formed during the ionization of compounds in solutions. This would give support also to the hypothesis that atoms are held in combination by electrical forces.

URBANA, ILL.

THE EFFECTS OF SULFATES ON THE DETERMINATION OF NITRATES.

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Introduction.

As is well known, the determination of nitrates in the sanitary analysis of water is generally made with the aid of the phenoldisulfonic acid reagent. During recent years this reagent has found extensive application in soil investigation, particularly in studies on nitrification. The chemistry of the reactions involved in this determination has been extensively studied, and, as shown by Chamot and Pratt,[1] the yellow color that is produced depends upon the formation of the tri-salt of the phenoldisulfonic acid. It is not the purpose of this paper, however, to discuss the chemistry of this reaction, but rather to present some data bearing upon the effects of sulfates on the nitrate determination.

Natural waters, as well as the solutions obtained from soils, frequently contain various salts. Among these are the chlorides, carbonates and sulfates. The effects of chlorides and carbonates on the determination of nitrates have been studied in detail, especially the former; but the fact that the phenoldisulfonic reagent contains free sulfuric acid, which upon neutralization gives rise to sulfates has caused chemists to neglect to study the effect of sulfates.

Recently, Lipman and Sharp[2] published some investigations on this subject in which chlorides, carbonates and sulfates were studied. They found, in common with previous studies, that chlorides caused an apparent loss of nitrates, but, contrary to previous observations, carbonates have no effect. They further found that considerable loss of nitrate took place upon evaporating a nitrate solution containing sodium sulfate. The addition of dry sodium sulfate to the dry nitrate residue, however, occasioned no loss of nitrate. From these observations the claim is made that sulfates cause a loss of nitrate in this determination not by interfering with the phenoldisulfonic acid reaction, but by the expulsion of nitric acid during the time of evaporation on the water bath. Hence they conclude that nitrate determinations in solutions containing sulfate must be made by the use of other methods.

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[1] THIS JOURNAL, 21, 922; 32, 630; 33, 366.

[2] *Univ. Cal. Pub. Agr. Sci.*, 1, No. 2, pp. 21–37.

As above stated, soluble sulfates are frequently present in soils. In addition it is a common practice to employ a solution of alum as a coagulating agent in order to secure clear soil solutions. While it is true the use of alum as a coagulating agent may well be objected to for other reasons, as pointed out by Lipman and Sharp, the suggestion that sulfates in general cause a loss of nitrate during the time of evaporation merits further study. The more especially is it important that this subject be investigated, since in the numerous nitrification studies now being carried on in many parts of the world, ammonium sulfate is often used as a source of nitrogen, and, therefore, soluble sulfate is bound to occur in the water extracts in which the nitrate determinations are usually made.

For some time the writer, at the suggestion of Mr. S. S. Peck, of the Hawaiian Sugar Planters' Experiment Station, has made use of calcium sulfate as a coagulating agent in the determination of nitrates in Hawaiian soils. This material has proven to be a most efficient coagulating agent with the abnormal soils of the Islands, often being found to be far more effective than calcium oxide or carbonate. In fact, the last named compounds cause a deflocculation in some of the heavy upland soils, while calcium sulfate brings about rapid coalescence of the finely divided particles, thus effectively aiding in securing a clear solution. On account of the extensive use that has been made of calcium sulfate in this laboratory it became necessary to test the effect of this compound on the nitrate determination. The results proved to be so out of harmony with the conclusions reached by Lipman and Sharp that a study of some of the more common sulfates was also undertaken.

Experimental.

The nitrate solution used in this work was prepared by dissolving in distilled water potassium nitrate at the rate of 250 parts of nitrogen per million, and portions of the solution containing the amounts of nitrogen shown in the subjoined tables were taken in all of the determinations reported in this paper. The sulfates were employed in solution prepared by dissolving one gram in one liter of distilled water, and varying amounts were added to the nitrate solution, as shown in the tables. After evaporating on a water bath, and cooling, the residues were treated with 2 cc. of the freshly prepared phenoldisulfonic acid reagent, allowed to stand five minutes, diluted to about 30 cc., and the color developed by carefully adding strong ammonia until alkalinity was produced and a permanent color obtained. After diluting to 250 cc., aliquot portions were then used for making comparisons in a colorimeter with a standard nitrate solution prepared in the same way. All determinations were made in duplicate. The results follow:

EFFECTS OF SULFATES ON THE DETERMINATION OF NITRATES.

(0.275 mgs. nitrate nitrogen used in each determination.)

Sulphate added. Mg.	Na_2SO_4. Nitrate N found. Mg.	K_2SO_4. Nitrate N found. Mg.	$MgSO_4$. Nitrate N found. Mg.	$(NH_4)_2SO_4$. Nitrate N found. Mg.	$CaSO_4$. Nitrate N found. Mg.
None	0.275	0.275	0.275	0.275	0.275
1.00	0.275	0.280	0.272	0.237	0.270
5.00	0.265	0.270	0.277	0.203	0.270
10.00	0.225	0.210	0.270	0.235	0.273
20.00	0.180	0.265	0.275	0.225	0.273
40.00	0.140	0.260	0.277	0.225	0.280

It will be seen from the above data that when any considerable amounts of sodium, potassium, or ammonium sulfate were added considerable loss of nitrate took place, whereas neither calcium nor magnesium sulfate occasioned any loss. It will also be seen that the losses of nitrate from solutions containing sodium sulfate were roughly proportional to the amounts of sulfate present, and that important losses were sustained amounting to practically 50% of the nitrate originally present when the larger amounts of the sulfate were used. On the whole the losses from potassium or ammonium sulfates were also proportional to the amounts used, but not so great as in the case of sodium sulfate.

The fact that neither calcium nor magnesium sulfate produced any effect on this determination, while the other sulfates caused losses of nitrate, led to a further investigation of the question. A new solution of sodium sulfate was prepared and used in the same way as above outlined. The results proved to be decidedly different from those previously obtained, the loss of nitrogen being very slight in any case. Subsequent trials showed it to be difficult to secure concordant results when sodium, potassium or ammonium sulfate was employed, and that only when practically the same conditions of evaporation are maintained, such as the rate of evaporation, temperature, etc., were the results identical.

Lipman and Sharp hold that the loss of nitric nitrogen takes place during the time of evaporation, and consider the loss to be due to the expulsion of nitric acid, brought about by the combined action of heat and the sulfate radical. Theoretically, at the temperature obtained on the water bath no action should take place if the sulfate radical be completely combined in the normal sulfate combination. It was suggested, therefore, that probably the sodium sulfate contained small amounts of the acid sulfate, or that hydrolysis took place to a limited degree, resulting in the formation of small amounts of the acid sulfate.

With the view to throwing some light on this point varying amounts of sodium bisulfate were added to portions of the nitrate solution, evaporated, and the determinations completed as usual.

EFFECTS OF SODIUM BISULPHATE.

$NaHSO_4$ added. Mg.	Nitrate N added. Mg.	Nitrate N found. Mg.
None	0.275	0.275
1.00	0.275	0.195
5.00	0.275	0.047
10.00	0.275	0.003
20.00	0.275	0.003
40.00	0.275	0.005

It will be seen that the acid sulfate under the conditions of these experiments can cause a relatively large loss of nitrates, 10 mg. having been found to expel practically all of the nitric nitrogen present. The loss was due to expulsion of nitric acid, as was shown by passing the vapors through a dilute caustic potash solution. Similar results were also obtained with other bisulfates. Therefore, acid sulfates, as might be expected have the power of setting free nitric acid from nitrates during evaporation on the water bath.

The expulsion of nitric acid by acid sulfates ought to be preventable by the addition of caustic alkali or carbonate. Experiments on this point showed such to be the case, if sufficient carbonate be added to the solution to completely convert the acid sulfate into normal sulfate. In the following series of experiments sodium carbonate was added to solutions containing different sulfates, and these then added to the nitrate solution, evaporated, and the determination completed as usual. The results are shown in the following table:

EFFECTS OF SODIUM CARBONATE ON THE LOSS OF NITRATE N.

Sulphate added.	Mg.	Sodium carbonate added. Mg.	Nitrate N added. Mg.	Nitrate N found. Mg.
None	..	None	0.275	0.270
Na_2SO_4	20	None	0.275	0.185
Na_2SO_4	20	20.00	0.275	0.277
K_2SO_4	20	None	0.275	0.240
K_2SO_4	20	20.00	0.275	0.280
$(NH_4)_2SO_4$	20	None	0.275	0.190
$(NH_4)_2SO_4$	20	20.00	0.275	0.270
$NaHSO_4$	20	None	0.275	0.006
$NaHSO_4$	20	20.00	0.275	0.280
None	..	20.00	0.275	0.282

From the above data it is shown that sodium carbonate may prevent the loss of nitrates brought about by different sulfates just as would be expected if the loss is caused by the liberation of nitric acid.

In this connection it should be stated that Lipman and Sharp were unable to prevent the loss of nitrates occasioned by sodium sulfate by the addition of sodium carbonate. In the experiments reported above, however, the loss of nitrate during evaporation was entirely prevented by the addition of sodium carbonate. The experiments on this point have been repeated several times, and in no instance was any important loss of nitrate observed when an excess of sodium carbonate had been added to the solution. Indeed it seems difficult to believe that nitric acid could be volatilized and expelled from a carbonate solution under the conditions usually obtaining in this determination.

It is furthermore of interest that no loss of nitrate was observed from the use of sodium carbonate alone. As was pointed out by Chamot and Pratt[1] carbonates may occasion slight losses of nitrates, due to mechanical causes such as effervescence produced by the reaction of the phenoldisulfonic acid reagent on the carbonates. If sufficient caution be observed, however, such losses may become negligible.

The data submitted in this paper indicate that the making of broad generalizations from specific instances may be entirely unwarranted. The fact that sodium sulfate (supposed to be none other than the normal sulfate) causes a loss of nitrate nitrogen, does not justify the sweeping conclusion that the sulfate radical in any inorganic combination would act in the same way. Although the evidence is of an indirect nature, the above data seem to justify the conclusion that losses of nitrate during evaporation in the presence of sulfates are probably referable to acid sulfates which were either originally present in the solution or perhaps formed by hydrolysis during the evaporation process. The latter view seems the more tenable, since losses took place only in the presence of the sulfates that most easily give rise to the bisulfate.

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NOTE.

Zincoso-zincic Chloride. (Preliminary Paper.)—It has been shown by Borchers and Stocken[2] that when metallic calcium is melted in presence of calcium chloride, a mass of transparent, red, pleochroitic crystals are formed. This compound was proved by them to be sub-chloride of calcium. This suggested us to investigate the action of metals on fused salts generally. The first case that has been taken for study is the action of metallic zinc on fused zinc chloride. It has been found that zinc dissolves freely in fused zinc chloride to form a bluish white mass and this proved to be a zincoso-zincic salt of the formula, Zn_3Cl_5.

For a preparation of the compound, zinc chloride is melted in a crucible and then metallic zinc is gradually added, when it begins to dissolve. After some time of addition, the added zinc remains undissolved and forms a globule at the bottom of the crucible. The supernatant fluid is next poured in a basin and allowed to cool when it sets to a homogeneous,

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[1] THIS JOURNAL, 33, 25.

[2] *Z. Electrochem.*, 8, 757 (1902).