Separation of Sulphate and Hydrogen Sulphate Ions from Interfering Substances by Adsorption on Aluminium Oxide, Prior to Sulphate Determination

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The difficulties in satisfactorily precipitating barium sulphate from solutions containing certain strongly adsorbable ions or, generally, from solutions containing large amounts of foreign salts or acids are well known. A method of previously isolating the sulphate as free as possible from these interfering substances seems to be highly desirable. Using the commercially obtainable ion exchange resins it is in most cases possible to separate sulphate from cations and uncharged substances, but not from other anions, in a way sufficiently simple for practical analysis. Such separations will, however, be laborious to perform in the presence of larger amounts of foreign substances; large ion exchanger volumes will be necessary involving large volumes of solutions, large consumption of reagents for regeneration, and appreciable loss of time. The necessity of using large ion exchanger volumes is of course a consequence of the unspecificity of sulphate adsorption on these resins because in quantitative adsorption sulphate ions are accompanied by most other anions. The authors found, however, that *aluminium oxide* as used for chromatographic purposes will, under certain conditions, meet the required specificity for sulphate ions — particularly hydrogen sulphate ions — to a high degree; moreover, elution of adsorbed sulphate and regeneration of the adsorbent are easily carried out.

Aluminium oxide has been used by Schwab & Dattler¹ for chromatographic separation of anions. As a result of a series of qualitative experiments, in each of which two kinds of anions were introduced into the adsorption column, these authors could arrange a sequence of adsorption for the different anions.

Later on a few additional results were obtained by Kubli ^{2,3}, whose sequence is the following

The anions are arranged in order of decreasing adsorption. These experiments were carried out with dilute solutions containing only the sodium or potassium salts of the different anions. Kubli also performed some quantitative separations: determination of K in K_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ after adsorption of the anions, and separation of Fe and Mg from PO_4 and SO_4 followed by determination of the different constituents.

Dean ^{4,5} has used aluminium oxide for the separation of fluoride and sulphate from potassium in silicate analysis as well as for the isolation of the nitroso-R-salt complex of cobalt in the analysis of alloys.

The reaction mechanism at adsorption has been outlined as an anion exchange, e.g.,

The reaction generally proceeds towards the formation of the most difficultly soluble basic aluminium salt. Provided X^- is a hydroxyl ion and the not too weak acid H^+Y^- is added, the reaction will proceed to the right on account of formation of water. As all other anions are removed by an excess of hydroxyl ion (see adsorption sequence above) this gives an often applicable method of introducing different Y^- groups in the aluminium oxide.

EXPERIMENTAL

Preparations used.

All experiments cited below have been performed using Merck's "*Aluminiumoxyd nach Brockmann*". A few experiments not recorded here show that Riedel — de Haen's corre-

Table 1. Maximal capacity of the aluminium oxide for some different anions.

Anion	Anion added as	Capacity mmole anion/ml of column
ClO_4^-	HClO_4	0.17; 0.17
»	NaClO_4	0.17
Cl^-	HCl	0.21
»	NaCl	0.16
NO_3^-	HNO_3	0.20
»	NaNO_3	0.16
F^-	1 M NaF	0.10
»	0.1 M NaF	0.12
»	0.1 M NaHF	0.43
CH_3COO^-	CH_3COOH	0.22
»	0.1 M CH_3COONa	0.13
H_2PO_4^-	H_3PO_4	0.25
»	KH_2PO_4	0.21; 0.21
HSO_4^-	H_2SO_4	0.17
SO_4^{2-}	K_2SO_4	0.083

sponding preparation had essentially the same properties. For the column experiments the finer particles were removed by washing; the batch experiments were carried out with the original preparation.

All chemicals used were of reagent grade quality.

The maximal capacity of the aluminium oxide for some anions.

The maximal capacity of the aluminium oxide for some anions was determined. An adsorption tube was prepared from a glass tube, constricted at the lower end and plugged with Pyrex wool. It was filled by wet packing with a slurry of the adsorbent, forming an adsorption column of height 50 mm, volume about 2 ml. The adsorbent was converted into the desired anion form by washing with 10 ml of 0.1 M NaOH , 3×5 ml water, 5 ml of the 1 M acid in question, and finally with 3×5 ml of water. Gentle suction was applied.

In some cases the adsorbent was converted into the desired anion form by washing its perchlorate form with a neutral or slightly acidic solution of the anion.

The adsorbed anion was eluted by washing with 10 ml 0.1 M NaOH followed by 3×5 ml of water, and determined through titration of the eluate with 0.1 M HCl . Eluting a second time in the same way proved the elution to be quantitative.

The results (Table 1) show that the maximal capacity is variable. Thus it is generally higher when an acid rather than a neutral salt has been used for saturating the adsorbent, indicating a certain adsorption of acid molecules in addition to the ion exchange. While no such effect is observed for the noncomplex-forming perchloric acid, it is specially marked in the case of the strongly associative hydrofluoric acid.

Low values of the capacity have been obtained when treating the adsorbent with neutral salts of weak acids, *e.g.*, sodium fluoride or acetate. In these cases the hydroxyl ion concentration and the buffer capacity are sufficiently high for the conversion of an appreciable part of the adsorbent into its hydroxyl form. Qualitative experiments also show a considerable decrease in pH when neutral salt solutions are added to perchlorate-saturated aluminium oxide.

If we disregard these cases, the capacity is about 0.17 mmole/ml for univalent anions and half as large for bivalent (SO_4^{2-}). Consequently, the adsorbent is more advantageously used in acidic solution for sulphates.

Equilibrium experiments

The results published by Schwab and Dattler and Kubli elucidate only the order of adsorption of the different anions. Quantitative relations between the strength of adsorption of the anions may be obtained from equilibrium experiments. A small amount of the anion under investigation is allowed to compete with a fairly large, and therefore practically constant, concentration of a standard anion, and the adsorbed amount determined. Perchlorate ion was chosen as a proper standard, since it is one of the most weakly adsorbed.

10.0 g of the aluminium oxide was introduced into a 100 ml centrifuge tube and converted to its perchlorate form by washing with 0.5 M Na_2CO_3 , water, 1 M HClO_4 , and water. The water remaining after centrifuging was determined by weighing. A solution containing the competing anion and sodium perchlorate or perchloric acid was added and made up to a final volume of 90 ml. The concentration of the two latter constituents were kept at 1 M. The mixture was stirred for 10 minutes with a motor driven stirrer, centrifuged, and a convenient amount of the clear solution pipetted off for analysis. Chloride was determined argentometrically according to Mohr, nitrate as ammonia after reduction by Devarda's alloy, phosphate colorimetrically according to Scheel⁶, chromate colorimetrically, and sulphate gravimetrically as barium sulphate.

Table 2. Partition coefficients, K , of some anions by competition with 1 M sodium perchlorate or perchloric acid. $K = (\text{millimoles of anion in 10 g of aluminium oxide}) / (\text{millimoles of anion in 90 ml of solution})$. Percent adsorbed = $100 K / (1 + K)$. Total capacity of 10 g aluminium oxide about 2.3 milliequiv.

Millimoles of anion added in 90 ml of solution	Partition coefficient, K , in									
	1 M HClO_4					1 M NaClO_4 (pH 4)				
	NO_3	Cl	$\frac{1}{2} \text{Cr}_2\text{O}_7$	PO_4	SO_4	NO_3	Cl	$\frac{1}{2} \text{Cr}_2\text{O}_7$	PO_4	SO_4
2	0.35	0.47	—	2.3	5.2	0.09	0.12	—	—	—
1	0.48	0.71	3.6	13	76	0.10	0.13	3.1	240	4.8
0.5	0.61	0.95	7.7	58	180	0.12	0.15	9.7	510	29
0.25	0.71	1.4	17	110	>250	—	0.17	22	2500	99
0.125	—	—	34	—	>250	—	—	41	—	>250

Fig. 1. Adsorption tube. A: receptacle for sample solution, volume 50 ml. B: adsorption column, height 120 mm, diameter 11 mm. C: plug of Pyrex wool.

The different anions had been added as the corresponding acids to the perchloric acid solution, and as the sodium or potassium salts (NaNO_3 , NaCl , K_2CrO_4 , KH_2PO_4 , K_2SO_4) to the sodium perchlorate solution. In the latter case, the pH of the mixture was brought to about 4 by addition of perchloric acid in order to avoid the otherwise ensuing differences in hydroxyl ion adsorption.

Phosphate and sulphate hold an exceptional position among the anions investigated on account of their strong adsorption (Table 2). At pH 4 phosphate is much more strongly adsorbed than sulphate, in strongly acid solution the order is reversed — possibly due to the increasing ratio between the concentrations of HSO_4^- and H_2PO_4^- . Hydrogen sulphate ion is more strongly adsorbed than sulphate ion. As will be shown below, hydrogen sulphate ions may be quantitatively adsorbed and separated from large amounts of chloride and, at least, small amounts of dichromate; consequently it should be possible to separate hydrogen sulphate ions from the anions succeeding dichromate in the order of adsorption. Of course the break-through capacity for sulphate is increased when washing with solutions of anions situated in the lower end of the adsorption sequence. When separating sulphate from large amounts of metals, these should preferably be present as perchlorates.

The partition coefficient, K , increased with decreasing concentration of the adsorbed anion, although in a considerably higher degree for those which are most strongly adsorbed. This makes the adsorbent specially adapted for the isolation of traces; in any case only half the total capacity of the adsorbent should be used.

APPLICATIONS

The adsorption tubes (Fig. 1) used for all the following experiments were filled to a volume of 10–12 ml with washed aluminium oxide having a total capacity of about 2 milliequiv. The tube was placed in the neck of a filtering flask with the aid of a rubber gasket and suction applied to obtain a rate of flow of 10–15 ml/min. During this treatment gas bubbles often formed in the column, but they were disregarded.

Preliminary experiments proved that the elution could be performed with sodium carbonate as well as with the hydroxide. The carbonate has a smaller dissolving action on the adsorbent and was accordingly preferred. It was later found that ammonia would also be equally good which may be convenient if the eluate has to be further concentrated by evaporation.

The adsorption part of the experiments was performed in the following way unless otherwise indicated. An adsorption column which had not been previously used was washed with 50 ml 0.5 *M* sodium carbonate followed by 2×10 ml of water; washing until negative alkaline reaction is unnecessary. The adsorbent was now converted to its perchlorate form by sucking through 10 ml 1 *M* perchloric acid and washed with 2×10 ml of water; washing until negative acidic reaction is superfluous and may be disregarded in most cases.

The sample solution, generally having a volume of 100–200 ml, was now sucked through and the column washed with 2×10 ml 1 *M* perchloric acid and 3×5 ml of water. The adsorption tube was fitted into a clean filtering flask and the adsorbed anions eluted by washing with 5 ml 0.5 *M* sodium carbonate followed by 6×5 ml 0.05 *M* sodium carbonate and 2×10 ml of water. The eluate was transferred to a 250 ml beaker for analysis. After acidifying with perchloric acid, the column is ready for a new sample. Our adsorption columns did not show any changes in performance after 30–40 analyses each.

The eluate was properly acidified and the sulphate determined gravimetrically as barium sulphate, taking the usual precautions when precipitating in the presence of alkali salts.

Isolation of sulphate from pure solutions of acids and salts

Sulphate was isolated from the solutions recorded in Table 3 and determined as described above. Blanks were run and applied as corrections; no blank exceeded 0.5 mg BaSO₄.

In addition to sulphate the column will, after the adsorption process, contain small amounts of other anions which, such as for instance nitrate or chromate, may coprecipitate with barium sulphate. Those anions may generally be removed by washing, preferably with solutions of more strongly adsorbable anions. Thus nitrate is easily removed by washing with 10 ml of 1 *M* hydrochloric acid. Chromate is difficult to remove in this way on account of its strong adsorbability. It may, however, be transformed to cations by reduction to the tervalent state and then easily washed out. Reduction was carried out by washing the column with 20 ml 1 *M* perchloric acid containing about 3

Table 3. Determination of sulphate after isolation from pure acid or salt solutions. 0.499 milliequiv. H_2SO_4 , corresponding to 58.2 mg BaSO_4 , adsorbed from 100 ml of solution. Adsorption column 10–12 ml.

Solution	BaSO_4 found mg	Diff., mg
0.1 M HClO_4	59.0	+ 0.8
1 M »	58.2	± 0.0
2 M »	58.2	± 0.0
4 M »	58.2	± 0.0
0.1 M HCl	58.3	+ 0.1
1 M »	58.0	— 0.2
2 M »	58.1	— 0.1
4 M »	38.0	— 20.2
0.1 M HNO_3 *	59.0	+ 0.8
1 M »	60.0	+ 1.8
2 M »	59.4	+ 1.2
4 M »	55.7	— 2.5
0.1 M NaCl , 0.1 M HCl	58.3	+ 0.1
0.9 M » 0.1 M »	58.6	+ 0.4
1.9 M » 0.1 M »	58.5	+ 0.3
0.1 M NaNO_3 , 0.1 M HNO_3	58.1	— 0.1
0.9 M » 0.1 M »	58.1	— 0.1
1.9 M » 0.1 M »	58.2	± 0.0
0.01 M K_2CrO_4 1 M HClO_4	58.2	± 0.0
0.02 M » 1 M »	58.0	— 0.2
0.05 M CrO_3 , 1 M HClO_4	58.2	± 0.0
0.1 M » 1 M »	58.2	± 0.0
0.2 M » 1 M »	58.2	± 0.0

* Adsorbed nitrates not removed by washing with hydrochloric acid; coprecipitation of nitrate!

millimoles of hydroxylamine hydrochloride, and the chromic salts washed away with 10 ml 1 M perchloric acid followed by water. The last traces of chromate are difficult to remove even with this procedure and it requires prolonged standing with an excess of the reducing solution in the column. These traces do not, however, interfere with the sulphate determination if they are reduced by adding a drop of 1 M hydroxylamine hydrochloride solution before the sulphate precipitation. The recorded analyses were carried out in that way.

As expected, the break-through capacity for sulphate increases in the order HCl — HNO_3 — HClO_4 of accompanying anions. The break-through capacity in

acid chromate solutions is large enough to permit the use of the adsorption method for isolating sulphates from solutions of chromium steels.

Determination of sulphate in water

Water samples are usually concentrated by evaporation for the more accurate determination of their sulphate contents. This is more conveniently accomplished by adsorption on aluminium oxide. In this special case ion exchange resins can be used, but aluminium oxide has the advantage of more rapid elution.

A sample of the laboratory tap water was analyzed for sulphate. Amounts of 1 000 ml were made 0.1 *M* in perchloric acid, run through the adsorption column, and the adsorbed sulphate determined. For comparison, 1 000 ml of the water was evaporated in a platinum dish and sulphate determined according to a standard method. The results, expressed in mg SO₄/l, were: Adsorption method, 36.2, 36.2; Standard method, 36.9.

Determination of sulphur in biomaterials

Sulphur in ash containing biomaterials is generally determined as barium sulphate after ashing a mixture of the sample and some alkaline oxidizing agent. Thus the 6. Ed. of "Methods of Analysis" of the A.O.A.C. includes two official methods for the determination of sulphur in plant materials, *viz.*, after ashing with sodium peroxide or with magnesium nitrate. In both methods the resulting solution will be rather rich in salts; isolation of sulphate before its precipitation is therefore indicated.

Both methods were run on a sample of air dry hay with and without preliminary isolation of sulphate. The sample was ground to pass a 2 mm sieve. 1 g was weighed off for the magnesium nitrate method, 2 g for the sodium peroxide method. The solutions designed for adsorption of sulphate were prepared with perchloric instead of hydrochloric acid but otherwise after the manner of the standard method. The magnesium nitrate ashing gave 0.194 and 0.206 % S according to the official method and 0.196 and 0.192 % S according to the adsorption method. The corresponding results obtained after sodium peroxide ashing were 0.202 % S and 0.188 % S. The discrepancy between the latter two results is probably due to difficulties in controlling the ashing.

It has been suggested that sulphur could be determined in organic substances after wet ashing by nitric and perchloric acids, *e.g.*, in feed and biomaterials (Toepfer and Boutwell⁷) and rubber (Kahane⁸). Probably such a method would also be applicable for determination of total sulphur in soils. Provided the

oxidation of the sulphur compounds to sulphate proceeds quantitatively at these digestions, the subsequent analysis should be improved in speed and accuracy by applying the adsorption method as an intermediate step. A large excess of perchloric acid does not interfere.

Determination of sulphur in dolomite and glass

The U.S. Bureau of Standards' samples of dolomite and soda-lime glass were analyzed for sulphur using the adsorption method. The sample solution of the soda-lime glass was prepared exactly according to the method published in the certificate of analysis. The sample of dolomite (5 g) was dissolved in conc. nitric acid and bromine as in the certificate, but it was then evaporated with 20 ml of perchloric acid (sp.gr. 1.67) until the appearance of white fumes and diluted with water to about 100 ml. The following results were obtained: *Dolomite, No. 88.* Certificate values on total S: 0.033 % and 0.027 % (0.035 % SO_3 + 0.013 % S), found by adsorption method: 0.031 %; *Soda-lime glass, No. 80.* Recommended value on SO_3 : 0.41 % (highest result: 0.49 %, lowest result 0.36 %). Found by adsorption method: 0.38 % and 0.38 %.

Determination of sulphur in iron and steel

The "umpire" method for the determination of sulphur in iron and steel involves dissolving the sample, usually 4.57 g, in nitric acid, conversion of the nitrates to chlorides by evaporation with hydrochloric acid, reduction of the iron to the bivalent state, and determination of the sulphate as barium sulphate. The procedure is quite time-consuming and requires very skillful handling for accurate results.

Application of the adsorption method should simplify the procedure considerably. No reduction of the iron should be necessary. The nitric acid solution could possibly be run directly through the adsorption column but should preferably be evaporated with an excess of perchloric acid to oxidize carbon and chromic salts. The latter will, at least in larger amounts, interfere with the sulphate adsorption by formation of complexes. Evaporation with perchloric acid until the appearance of white fumes may be performed on a hot plate, thus avoiding the time-consuming steam bath. The final determination in the presence of only small amounts of sodium chloride should be more accurate.

On account of these considerations some preliminary experiments were performed. A sample of 4.57 g of electrolytic iron was dissolved in dilute perchloric acid, oxidized with nitric acid, and evaporated to white fumes with a total of 50 ml perchloric acid (sp.gr. 1.67). The residue was dissolved in

Table 4. Determination of sulphate in synthetic iron solutions.

Red. of chromate	S added, mg BaSO ₄	S found, mg BaSO ₄	Diff., mg
Before adsorption	58.2	58.0	— 0.2
» »	58.2	57.7	— 0.5
» »	11.64	11.57	— 0.07
» »	11.64	11.41	— 0.23
After »	58.2	58.3	+ 0.1
» »	58.2	58.0	— 0.2
» »	11.64	11.57	— 0.07
» »	11.64	11.59	— 0.05

water to a volume of about 125 ml. This solution was purified from traces of sulphate by passing through an adsorption column. After washing the column with 1 *M* perchloric acid, the solution amounted to a volume of 150 ml. To this sulphate-free solution was now added 1.003 millimoles of sulphuric acid corresponding to 23.41 mg BaSO₄ and the sulphate was determined by the adsorption method. Four determinations gave 23.45, 23.19, 23.23, 23.47, average 23.35 mg BaSO₄ (blanks: 0.38 and 0.36 mg BaSO₄).

In further experiments, sulphate-free pure iron solutions were prepared in exactly the same way as above, and solutions of the common constituents of iron and steel added. The salts used were K₂CrO₄, MnCl₂, KH₂PO₄, NiCl₂, Na₂MoO₄, Co(NO₃)₂, NH₄VO₃, CuCl₂ and Na₂HAsO₄. The samples corresponded to a steel with 0.1 % Cr, 0.5 % Mn, 0.03 % P, 0.1 % Ni, 0.01 % Mo, 0.01 % Co, 0.001 % V, 0.2 % Cu, and 0.05 % As. After addition of measured amounts of sulphuric acid, the solution was again evaporated to white fumes, diluted with water to 150 ml and the sulphate determined by the adsorption method. In some experiments the chromate was reduced before adsorption by addition of ferrous chloride; in the other experiments chromate was reduced in the column by the hydroxylamine procedure previously described.

The results (Table 4) show good agreement between added and found amounts of sulphur. At this low percentage of chromium there is no significant difference between results obtained when chromate is reduced before or after adsorption. A further study on sulphur determinations in iron and steel will be published in another paper.

SUMMARY

The adsorption properties of aluminium oxide have been investigated with special reference to its use for isolating small amounts of certain anions from fairly concentrated salt or acid solutions. Experiments show that sulphate, hydrogen sulphate and dihydrogen phosphate ions (and, it is concluded from other papers, also fluoride ions) are exceptionally strongly adsorbed and may easily be isolated from most of the other common anions. This paper deals with the isolation of sulphates only.

Adsorbed sulphate is easily eluted with small amounts of dilute sodium hydroxide, sodium carbonate, or ammonia. This fact, together with the specificity of adsorption, makes aluminium oxide preferable to ion exchange resins for the isolation of small amounts of sulphate.

Some practical applications have been demonstrated; others have been indicated. Thus the adsorption method has been applied to the determination of sulphur or sulphates in pure salt or acid solutions, in water, in biomaterials, in dolomite, in glass, and in iron and steel. The results are generally good and show the practical applicability of the method.

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