

ORKUSTOFNUN
Jarðhitadeild

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GREINING Á SÚLFATI.

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GREIÐING Á SÚLFATI

0. Almenn
1. Thorin títrun
 - 1.1 Áhöld
 - 1.2 Efni
 - 1.3 Framkvæmd
2. Felling á súlfati
 - 2.1 Framkvæmd
 - 2.2 Staðalfrávik
3. Samanburður á thorin títrun á Orkustofnun og gravimetriskri ákvörðun á Rannsóknastofnun Iðnaðarins.

0. Almenn

Nokkrar aðferðir eru til fyrir greiningu á súlfati. Felling með barium er víðast notuð, en hún er seinleg og hentar því illa í rúttínu efnagreiningu. Á Orkustofnun hafa verið reyndar aðrar aðferðir svo sem títrering með blýperklórati og notkun blýelektróðu og núna síðast thorin títrun. Fyrri aðferðin gafst ekki vel en þeirri síðari er lýst hér á eftir. Thorin títrun hentar vel við ákvörðun á súlfati í vatni ef það er ekki salt. Gerður hefur verið samanburður á thorin títrun og fellingu framkvæmdri hjá Rannsóknastofnun Iðnaðarins. Tekin voru 15-20 sýni og þau greind í tvítaki, þannig að sá sem efnagreindi vissi ekki hvaða tvö númer voru sama sýnið. Niðurstöður þessarar athugunar fylgir hér með.

1. Thorin títrun.

Súlfat í litlu magni má ákvarða með því að títrera með 0.005M barium perklórati og nota thotin sem indikator. Títreringin fer fram í 80% alkahóli og á pH sviði 2,5 til 4.0. Fyrir títrunina þarf að fjarlægja katjóna með því að láta sýnið streyma gegnum jónskipta súlu. Ef fosfat er til staðar í sýninu gerir það ákvörðunina ónákvæma.

1.1 áhöld. Þau áhöld sem þarf við þessa ákvörðun eru:

- 1) byrettur fyrir katjónaskipta.
- 2) postulínsskálar
- 3) segulhrærari
- 4) byretta fyrir títur vökva (10 ml kvörðuð upp á 0,02ml)

1,2 efni.

- 1) katjónaskiptir (Ionenaustauscher I, Merck Art 4765)
- 2) 2-própanol, absalut ethyl alkahól eða metanól geta öll gengið jöfnum höndum.
- 3) barium perklórat, 0.005M. Leysa 2.0 g af bariu perklórati trihydrate í 200 ml af vatni og 800 ml af 2-propanol eða ethyl alkahóli. Stillu pH á 3.5 með perklórsýru. Staðla lausnina með 0.005M brennisteinssýru eða súlfat standard.

4) 0.005M brennisteinssýra. Útbúa lausn og staðla hana með 0.02 N NaOH.

5) Thorin indikator. Útbúa 0.2 % lausn í vatni.

1.3 Framkvæmd. Eftir að jónskiptaranum hefur verið komið fyrir í byrettu (ca 15 ml af jónskiptara) er byrettan fyllt af sýni og það látið renna í gegn. Aftur er byrettan fyllt og sýnið látið renna í gegn. Þegar byrettan er fyllt í þriðja skipti er sýnið látið streyma í gegn í dropatali, niður að 0 ml marki. 10 ml sýnis (minna ef magn SO_4 er hátt) er látið streyma í gegn í dropatali. Í 10 ml sýnis er bætt 40 ml af propanoli (hlutfallið sýni:propanol 1:4) og 1 dropi af thorin indikator. Þetta er títrerað með barium perklórati og notaður segulhrærari, þar til fyrsta breyting úr gul eða gulrauðu yfir í bleikt kemur fram. Útreikningar á sulfati eru þá eftirfarandi:

$$\text{ppm } SO_4 = \frac{\text{ml}(\text{títrant}) \cdot N(\text{títrant})}{\text{ml}(\text{sýnis})} \cdot 96062$$

Reiknað hefur verið út staðalfrávik fyrir þessa aðferð og reyndist það vera 5.22%.

2. Felling á sulfati.

Hjá Rannsóknastofnun Iðnaðarins er sulfat greint með fellingunni. Sú stutta lýsing sem hér fylgir er tekin úr skýrslu RI sem ber nafnið "Efnarannsóknir á vatni Elliðaárna og aðrennslis þeirra" og er eftir Halldór Armannsson (maí 1970). Við ákvörðunina fást jafnframt uppleyst efni og kísill.

2.1 Framkvæmd.

250 ml vatnssýni er fyltrerað og síðan þurreimað í platínudeiglu við 105 °C og það sem eftir situr er vegið. Er þar með fengin uppleyst efni. Samkvæmni mælingarinnar er metin ±5% með 95 % vissu. Þurrefnin eru leyst í HCl lausn. Botnfallið sem eftir er er glætt og vegið. SiO_2 er síðan reykt burt með HF og það sem eftir er er glætt og vegið. Þar með fást ákvörðun á SiO_2 . Samkvæmni er metin ± 27.4 % með 95% vissu. Í filtratið er bætt 10 % $BaCl_2$ lausn og botnfallið sem myndast er glætt og vegið.

Fæst þannig tala fyrir súlfat ákvarðað gravimetrískt.

2.2 Staðalfrávik

Send voru um 20 sýni í tvítaki til súlfat ákvörðunar á RI. Ut frá þeim greiningum hefur verið hægt að reikna staðalfrávik og reyndist það vera 5.17%.

3. Samanburður á thorin títrun á Orkustofnun og gravimetriskri ákvörðun á Rannsóknastofnun Iðnaðarins.

I 20 sýnum var súlfat greint í tvítaki bæði hjá RI og OS. Reynt var að láta sýnin spanna yfir þann styrkleika sem um er að ræða í vatni svo og sem flestar vatnsgerðir. Niðurstöður eru sýndar í meðfylgjandi töflu (tafla 1). Í heildina eru greiningar RI lægri en greiningar OS. Reiknað hefur verið út staðalfrávik og óvissa hverrar mælingar. Mismunur á greiningum RI (gravimetrískt) og OS (thotin títrum) er innan skekkjumarka greiningaaðferðanna. Þrátt fyrir það er um kerfisbundinn mun að ræða, eins og sést á meðfylgjandi mynd. Þennan mun má skýra á tvennan hátt. Gravimetriskar fellingar hafa frekar tilhneigingu til að sýna of lág gildi ef fyllsta hreinlætis er gætt. Á hinn bóginn hafa niðurstöður títreringar tilhneigingu til að sýna frekar of hátt magn. Þessi samanburður má því teljast vel viðunandi, en ef til vill væri rétt að athuga hvort ekki mætti nota þynnri lausn af $BaCl_4$ en nú er notuð og minnka þar með áhrif síðasta dropa títurvökva.

I ljós kom við þessa athugun að greiningu SO_4 í söltu vatni er ekki hægt að framkvæma með thorin títrun. Tafla 2 sýnir niðurstöður saltra sýna. Hvert tvítak var títrerað 3-8 sinnum, eða þar til tvö viðunandi gildi fengust. Í hluta I eru valin tvö til þrjú þau gildi sem best passa saman, en í hluta II er tekið meðaltal allra mælinga af sama tvítaki. Samkvæmni þessara mælinga er slæm og greinileg truflun kemur fram (allt of háar niðurstöður) miðað við gildi fengin á RI, en þeim ber saman við eldri mælingar gerðar á OS á sýnum frá sömu svæðum. Það er því ljóst að thorin títrun hentar ekki fyrir salt vatn.

GREINING Á SÚLFATI.

Rannsóknastofnun Iðnaðarins gerði greininguna með fellingu en á Orkustofnun var súlfat greint með Thorin titrun

Sýni	Rannsóknastofnun Iðnaðarins		Orkustofnun		RI og OS				
	I	II	I	II	meðaltal	meðaltal			
KRADO1771003	192.1	187.2	189.7±	9.8	198.3	196.4	197.4±	10.3	193.6
KRADO2771015	228.0		11.8		239.1	239.1	239.1	12.5	233.6
KRADO1771002	102.6		5.3		109.9			5.7.	106.3
NAMDO1771009	37.7		1.9		48.0	38.9	43.5	2.3	40.6
NAMDO9771163	24.1		1.2		25.3	24.9	25.1	1.3	24.6
NAMDO9771170	18.7		1.0		25.7	20.9	23.3	1.2	21.0
NAMDO2771000	53.7		2.3		60.9	60.6	60.8	3.2	57.3
REYVO3770033	146.9	141.0	144.0	7.4					
REYD10770147	88.1	78.0	83.1	4.3					
SVAVO6770043	34.2	35.8	35.0	1.8					
SVADO3770040	40.3	44.4	42.4	2.2					
SVADO2770012	47.7	47.3	47.5	2.5					
SKFV10770153	206.2	213.0	209.6	10.8	219.1	212.4	215,8	11.3	212.7
SNAV11770073	76.5	78.6	77.6	4.0	82.8	85.4	84.1	4.4	80.9
OS-kranavatu	3.7	5.3	4.5	0.2	9.5	7.4	8.5	0.4	6.5
HÖFV10772059	204.9	207.0	206.0	10.7	214.1	200.5	207.3	10.8	206.7
Spóastaðir	55.1	54.7	54.9	2.8	61.5	61.9	61.7	3.2	58.3
KJÓVO4772036	14.4	17.1	15.8	0.8	19.6	17.8	18.7	1.0	17.3
SNAVO5770074	2.9	3.7	3.3	0.2	4.2	3.5	3.9	0.2	3.5
SNAVO5770085	6.0	6.2	6.1	0.3	5.9	7.0	6.5	0.3	6.3
Staðalfrávik			5.17%						5.22%

TAFLA II. Súlfat í söltum sýnum.

sýni	Rannsóknastofnun Iðnaðarins		Orkustofnun I		Orkustofnun II						
	a	b	a	b	a	b					
REYV03770033	146.9	141.0	144.0 ± 7.4	443.9	345.1	394.5 ± 20.0	514.9 ± 22.2	370.0 ± 14.6	442		
REYD10770147	88.1	78.0	33.1	4.3	277.2		397.8	30.1	297		
SVAVC6770043	34.2	35.8	35.0	1.8	271.1	298.6	15.1	299.8	17.2	231.3	24.6
SVADC3770040	40.3	44.4	42.4	2.2	287.1	294.6	14.9	262.0	27.8	232.2	22.5
SVAD02770012	47.7	47.3	47.5	2.5				264.9	15.6	141.7	203

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Rapid Microtitration of Sulfate

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Small concentrations of sulfate can be determined by a direct titration with 0.005M barium perchlorate using Thorin [2(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid] as the indicator. The titration is carried out in 80% alcohol, in the apparent pH range 2.5 to 4.0. The end point is sharp and equilibrium is rapidly attained, so that the titration can be rapidly carried out. The method is more versatile when cations are removed by passage of the sample through an ion exchange column prior to the titration. Phosphate makes the method inaccurate, but can be removed by a rapid precipitation with magnesium carbonate. The method has been applied to the determination of sulfate in raw water, treated city water, and boiler water. Concentrations of sulfate as low as 10 p.p.m. can be determined which are accurate to ± 1 p.p.m. Higher concentrations can be determined with an error of 1% or less. In the absence of phosphate the time required for a complete single determination is only 3 to 5 minutes.

NO REALLY satisfactory method is available for the determination of small amounts of sulfate. Gravimetric methods are time-consuming and unsuited for the determination of very low concentrations of sulfate. Turbidimetric procedures are rapid, but are often unreliable and difficult to reproduce. The direct titration of sulfate with barium using tetrahydroxyquinone (THQ) or rhodizonic acid indicator has been widely used by some but rejected by others, largely because of the poor end point (1, 3, 5).

A rapid titrimetric method for macro amounts of sulfate has recently been reported (2). This involves direct titration of sulfate in 40% alcohol with barium chloride using Alizarin Red B as the indicator. The end point is sharp and easily detectable.

p. 1439, Oxford Univ. Press, London, 1950.
(20) Sieburg, E., *Biochem. Z.*, **74**, 371 (1916).
(21) Stuewe, W., *Arch. Pharm.*, **252**, 430 (1914).

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This method can only be applied for the determination of macro quantities of sulfate, however, because a certain minimum of precipitate is required to provide enough surface for the end point reaction.

The present method is applicable to very low concentrations of sulfate. The determination is carried out by first removing cations by means of a small ion exchange column in the hydrogen form. Alcohol is added to bring the alcohol concentration to 80% by volume and the resulting solution is titrated with 0.005M barium perchlorate using Thorin [2(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid] as the indicator. The end point is marked by a sharp change from yellow to pink.

CONDITIONS FOR TITRATION

The titration is successful only if a high concentration of some nonaqueous solvent is present. Using the lower alcohols the concentration of nonaqueous solvent should be between 70 and 90% by volume. Ethyl alcohol, 2-propanol, or methanol serves equally well. Barium sulfate precipitated from solutions containing a high concentration of alcohol appears to be gelatinous and not at all like the familiar fine crystalline precipitate which is obtained from aqueous solution. Titration of very low concentrations of sulfate is rapid in alcohol-water, indicating that the induction period observed in water for precipitation of small concentrations of sulfate is not encountered here.

The titration can be successfully carried out anywhere in the "apparent" pH range 2.5 to 4.0. Passage of the sample through the cation exchange column automatically brings the apparent pH within this range after the addition of the alcohol unless the foreign salt concentration is too high. The maximum foreign salt concentration permissible is approximately five to ten times the molar concentration of sulfate. The pH is controlled by adjusting the quantity of sample taken so that the total salt concentration will not be great enough to lower the

pH excessively after passage through the hydrogen form ion exchange column.

The titrant used in barium perchlorate in 80% alcohol. The perchlorate ion introduced with the barium causes less coprecipitation error than chloride; also barium perchlorate is much more soluble in alcohol than is barium chloride. Preparing the titrant in alcohol-water solution keeps the alcohol concentration constant throughout the titration.

The optimum concentration of the titrant and of sulfate depends on the size of the increments of titrant added near the end point and on the total volume of sulfate solution taken for titration. Adding approximately 0.01-ml. increments of barium perchlorate near the end point and taking 10 ml. of sulfate solution (plus 40 ml. of alcohol) for titration, it is best to use 0.005M barium perchlorate. Using these conditions, the range of sulfate titrated is 0.05 to 5.0 mg. or approximately 5 to 500 p.p.m. (before addition of alcohol).

The rate of titration is not critical. Equilibrium is rapidly attained, so that the titration can be quickly carried out. It is best to allow 2 or 3 seconds between addition of the last few increments of titrant before the end point. Efficient magnetic stirring improves the speed and convenience of the titration.

EFFECT OF FOREIGN IONS

The effect of foreign cations was studied by titrating sulfate in the presence of various ions added as the perchlorate or chloride. The results given in Table I show that several metal ions cause errors of 2 to 3% due to coprecipitation. Numerous other metal ions completely interfere with the titration by forming a colored complex with the Thorin indicator. Many metal ions which do

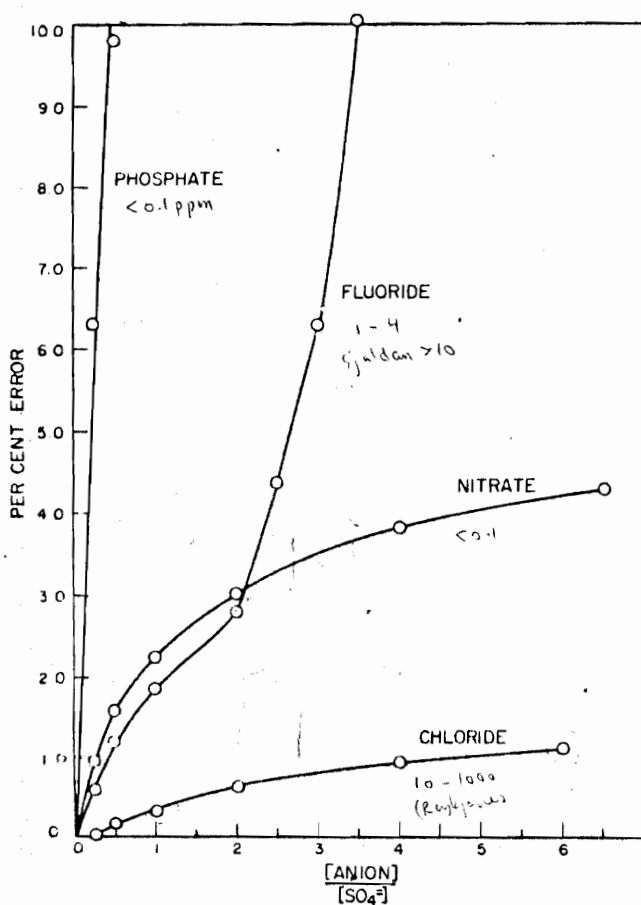


Figure 1. Results of titration of sulfate in presence of different concentrations of common anions

Table I. Effect of Cations

Salt Added, ($\approx 2[\text{SO}_4^{2-}]$)	Ba ⁺⁺ Theory, MI.	Ba ⁺⁺ Actual, MI.	Difference, %
NaClO ₄	4.83	4.69	-2.9
KCl	6.76	6.32	-6.6
NH ₄ ClO ₄	6.76	6.62	-2.0
Zn(ClO ₄) ₂	4.83	4.71	-1.9
Mg(ClO ₄) ₂	2.95	2.90	-1.7

Table II. Sulfate Titration after Ion Exchange Removal of Cations

Added	Ba ⁺⁺ Theory, MI.	Ba ⁺⁺ Actual, MI.	Difference, %
NaClO ₄	2.42	2.42	± 0.0
KCl	2.637	2.64	+0.1
LiClO ₄	2.42	2.42	± 0.0
NH ₄ ClO ₄	2.637	2.635	-0.1
Cu(ClO ₄) ₂	2.637	2.64	+0.1
Ca(ClO ₄) ₂	2.637	2.64	+0.1
Zn(ClO ₄) ₂	2.637	2.635	-0.1
LaCl ₃ + HCl	2.637	2.685	+1.8
Al(ClO ₄) ₃	2.637	2.635	-0.1

not form colored complexes with Thorin in aqueous solution do so in solutions containing a high percentage of alcohol.

The preliminary removal of cations by means of an ion exchange column is recommended in almost every case. This operation can be quickly accomplished and permits excellent results in the sulfate titration. Table II gives data for the titration of small amounts of sulfate following the ion exchange removal of various cations. Virtually all cations can be successfully removed by this process; only metals such as chromium (4) and zirconium, which form anion complexes with sulfate, cause difficulty.

Sulfate was titrated in the presence of common anions added as the appropriate acid. The error caused by different concentrations is plotted in Figure 1. Of the anions commonly associated with sulfate, the error due to phosphate is by far the most serious. It was found, however, that phosphate can be removed by precipitation with magnesium carbonate. Apparently the excess magnesium carbonate serves as a carrier to ensure complete precipitation of the phosphate. Table III gives results for titration of sulfate following the removal of phosphate by this method. Phosphate removal is essentially complete if the precipitate is filtered cold, but a small amount of phosphate apparently remains if the filtration is carried out at room temperature.

Table III. Titration of Sulfate Following Removal of Phosphate

Method of PO ₄ ⁻⁻⁻ Removal	Ba ⁺⁺ Theory, MI.	Ba ⁺⁺ Actual, MI.	Difference, %
MgCO ₃ cooled to 10° C.	0.74	0.74	± 0.0
	0.74	0.74	± 0.0
	0.74	0.743	+ 0.4
MgCO ₃ cooled to 25° C.	0.74	0.757	+ 2.3
	0.74	0.747	+ 1.0
Phosphate not removed	0.74	0.85	+ 15.0

Sulfate interferes seriously. Attempts to remove the sulfite by acidifying and boiling were unsuccessful. Interference can be avoided, however, by titrating the sulfite to sulfate with a standard iodine solution, and determining the total sulfate by the general procedure. The original sulfate can then be calculated by subtracting the amount of sulfate equivalent to the amount of iodine used.

APPLICATION TO WATER ANALYSIS

The titrimetric microprocedure has been adapted to the determination of sulfate in raw water, treated city water, and

in boiler water. As in the general method, cations are first removed by passage of the sample through an ion exchange column. In the conventional ion exchange method, the sample is diluted on rinsing through the column. To avoid this a continuous flow technique has been adopted. The apparatus employed is shown in Figure 2. The use of a rather coarse resin, and of a water sample large enough to give a head of pressure, permits a very rapid rate of flow through the column. After the first 30 to 50 ml. of effluent are discarded, a portion of the next effluent (which has the same sulfate concentration of the original sample) is taken for the sulfate titration. Using this method, a complete single determination of sulfate in water requires only 3 to 5 minutes.

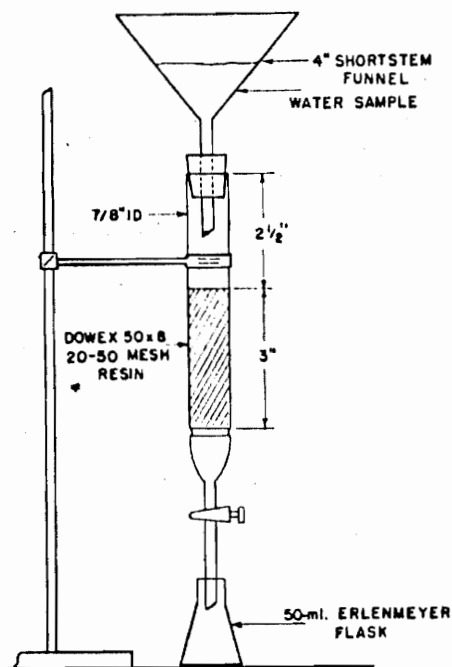


Figure 2. Apparatus used for determination of sulfate in water

Tables IV and V compare the results obtained in the analysis of several water samples by gravimetric and titrimetric methods. In the gravimetric method a 500-ml. sample was first passed through an ion exchange column, then concentrated by evaporation to about 250 ml. before precipitation. The samples of boiler water had been titrated with sodium phosphate and contained a slight excess over that required to treat the hardness.

APPARATUS

The apparatus used in the general procedure for sulfate is shown in Figure 3 and that for the determination of sulfate in water is described in Figure 2. The capacity of the small column is approximately 30 meq. The columns should be regenerated when about two thirds of the capacity has been exhausted, as indicated by the progress of the lighter colored upper band.

Table IV. Determination of Sulfate in Water

Sample Source	SO ₄ Gravimetric, P.P.M.	SO ₄ Titrimetric, P.P.M.	Difference, P.P.M.
ISC water	118.8	120.2	1.4
ISC water	109.2	109.4	0.2
Diluted ISC	43.8	44.1	0.3
Diluted ISC	10.9	11.2	0.3
Boiler water	918	926	8
Boiler water	1203	1210	7
Boiler water	1203	1240*	37

* Phosphate not removed.

Regeneration is carried out by passing about 100 ml. of 2 to 3N hydrochloric acid through the column. After thorough washing with distilled water, the column is ready for use.

REAGENTS AND SOLUTIONS

Alcohol. Absolute ethyl alcohol, 2 propanol, methanol, or mixed ethyl alcohol and methanol as purchased commercially.
Barium perchlorate, 0.005M. Dissolve 2.0 grams of barium perchlorate trihydrate in 200 ml. of water and add 800 ml. of

Table V. Titration of Diluted Samples of Raw Water

Dilution	Ba ⁺⁺ , Ml.	SO ₄ ⁻² , P.P.M.	SO ₄ ⁻² Gravimetric, P.P.M.	Difference, P.P.M.
None	2.46	115.8	114.9	+0.9
	2.47			
	Av. 2.47			
10:100	0.25	11.7	11.5	+0.2
	0.25			
	Av. 0.25			
20:100	0.49	23.4	23.0	+0.4
	0.50			
	Av. 0.50			
40:100	1.00	46.9	46.0	+0.9
	1.00			
	Av. 1.00			
70:100	1.73	81.1	80.4	+0.7
	1.72			
	Av. 1.73			

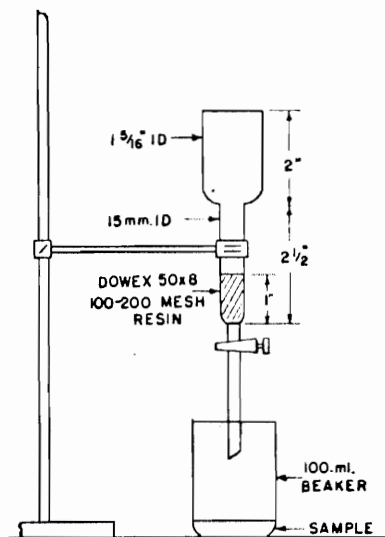


Figure 3. Apparatus used in the general procedure for sulfate

2-propanol or ethyl alcohol. Adjust the apparent pH to about 3.5 with perchloric acid. Standardize against 0.005M sulfuric acid according to the general procedure.

Sulfuric acid, 0.005M. Prepare a 0.005M solution and standardize by titration with 0.02N sodium hydroxide.

Thorin. Prepare a 0.2% solution in water. The Thorin used was purchased from the Bach Chemical Co., Ames, Iowa.

Starch. To 1 gram of starch add sufficient water to make a paste. To this add 100 ml. of boiling 50% glycerol.

Iodine, 0.01M. Dissolve 1.27 grams of recrystallized iodine and 10 grams of potassium iodide in 100 ml. of water. Dilute to 500 ml.

PROCEDURES

General Procedure. Take a sample for analysis which is 10 ml. or less in volume and which contains 0.12 to 120 mg. of sulfate. Pass the sample through the small ion exchange column (Figure 3) and wash through with 12 to 15 ml. of wash water added in three or four portions (the liquid level should be allowed

to recede to the top of the resin before each portion of wash water is added). Receive the effluent from the column in a 25-ml. volumetric flask and dilute exactly to volume. Pipet a 10-ml. aliquot of the effluent into a 100-ml. beaker, and add 40 ml. of alcohol and 1 drop of Thorin indicator. Titrate with 0.005M barium perchlorate, taking the first permanent change from yellow or yellow-orange to pink as the end point. Add the bulk of the titrant rapidly, but allow 2 or 3 seconds between addition of the last few increments.

The total salt content of the sample (including sulfate and foreign salts) should not exceed about 0.6 meq.; otherwise the pH of the solution after passage through the ion exchange column will be too low. If the salt concentration is not known, determine the pH of a small portion of the 25-ml. effluent; a pH lower than 1.5 indicates that additional dilution is required. Discard this portion of the effluent, as it will be contaminated with potassium chloride from the calomel electrode.

Procedure for Sulfate in Water. Fill the reservoir of the larger ion exchange column (Figure 2) with the water sample and pass through the column at a rapid rate. Discard the first 40- or 50-ml. portion of the effluent. Pipet 10 ml. of the next portion into a small beaker or flask, add 40 ml. of alcohol and 1 drop of Thorin indicator, and titrate with 0.005M barium perchlorate as described in the general procedure.

In the presence of sulfite and phosphate (as in boiler water), pipet 25 ml. of the water into a 100-ml. beaker. Titrate the sulfite with 0.01M iodine solution using 1 ml. of starch solution as the indicator. Add 10 drops of 0.1M perchloric acid and 0.3 gram of magnesium carbonate. Boil gently for 5 minutes, cool to 10° C., and filter (using Schleicher & Schuell No. 589 filter paper or equivalent) directly into the small ion exchange column (Figure 3). Titrate a 10-ml. aliquot with 0.005M barium perchlorate according to the general procedure. This gives the total sulfate. The original sulfate is the total sulfate less the amount of sulfite determined iodometrically.

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Determination of Carboxylic Acid Anhydrides by Reaction with Morpholine

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A titrimetric method employing an indicator was sought for the direct determination of carboxylic acid anhydrides in the presence of and to the exclusion of the corresponding acids. A satisfactory method was developed based on the reaction of the anhydride with morpholine and titration of the excess reagent with methanolic hydrochloric acid. Data are presented on the determination of the purity of eight anhydrides and the determination of low concentrations of acetic anhydride in glacial acetic acid. The procedure is rapid, generally applicable to a variety of acid anhydrides, and accurate and precise over a wide range of concentrations.

Round Table Discussions on Titrations in Nonaqueous Solutions (7), and later its application to the determination of chrysanthemum acid anhydride in commercial allethrin was reported (5).

Morpholine reacts with carboxylic acid anhydrides to produce equimolar quantities of amide and acid. In a methanolic medium using mixed methyl yellow-methylene blue indicator, all the components of the reaction are neutral except morpholine. If a measured excess of morpholine reacts with a sample containing anhydride, the anhydride reacts preferentially with morpholine, and the excess can be titrated with standard methanolic hydrochloric acid. The morpholine consumed, represented by the difference in titration between a blank and sample, is a measure of anhydride.

TABLE I. Methods for the determination of carboxylic acid