent remains as sulfuric acid. Other insoluble sulfates such as those of barium and strontium will behave similarly (2).

EXPERIMENTAL

Apparatus. The apparatus consists of a mixing chamber, an ion exchange column, a 500-ml. vacuum flask, and a source of hot, 90° C. distilled water. The mixing chamber is a 75-ml. Buechner funnel with a coarse grain sintered glass bottom, and the ion exchange column is a 65-ml. cylindrical separatory funnel with a stopcock drain.

Procedure. For analyses the ion exchange column is completely filled with moist hydrogen-form resin and the mixing chamber is partially filled with approximately 25 grams of resin. A 0.2- to 0.3-gm. sample of finely pulverized solids is stirred with the resin and 50 ml. of hot distilled water for 15 minutes in the mixing chamber. The hot solution is then drawn out of the mixing chamber through the ion exchange column by vacuum. Finally, the system is rinsed twice with additional hot water.

Most of the cations are replaced by hydrogen ions in the mixing chamber but the ones remaining are replaced in the ion exchange column. With this arrangement several samples can be analyzed before the resin needs to be replenished. To ensure an excess of resin at all times the mixing chamber is replenished with fresh resin after every five determinations and the ion ex-

Table I. Comparison of Sulfate Determinations by the Present Method and the Gravimetric Method

Other main components present		SO₃, %					
		Gravimetric Method			Present Method		
CaO, %	CaS, %	1st	2nd	Av.	1st	2nd	Av.
74.0	5.6	6.00	5.95	5.97	5.74	6.16	5.95
69.1	10.4	4.50	4.82	4.66	4.89	4.46	4.67
56.8	13.7	11.03	10.79	10.91	10.79	10.42	10.61
62.9	11.9	9.79	9.70	9.75	10.60	10.72	10.66
60.2	11.7	9.57	9.80	9.68	9.56	7.63	8.59
45.9	35.1	5.01	4.91	4.96	5.12	4.79	4.95
38.8	36.9	8.44	8.48	8.46	8.56	8.73	8.64
34.4	43.5	7.87	7.96	7.91	8.26	8.50	8.38
28.4	49.5	7.63	7.70	7.66	7.77	7.60	7.68
25.9	52.8	6.43	7.46	6.94	6.44	6.67	6.55
22.3	54.9	6.33	5.93	6.13	7.14	7.08	7.11
29.6	49.7	7.87	7.67	7.77	7.88	7.87	7.87
33.4	47.3	6.42	6.24	6.33	6.71	6.43	6.57
31.3	50.9	5.26	5.13	5.19	5.48	5.21	5.34

change column is replenished after every ten determinations.

Most of the sulfide present in the sample is vaporized from the hot mixing chamber as hydrogen sulfide but positive removal of hydrogen sulfide is assured by heating the filtrate to boiling and then subjecting the solution to an aspirator-produced vacuum. The remaining solution is titrated with $0.1N$ sodium hydroxide to a pink end point using phenophthalein indicator.

RESULTS AND DISCUSSION

When this method was adopted for routine analysis some of the pilot plant samples were analyzed by both the present method and the gravimetric method for comparison. The results for a series of fourteen samples are shown in Table I. The oxide and sulfide contents of these samples varied over a wide range while the sulfate content varied between 5 and 11% expressed as SO_3. The mean sulfate content of all samples found by the present method was 7.40% as compared to 7.31% by the gravimetric method. An analysis of variance for each method showed the standard deviation between determinations within samples for the present method to be 0.41% and for the gravimetric method to be 0.24%. The corresponding relative standard deviations were 5.5 and 3.2%.

If it is assumed that tests of significance are valid and applicable to this situation, it can be shown that there is no significant difference between the means found by the two analytical methods. However, the difference in the standard deviations is significant. The accuracy of the two methods appears to be the same but the present method does not have as great a precision.

For this series of samples the precision of either method was not great and this is probably due to the relative inexperience of the analyst who was a freshman college student with very little formal training in quantitative analysis. Possibly better results would have been obtained with methyl orange indicator since it would not have permitted any unvaporized sulfide to be titrated. Hence, it appears likely that better results can be obtained with the present method than are reported here.

Nonvolatile anions, where present, can interfere with the determination.

These would have to be determined separately and corrections applied for them. With the samples analyzed here, the chloride ion content required less than 0.1 ml. of sodium hydroxide, so no correction was made.

LITERATURE CITED

(1) Kniestedt, H., Wahle, J., *Chem. Tech. Berlin* **13**, 110 (1961).
(2) Perry, J. S., U. S. Gypsum Co., private communication, 1963.
(3) Samuelson, O., "Ion Exchangers in Analytical Chemistry," p. 122, Wiley, New York, 1953.

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Determination of Oxygen in Potassium

SIR: Much interest has been evidenced recently in the use of potassium as a thermodynamic working fluid in nuclear turboelectric power systems. Since oxygen impurities in alkali metals (even below 20 p.p.m. in some cases) have been recognized as promoting and accelerating corrosion attack on containment materials, it is important that a reliable method for determining the oxygen content of potassium be available.

Currently the technique most widely used for the measurement of oxygen in potassium is the Pepkowitz-Judd amalgamation technique (2). It is our belief that a major source of error in this technique is the inadvertent introduction of oxygen or water contamination during the processes of sampling, transfer, and analysis. This should not be unexpected in view of the reactivity of potassium with oxygen and water and the questionable handling techniques currently employed. It then follows, if the above contention is correct, that extreme care must be exercised in the handling and analytical procedures. One way to prevent oxygen pickup is to carry out all steps in a high vacuum environment with a continuous monitoring of the pressure by means of a high vacuum gauge.

In our attempt to improve the analytical precision of the Pepkowitz-

Judd technique for determining oxygen in potassium, five innovations were made: the entire system complex—sample tube, transfer section, and amalgamation system—was maintained under a high vacuum; the amalgamation reaction system volume was made small; a ball check valve was used to contain the vigorous amalgamation reaction; flanged O-ring joints were used to eliminate greased or waxed joints; and replicate samples were taken from a single sample tube.

The apparatus, shown in Figure 1, consists of two major components: a metal extruder and a glass extraction system. The glass and metal components are connected by O-ring joints, and the entire apparatus is evacuated to a pressure between 2×10^{-5} and 4×10^{-6} torr.

The sample container is a stainless-steel tube $6^3/_4$ inches by $^5/_{16}$-inch i.d.

It is vacuum filled with liquid metal, capped, and stored under vacuum until used. For analyses, the sample tube is mounted in the extruder section apparatus.

After the apparatus has attained operational vacuum, a small portion of the potassium is extruded from the sample tube, cut with a hot wire, and discarded in the waste tray. The analytical sample is then extruded, cut off, and dropped into the glass extraction system. The extruder is valved-off from the extraction system and the ball check valve is seated in place to confine the amalgamating reaction. Triple distilled mercury is then admitted to the extraction system. After the reaction has occurred, manipulation of a glass-covered magnetic bar within the extraction system removes all film from the chamber walls. By means of a valve on the restricted end of the extraction system, the amalgam is slowly removed into the receiving flask. The exit valve is

Table I. Oxygen Content of Potassium

Lot	Tube number	Oxygen, p.p.m.	Sample weight, grams
A	1	13, 18, 18	1.06, 1.22, 1.13
	2	23, 21, 22	0.61, 1.40, 2.06
B	3	88, 96, 88	1.15, 1.14, 1.16
C	4	88, 93, 93	0.66, 0.88, 1.22
D	5	186, 198	0.74, 1.00
E	6	207, 200, 196	1.07, 1.03, 1.06