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THE DEVELOPMENT AND APPLICATION OF SOME RAPID  
ANALYTICAL CONTROL METHODS IN THE  
MANUFACTURE OF WET PROCESS PHOSPHORIC ACID

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## 1. GENERAL INTRODUCTION.

This paper describes the development and application of some rapid methods of chemical control analysis in the production of wet process phosphoric acid.

The work described was carried out to improve the accuracy of analytical methods being used in the routine control of phosphoric acid production. A further aim was to reduce the time required for analytical determinations.

Normally the essential analyses required for plant control are the determination of phosphoric acid, sulphuric acid and dilution ratio. In addition the examination of gypsum filter cake for free water and water soluble phosphate content gives information on the filtration efficiency.

The determination of phosphoric acid is carried out using the differential vanadophosphomolybdate method previously described by Donald, Schwehr and Wilson (1), and with only slight modification has been adapted for this particular determination. As such it will not be described further.

The analytical methods replaced by those described in this paper were lengthy and in the case of the determination of sulphate and free water in gypsum filter cake of doubtful accuracy. The studies carried out and the work involved were required to remedy the defects already existing and outlined above, namely to decrease the time required for an analysis with improvement in accuracy when compared with previous methods.

A study was made of the turbidimetric method for the determination of sulphate in phosphoric acid. The stabilisation of the barium sulphate precipitate was accomplished by the use of a suitable surface active agent and the formation of a precipitate of reproducible particle size and conforming to the Beer-Lambert Law, by the addition of solid barium chloride of known particle size.

The determination of the dilution ratio of phosphoric acid-gypsum slurries departs from the usual chemical methods and the method described involves the rapid centrifugal separation of solid and liquid phases. The accuracy of the method may be checked using usual chemical methods or alternatively a new concept of dilution ratio may be adopted using the results obtained by the method.

Free and combined water in gypsum filter cake are determined by extraction with suitable organic solvents followed by ignition or azeotropic distillation using xylene.

Marked improvements in both the accuracy and reproducibility of the method for the determination of sulphate in phosphoric acid are claimed and the time required for a complete analysis in the routine control laboratory was reduced from 90 minutes to 15 minutes. The average coefficient of variation at the 3% sulphate level is about 6% when used as a rapid routine control method.

The investigation of the method for the determination of dilution ratio resulted in a very rapid and accurate method being developed. The time required for an analysis, an important factor in routine control was reduced from several hours of manipulative chemical work to approximately 15 minutes in which most of the time was utilised in centrifuging the sample. A feature of the method is that with the equipment available four individual tests or one test in quadruplicate or two tests in duplicate can be carried out at the same time.

The method developed for the determination of free water in gypsum filter cake is considered to be the most reliable and also the most rapid of those available at the present time. The determination of combined water is carried out rapidly by ignition and although slightly high results are obtained due to the presence of organic matter the results are of sufficient accuracy for routine control purposes. The azeotropic distillation method while being more time consuming is of similar accuracy and this determination can be completed in 30 minutes.

The development of the three analytical methods is described in separate sections. In addition to the work described a statistical examination of series of results obtained by laboratory personnel engaged on routine control have been made and are also presented in the paper.

## 2. THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID.

### 2.1. Introduction.

A survey of the method available for the determination of sulphate suggested that under controlled conditions a turbidimetric method would be of sufficient accuracy for plant control purposes and more rapid than both classical and modified gravimetric procedures.

Colorimetric and titrimetric procedures were considered, but all method available suffered from interference by phosphate ion and, therefore, a re-examination of the turbidimetric method was made.

It was evident that to obtain reproducible results uniform particle size of precipitate was required. In addition it was considered essential to keep the precipitate in stable suspension for a sufficient length of time to permit reproducible measurement of optical density by the spectrophotometer.

A number of points were considered worthy of further investigation and the effects of acidity, temperature, particle size of solid barium chloride and surface active agents on the formation and stabilisation of barium sulphate were examined.

### 2.2. Experimental.

Early attempts to utilise a turbidimetric method resulted in the formation of a variable and rapidly deposited barium sulphate precipitate. Even with rapid measurement of the optical density of the suspension the variation in particle size of precipitate did not permit reproducible measurements to be made.

A number of compounds were examined in an effort to stabilize the precipitated barium sulphate and maintain it in suspension. Starch, gelatine and glycerol had little effect, but it was found that the addition of a low concentration of a non-ionic surface active agent Nonex stabilised the precipitate both with regard to particle size and effective suspension in aqueous solution.

The following reagents were used in the investigation:-

- |                            |   |  |
|----------------------------|---|--|
| Sulphuric acid             | - | Analar. Diluted with distilled water to give a solution containing 1.0 mg. $\text{SO}_4^{--}$ per ml.    |
| Phosphoric acid            | - | Analar. Diluted with distilled water to give a solution containing 5 mg. $\text{H}_3\text{PO}_4$ per ml. |
| Nonex surface active agent | - | B.D.H. Diluted with distilled water to give the required concentration.                                  |
| Barium chloride            | - | 10% solution in distilled water.   |
| Barium chloride            | - | Analar. Solid. Sieved when necessary to give the required particle size.                                 |

#### 2.2.1. Effect of surface active agent on precipitation.

Aliquots of standard sulphuric acid containing from 1.0 mg. to 5.0 mg.  $\text{SO}_4^{--}$  were transferred to graduated tubes each containing 40 mg. phosphoric acid. 1 ml. of a 0.1% solution of Nonex was added and the volumes were adjusted to 15 ml. 5 ml. of 10% barium chloride solution was then added and the contents of each tube well mixed. The optical density of the suspension was then measured at a wavelength of 470m $\mu$ . Six replicate determinations were carried out, the results obtained are presented in Table 1 :-

2. THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID (Contd.)

2.2. Experimental (Contd.)

2.2.1. Effect of surface active agent on precipitation (Contd.)

Table 1.

mg. SO <sub>4</sub>	Number of experiment.					
	1	2	3	4	5	6
	<u>Optical density.</u>					
1	0.372	0.355	0.326	0.282	0.315	0.299
2	0.574	0.494	0.514	0.594	0.450	0.522
3	0.780	0.664	0.656	0.878	0.608	0.743
4	0.985	0.860	0.856	1.085	0.731	0.908
5	1.182	1.020	1.040	1.190	0.816	1.003

The reproducibility of the series was obviously unsatisfactory. In each case, however, the precipitate remained in stable suspension for a sufficiently long period to enable a satisfactory optical density measurement to be made.

The amount of Nonex required to effect satisfactory stabilisation of the precipitate was investigated and a series of standard solutions containing 2.5 mg. SO<sub>4</sub> and varying quantities of Nonex were prepared and treated with 5 ml. of 10% barium chloride solution. However, in view of the high optical densities obtained when using a final volume of 20 ml. it was decided that in future work the dilution would be made to 100 ml.

The optical densities of the suspensions prepared above and diluted to a volume of 100 ml. were measured. The results are given in Table 2 below :-

Table 2.

Nonex g. per 100 ml.	<u>Optical density 2.5 mg. SO<sub>4</sub></u>	
	1	2
0.01	0.192	0.188
0.001	0.199	0.195
0.0001	0.182	0.175
0.00001	0.178	0.176
Nil	0.171	0.169

The stability of the precipitate at concentrations of 0.001 g. Nonex per 100 ml. and above was very good and, therefore, it was decided to use this concentration in future work. At the 0.0001 g. per 100 ml. level and below, and particularly in water solution only, optical density measurements were found to decrease rapidly due to settling of the barium sulphate precipitate.

There was a marked variation in the optical densities of standard solutions of equivalent concentration, although the suspensions once prepared remained in stable suspension. In an effort to overcome this variation it was decided to investigate the use of solid barium chloride as precipitant.

2.2.2. The use of solid barium chloride as precipitant.

In order to eliminate errors due to an excessive variation in particle size, solid Analar barium chloride dihydrate was sieved to give crystals of particle size 0.251 mm. to 0.124 mm.

2. THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID (Contd.)

2.2. Experimental (Contd.)

2.2.2. The use of solid barium chloride as precipitant (Contd.)

Suitable aliquots of standard sulphate solution were transferred to 100 ml. graduated flasks together with 40 mg. of phosphoric acid and 1 ml. of 0.1% Nonex solution. The solutions were diluted to about 20 ml. 0.2 g. of solid barium chloride was added to each flask and the flask contents were shaken until the barium chloride dissolved. The volume was then made up to 100 and the optical density measured. The results are given in Table 3 below :-

Table 3.

<u>mg. SO<sub>4</sub></u>	<u>Optical density.</u>
1	0.105
2	0.232
3	0.367
4	0.479
5	0.572

To eliminate errors arising from slight departures from a volume of 20 ml. prior to adding the solid barium chloride the volume was made up to 100 ml. A standard curve was then prepared using the method as described fully in the appendix; Appendix 1. The results obtained are given in Table 4 below :-

Table 4.

<u>mg. SO<sub>4</sub></u>	<u>Optical density.</u>
0.5	0.053
1.0	0.103
1.5	0.129
2.0	0.205
2.5	0.250
3.0	0.320
3.5	0.358
4.0	0.411
4.5	0.473
5.0	0.495

These results show a linear relationship between sulphate concentration and optical density between 0.5 mg. and 5.0 mg. SO<sub>4</sub>.

The effect of particle size of barium chloride on precipitation was further investigated. For this purpose Analar barium chloride was sieved to give a sufficient amount of the following particle size ranges:-

2.057	-	1.405 mm.
1.405	-	1.003 mm.
1.003	-	0.500 mm.
0.500	-	0.251 mm.
0.251	-	0.124 mm.
0.124	-	0 mm.

Duplicate determinations were then carried out using 2.0 mg. of standard sulphate in the test as described in the appendix, Appendix 1, but replacing Analar barium chloride with prepared material of particle size ranges given above. The results of the determinations are given in Table 5 :-

2. THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID (Contd.)

2.2. Experimental (Contd.)

2.2.2. The use of solid barium chloride as precipitant (Contd.)

Table 5.

<u>Particle size - mm.</u>	<u>Optical density</u> <u>2.0 mg. SO<sub>4</sub> present.</u>	
2.057 - 1.405	0.197	0.195
1.405 - 1.003	0.175	0.180
1.003 - 0.500	0.193	0.190
0.500 - 0.251	0.165	0.170
0.251 - 0.124	0.211	0.210
0.124 - 0	0.130	0.128

The particle size was seen to be clearly important in the test and capable of markedly affecting the final optical density. However, the original Analar barium chloride from which the fractions were obtained gave optical density readings close to that given by the 0.251 - 0.124 mm. fraction. This was found to be true of a number of samples of Analar barium chloride examined. A typical particle size analysis of a satisfactory Analar barium chloride is given below in Table 6:-

Table 6.

<u>Particle size - mm.</u>	<u>%</u>
> 2.057	Nil
2.057 - 1.405	0.3
1.405 - 1.003	0.6
1.003 - 0.500	14.7
0.500 - 0.251	68.6
0.251 - 0.124	15.0
< 0.124	0.8

2.2.3. Effect of acid concentration.

The acid concentration has been stressed as being important when precipitating barium sulphate and the addition of hydrochloric acid has been regarded as essential. The effect of excess acidity from added hydrochloric acid was investigated. 3 mg. aliquots of standard sulphate solution were transferred to 100 ml. graduated flasks together with 1 ml. of 0.1% Nonex solution, 40 mg. of phosphoric acid and the required amount of hydrochloric acid. Hydrochloric acid was added in the basis of hydrogen ion concentration and was in addition to that contributed by phosphoric and sulphuric acids. Barium sulphate was precipitated by the addition of solid Analar barium chloride and the optical density was measured. The results are given in Table 7 below:-

Table 7.

<u>mg. H<sup>+</sup> from hydrochloric acid.</u>	<u>mg. H<sup>+</sup> from phosphoric and sulphuric acids.</u>	<u>pH</u>	<u>Optical density</u> <u>3 mg. SO<sub>4</sub> present.</u>
Nil	1.297	2.40	0.311
2.594	1.297	1.60	0.311
6.485	1.297	1.40	0.310
12.97	1.297	1.20	0.330
32.425	1.297	0.85	0.320
64.850	1.297	0.60	0.265
97.275	1.297	0.40	⊠
129.7	1.297	0.30	⊠

⊠ In these cases turbidity developed very slowly over a period



2. THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID (Contd.)

2.2. Experimental (Contd.)

2.2.3. Effect of acid concentration (Contd.)

The results indicated that the use of up to 25 times the hydrogen ion concentration contributed by phosphoric acid and sulphuric acid present did not affect precipitation or the optical density of the barium sulphate suspension. Concentrations in excess of this tended to reduce the optical density of the barium sulphate suspension. On the basis of these results it was decided that the addition of hydrochloric acid was unnecessary and accordingly a calibration curve was prepared appropriate to the omission of additional hydrochloric acid.

2.2.4. Effect of temperature on precipitation.

The effect of temperature on precipitation between 15°C. and 30°C. was determined by carrying out the precipitation of barium sulphate after heating or cooling the solution in a constant temperature bath, prior to adding the solid barium chloride. The relationship between temperature and optical density for a solution containing 3.3 mg. of  $\text{SO}_4^{--}$  is given in Table 8 below:-

Table 8.

<u>Temperature °C.</u>	<u>Optical density</u> <u>3.3 mg. <math>\text{SO}_4^{--}</math> present.</u>	
15	0.303	0.306
20	0.336	0.346
25	0.344	0.332
30	0.364	0.346

The results indicate that a small temperature coefficient exists and that for best results the temperature should be maintained close to the temperature of standardisation. Determinations were normally carried out between 20°C. and 25°C.

2.2.5. Examination of production samples by the proposed method and a comparison of results with the classical gravimetric method for the determination of sulphate.

Prior to introducing the method as a routine procedure six Shift Laboratory Assistants with no previous experience of the method carried out the preparation of standard curves at the concentration levels of 1.0, 2.0, 3.0, 4.0 and 5.0 mg.  $\text{SO}_4^{--}$  using the method described in full in the appendix. One determination only at each level was carried out. The results obtained are given in Table 9 below:-

Table 9.

<u>Analyst</u>	<u>mg. <math>\text{SO}_4^{--}</math></u>				
	1	2	3	4	5
	<u>Optical density</u>				
1	0.108	0.195	0.282	0.400	0.545
2	0.093	0.209	0.299	0.397	0.510
3	0.090	0.197	0.293	0.390	0.495
4	0.102	0.200	0.293	0.426	0.470
5	0.103	0.203	0.331	0.418	0.532
6	0.116	0.209	0.339	0.447	0.526
Average	0.102	0.202	0.306	0.407	0.513
Standard deviation	0.0095	0.00578	0.0231	0.0214	0.0273
Coefficient of variation	9.30%	2.86%	7.55%	5.05%	5.32%

THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID (Contd.)

2.2. Experimental (Contd.)

2.2.5. Examination of production samples by the proposed method and a comparison of results with the classical gravimetric method for the determination of sulphate (Contd.)

The average coefficient of variation of 6.01% for the whole series was considered to be satisfactory for this particular determination. From the average results given in the Table 9 a calibration curve was prepared. The curve reproduced in the appendix, Figure 1, shows excellent linear relationship between optical density and  $SO_4^{--}$  concentration, and agrees well with that obtained during the preliminary investigation of the method.

At this stage the method was put into routine use and for several weeks checks on random samples were made using the classical gravimetric technique of precipitation as barium sulphate and the rapid gravimetric technique previously used as a routine method. The results are given in Table 10 below :-

Table 10.

<u>Sample</u>	<u>Classical gravimetric.</u> <u>% <math>SO_4^{--}</math></u>	<u>Rapid gravimetric.</u> <u>% <math>SO_4^{--}</math></u>	<u>Turbidimetric</u> <u>% <math>SO_4^{--}</math></u>
O	3.36	4.01	3.44
O3	0.96	1.01	0.92
SA	2.58	2.85	2.52
F6	2.51	2.43	2.62
RAVI	1.79	2.78	1.63
RAVB	0.94	1.48	0.72
RAVO	0.43	1.08	0.34
1	2.06	2.30	1.98
2	3.87	4.19	3.79
3	0.42	1.00	0.30

Further comparisons made on samples taken at random during the first few months after putting the turbidimetric method into routine use are given in Table 11 below:-

Table 11.

<u>Classical gravimetric</u> <u>% <math>SO_4^{--}</math></u>	<u>Turbidimetric</u> <u>% <math>SO_4^{--}</math></u>	<u>Difference</u> <u>%</u>	<u>Classical gravimetric</u> <u>% <math>SO_4^{--}</math></u>	<u>Turbidimetric</u> <u>% <math>SO_4^{--}</math></u>	<u>Difference</u> <u>%</u>
4.90	5.20	- 0.30	6.35	6.70	- 0.35
2.44	2.80	- 0.36	2.80	2.90	- 0.10
2.81	2.90	- 0.09	4.40	4.50	- 0.10
4.43	4.45	- 0.02	4.90	5.20	- 0.30
3.20	3.20	+ 0	3.20	3.20	+ 0
3.30	3.30	+ 0	3.30	3.30	+ 0
2.91	2.65	+ 0.26	2.20	2.60	- 0.40
3.70	3.90	- 0.20	2.90	2.60	- 0.30
2.15	2.00	+ 0.15	2.70	2.90	- 0.20
0.86	1.02	- 0.16	3.80	3.90	- 0.10
1.02	1.20	- 0.18	3.15	3.10	+ 0.05
3.70	3.70	+ 0	4.20	4.10	+ 0.10

A comparative plot of the results given in Table 10 is given in the appendix, Figure 2. An inspection of this graph indicates the wide divergence of the results obtained by the rapid gravimetric method from those obtained by classical gravimetric method; good agreement is evident between the classical gravimetric method and the turbidimetric method. These observations are confirmed by the numerical calculation of the statistical t test for measuring the comparison of slopes. Results are tabulated in Table 12:-

2. THE DETERMINATION OF TOTAL SULPHATE IN WET PROCESS PHOSPHORIC ACID (Contd.)

2.2. Experimental (Contd.)

2.2.5. Examination of production samples by the proposed method and a comparison of results with the classical gravimetric method for the determination of sulphate (Contd.)

Table 12.

<u>Method</u>	<u>t value</u>	<u>t crit (9 DF)</u>
Rapid gravimetric	3.350	3.25
Turbidimetric	0.105	3.25

The t value obtained for the rapid gravimetric method exceeds the critical value of t, thus indicating that the slope differs from unity by more than a reasonable multiple of the standard deviation.

The small t value obtained for the turbidimetric method is satisfactorily small and indicates that the slope of the line is acceptably close to 1.

2.3. Conclusions.

The turbidimetric method developed for the determination of sulphate ion in phosphoric acid is both rapid and of sufficient accuracy for routine control use.

It has been shown to have a number of advantages over the rapid gravimetric method for the determination of sulphate particularly with respect to speed and accuracy. A determination in duplicate can readily be carried out in 10 minutes.

The coefficient of variation of about 6% is considered satisfactory for the method described and the statistical t tests shows it to be far superior to the rapid gravimetric method previously employed.

2.4. Summary.

The classical method of precipitation as barium sulphate is an accurate and satisfactory method for determining sulphate in phosphoric acid providing acidity and sulphate concentrations are satisfactory. The method, however, is lengthy and requires careful manipulation.

A more rapid variation of the classical method had been used for some years but although an analysis could be completed in 75 to 90 minutes it was found to be characterised by low accuracy and poor reproducibility.

A number of methods for the determination of sulphate were considered, but only a turbidimetric method was investigated further since phosphate ion interference in other methods appeared difficult to overcome.

The proposed method is suitable for the rapid routine determination of sulphate in phosphoric acid solutions. Comparison of the method with the classical gravimetric procedure on a range of process samples indicated that it is more precise than the rapid gravimetric procedure previously employed.

### 3. THE DETERMINATION OF THE DILUTION RATIO OF WET PROCESS PHOSPHORIC ACID SLURRY.

#### 3.1. Introduction.

A number of methods were available for the determination of the dilution ratio of phosphoric acid slurry. All the methods available involved the physical separation of solid and liquid followed by chemical analysis of the separated entities, or the careful drying of the solid, or the determination of the gypsum content of the wet solid.

All these methods possess the great disadvantage that they are lengthy and require constant operator attention during the test. A single analysis may take up to 1½ hours and unless conditions are carefully controlled, particularly when drying of gypsum is resorted to, the results may not be of satisfactory accuracy.

In an effort to reduce the time taken for analysis without loss of accuracy some thought was given to an alternative method and experimental work confirmed that a physical separation of solid and liquid by centrifuging enabled the accurate determination of the dilution ratio to be carried out.

#### 3.2. Experimental.

Three methods were available for the determination of the dilution ratio of wet process phosphoric acid slurry. The three methods may be described as the physical method, the  $P_2O_5$  method and the acidity method. Brief details of these methods are as follows:-

##### 3.2.1. Physical method.

100 ml. of the slurry is transferred to a tared weighing bottle and weighed. The slurry is then washed into a Hartley funnel and filtered under suction using a No. 30 Whatman filter paper. The residue is then washed with distilled water until free from phosphoric acid, transferred to a tared porcelain or silica dish and dried at 60°C. for a period of 12-14 hours. The weight of dry gypsum is then calculated and the dilution ratio is obtained from the following expression:-

$$\text{Dilution ratio} = \frac{\text{Weight of acid}}{\text{Weight of dry gypsum}}$$

##### 3.2.2. $P_2O_5$ method.

10 g. of the slurry is weighed and transferred to a 500 ml. graduated flask and diluted to 500 ml. with distilled water. The contents of the flask are mixed well and a portion filtered through a dry No. 30 Whatman filter paper. A suitable aliquot is then analysed for  $P_2O_5$  content by the differential spectrophotometric vanadophosphomolybdate method.

A portion of the original slurry is then filtered and 6 g. of the clear filtrate is transferred to a 500 ml. graduated flask and diluted to 500 ml. with distilled water. The contents of the flask are mixed well and the  $P_2O_5$  content of a suitable aliquot is determined by the vanadophosphomolybdate spectrophotometric method.

Alternatively the  $P_2O_5$  contents are determined by the Wilson quinoline phosphomolybdate method.

The dilution ratio is then calculated from the following expression

$$\text{Dilution ratio} = \frac{\% P_2O_5 \text{ in slurry}}{\% P_2O_5 \text{ in acid} - \% P_2O_5 \text{ in slurry.}}$$

3. THE DETERMINATION OF THE DILUTION RATIO OF WET PROCESS PHOSPHORIC ACID SLURRY. (Contd)

3.2. Experimental. (Contd).

3.2.3. Acidity method

15 g. of slurry is weighed, transferred to a 500 ml. graduated flask and diluted to 500 ml. with distilled water. The contents of the flask are mixed well and a portion filtered through a dry No. 30 Whatman filter paper. A suitable aliquot is then analysed for acid content by titration with standard alkali using mixed methyl red bromocresol green indicator pH 4.5 and the acid content of the slurry is calculated. A portion of the original slurry is then filtered and 10 g. of the clear filtrate is weighed and transferred to a 500 ml. graduated flask. The contents of the flask are mixed well and the acid content of a suitable aliquot is then determined by titration with standard alkali. The acid content of the liquid fraction of the slurry is then calculated. The dilution ratio is then obtained from the following expression.

$$\text{Dilution ratio} = \frac{\% \text{H}_2\text{PO}_4 \text{ in slurry}}{\% \text{H}_3\text{PO}_4 \text{ in acid} - \% \text{H}_2\text{PO}_4 \text{ in slurry.}}$$

Experience of the three methods suggested that the  $\text{P}_2\text{O}_5$  method was the most accurate but in fact that requiring the longest operator time for the completion of a determination. This method was accepted as a basis for comparison of other methods, but in addition careful determinations carried out by the physical method were also included as a basis of standardisation for the new method.

3.2.4. Extension of the physical method using isopropanol/ether extraction.

Sometime after this standardisation had been made based on the  $\text{P}_2\text{O}_5$  method the isopropanol/ether method for the determination of free water in gypsum filter cake was introduced, and it was found that this could be extended to give a method suitable for the determination of dilution ratio. A suitable quantity of sample was transferred to a sintered glass crucible of average pore size 20-30 microns and excess acid removed under suction. The gypsum residue was then washed with isopropanol followed by ether as described in the method for the determination of free water in gypsum filter cake. The dilution ratio was then calculated from the following expression

$$\text{Dilution ratio} = \frac{\text{Weight of acid}}{\text{Weight of gypsum}}$$

3.2.5. Centrifugal method.

After considering the possibility of a centrifugal separation of solid and liquid little experimental work was required to confirm that such a separation was rapid and yielded reproducible results.

The speed of separation was determined by transferring portions of slurry to four 10 ml. centrifuge tubes and placing in centrifuge baskets in a I.L.S.E. "Super-Minor" Centrifuge. Centrifuging was then carried out for intervals of 2.5 minutes at 4,500 r.p.m. Typical results from a series of determinations are given in Table 13 :-

3. THE DETERMINATION OF THE DILUTION RATIO OF WET PROCESS PHOSPHORIC ACID SLURRY (Contd.)

3.2. Experimental (Contd.)

3.2.5. Centrifugal method (Contd.)

Table 13.

Time Minutes.	Sample 1.		Sample 2.	
	Vol. liquid. ml.	vol. sediment. ml.	vol. liquid. ml.	vol. sediment. ml.
2.5	3.8	5.1	4.2	5.7
5.0	3.9	5.0	4.3	5.6
7.5	4.0	4.9	4.5	5.4
10.0	4.0	4.9	4.5	5.4
15.0	4.0	4.9	4.5	5.4
20.0	4.0	4.9	4.5	5.4

The experiments showed that centrifuging for a period of ten minutes was sufficient to ensure maximum separation of solid and liquid and future tests were carried out for a period of ten minutes at 4,500 r.p.m.

To examine the proposed method further samples were obtained from the production unit having varying dilution ratios. Initially the range of samples was limited. Therefore, a number of the samples were adjusted to give intermediate dilution ratios by the addition of separated phosphoric acid or gypsum. Sufficient sample of each dilution ratio was prepared to enable the dilution ratio to be determined by the physical method, the  $P_2O_5$  method and the proposed centrifuge method.

One of the difficulties encountered in the analysis of slurries is that of obtaining homogeneous samples and it was found necessary to employ vigorous mechanical stirring to prevent the separation of solid and liquid prior to transferring samples to centrifuge tubes or weighing bottles.

The dilution ratios of the six prepared samples were determined by the physical method and the  $P_2O_5$  method as previously described. The centrifuge method was then carried out as follows:-

Four graduated 10 ml. centrifuge tubes were filled with the previously well mixed slurry and the tubes were transferred to a M.S.E. "Super-Minor" Centrifuge. The tubes were then centrifuged for a period of ten minutes at 4,500 r.p.m. and after being removed from the centrifuge the volumes of solid and liquid were measured. The dilution ratio was expressed as

$$\text{Dilution ratio} = \frac{\text{volume of liquid}}{\text{volume of solid}}$$

The results of the comparative determinations by the three methods are given in Table 14 below:-

Table 14.

Sample	Physical method.	$P_2O_5$ method.	Centrifuge method.
A	1.59	1.49	0.52
B	2.19	2.09	1.00
C	3.22	3.01	1.67
D	4.03	3.88	2.14
E	4.32	3.97	2.32

In order to use the centrifuge method it was essential to establish some correlation between the methods at different levels of dilution ratio.

3. THE DETERMINATION OF THE DILUTION RATIO OF WET PROCESS PHOSPHORIC ACID SLURRY (Contd.)

3.2. Experimental (Contd.)

3.2.5. Centrifugal method (Contd.)

A graphical plot of dilution ratio by the  $P_2O_5$  method and physical method versus centrifuge method was made. The graph is reproduced in the appendix, Figure 3. From this it can be seen that a straight line relationship exists and that it is a simple matter to convert dilution ratios obtained by the centrifuge method to those by the  $P_2O_5$  method and the physical method.

The reproducibility of the three methods already described was then investigated. Five plant samples were obtained and examined by the physical method, the  $P_2O_5$  method and the centrifuge method for dilution ratio. Replicate determinations were carried out and the standard deviation and coefficient of variation for the three methods were calculated. The results are given in Table 15 below:-

Table 15.

Number of sample	Number of determinations	<u>Physical method.</u>		<u><math>P_2O_5</math> method.</u>		<u>Centrifuge method.</u>	
		Stan- dard devi- ation	Coeffi- cient of vari- ation %	Stan- dard devi- ation	Coeffi- cient of vari- ation %	Stan- dard devi- ation	Coeffi- cient of vari- ation %
1	17	0.037	2.52	0.052	3.74	0.078	5.00
2	7	0.130	8.38	0.004	2.86	0.045	2.90
3	4	0.045	2.58	0.146	9.24	0.071	4.23
4	5	0.039	2.09	0.228	7.71	0.112	6.50
5	4	0.251	11.15	0.041	2.01	0.126	6.56
Average		0.100	7.32	0.074	5.11	0.088	5.04

After introducing the centrifuge method it was found that the technique of transferring slurry to the centrifuge improved and a series of thirty four tests were carried out on the same sample. This sample was continuously stirred by a mechanical stirrer while the samples were removed. The standard deviation and coefficient of variation were calculated from the results obtained. These together with other pertinent data are given below in Table 16:-

Table 16.

<u>No. of deter- minations.</u>	<u>Average.</u>	<u>Maximum.</u>	<u>Minimum.</u>	<u>Standard deviation.</u>	<u>Coefficient of variation. %</u>
34	1.79	1.86	1.72	0.0416	2.32

With a further method available; described in Section 3.2.4., suitable for calibration purposes, arrangements were made to obtain a further series of production samples and examine them using this and the  $P_2O_5$  method together with the centrifuge method.

Each dilution ratio by the  $P_2O_5$  method and isopropanol/ether method was carried out in duplicate, those by the centrifuge method were carried out in quadruplicate. The average results obtained on seven samples with dilution ratios between 1.0 and 4.0 are given in Table 17:-

3. THE DETERMINATION OF THE DILUTION RATIO OF WET PROCESS PHOSPHORIC ACID SLURRY (Contd.)

3.2. Experimental (Contd.)

3.2.5. Centrifugal method (Contd.)

Table 17.

<u>P<sub>2</sub>O<sub>5</sub> method.</u>	<u>Isopropanol/ether method.</u>	<u>Centrifuge method.</u>
0.99	1.02	0.21
1.42	1.55	0.53
1.94	2.04	0.80
2.44	2.53	1.12
2.72	2.92	1.45
3.55	3.35	1.76
4.03	3.96	2.12

These results again show that a straight line relationship exists between the centrifuge method, the P<sub>2</sub>O<sub>5</sub> method and the isopropanol/ether method respectively, and the second calibration curve differs only slightly from that originally obtained. The results are shown graphically in the appendix, Figure 3.

3.3. Conclusions.

The method described employing centrifugal separation of solid and liquid is a rapid and accurate method for the determination of dilution ratio. The accuracy is equal to, if not better than, that of previous methods and the time required for a determination is 15 minutes of which only five minutes is operator time. Using a mechanical centrifuge accommodating four tubes it is possible to carry out four single determinations, two determinations in duplicate or one determination in quadruplicate within 15 minutes.

The work has indicated that a linear relationship exists between the results obtained by the centrifuge method and other methods at all levels of dilution ratio likely to be encountered in the production of wet process phosphoric acid.

3.4. Summary.

Normal methods for the determination of dilution ratio involving separation of liquid and solid phases and consequent chemical analyses are described and these methods are compared with a method developed utilising solid-liquid separation by centrifuging. The centrifuge method is shown to be more accurate and rapid than methods previously employed and to be very suitable for routine process control of the dilution ratio of wet process phosphoric acid slurries.

4. THE DETERMINATION OF FREE WATER AND COMBINED WATER IN GYPSUM FILTER CAKE.

4.1. Introduction.

A number of methods have been described for the determination of free water in gypsum filter cake. The most widely used are those involving oven drying at controlled temperatures or azeotropic distillation using a suitable organic liquid. Both methods had been used in our Laboratories but neither had proved very satisfactory. Loss of water of crystallisation occurred by oven drying even at relatively low temperatures. At 75°C. a temperature recommended for this determination, drying was found to progress to the hemihydrate stage.

A method similar to that described by Haral and Talmi (2) using azeotropic distillation with xylene had been used for some time to determine total water in filter cake samples, but an extension of the method using benzene to determine free water was unsuccessful, and the apparent free water content increased with time of distillation.



4. THE DETERMINATION OF FREE WATER AND COMBINED WATER IN GYPSUM FILTER CAKE (Contd.)

4.1. Introduction (Contd.)

In view of these difficulties and in order to reduce the time required for a determination it was decided to investigate the use of organic solvents for the removal of free water from gypsum, a method previously used by the Author for the determination of free water in other heat sensitive hydrates.

4.2. Experimental.

4.2.1. Selection of organic solvents.

A number of organic solvents miscible with water have been suggested as suitable for removing free water from hydrates. However, some hydrates with loosely bound water lose their hydrate water in addition to free water when treated with organic solvents. Two solvents, ethanol and isopropanol showed most promise in preliminary tests and both were readily available and relatively inexpensive. Further work was, therefore, carried out with these solvents.

An examination of the solubility of gypsum in ethanol and isopropanol showed that some dissolution of gypsum in ethanol was likely to take place whereas with isopropanol solubility effects could be neglected.

Experiments were carried out on a number of samples which appeared to have widely varying free water contents by an examination of their physical condition. The samples obtained from a wet process phosphoric acid plant in which the acid concentration did not exceed 40%  $H_3PO_4$  and the reaction temperature did not exceed  $80^\circ C$ . were considered to be free from hemihydrate; a supposition supported by microscope examination of samples which did not detect hemihydrate crystals in any of the samples.

In view of this it was considered that an examination of the residual gypsum for combined water content after treatment with organic solvents would be sufficient evidence of removal of free water. Preliminary examination of a number of samples indicated that at least 30% of free water in 10 g. of filter cake could be removed by three washings with 15 ml. aliquots of isopropanol. However, the removal of all the isopropanol by the passage of air through the sample to effect volatilisation was of relatively long duration and it was found that a further treatment of the residue with ether readily removed the isopropanol. The ether remaining in the residue was then rapidly removed, due to its greater volatility, by a stream of air passed through the sample for about ten minutes.

4.2.2. Examination of plant samples.

Eleven samples selected for their variable free water contents were examined as described above for free water content. The details of the method are described more fully in the appendix, Appendix 2. Portions of the sample were also examined for total water, using an azeotropic distillation method with xylene. Hydrate water remaining in the samples after removal of free water with isopropanol and ether was determined by ignition at  $500^\circ C$ . Results are given in Table 18 :-

THE DETERMINATION OF FREE WATER AND COMBINED WATER IN GYPSUM FILTER CAKE (Contd.)

4.2. Experimental (Contd.)

4.2.2. Examination of plant samples (Contd.)

Table 18.

<u>Free H<sub>2</sub>O %.</u> <u>Isopropanol/ ether method.</u>	<u>Hydrate H<sub>2</sub>O %.</u> <u>Ignition at 500° C.</u>	<u>Total H<sub>2</sub>O %.</u>	<u>Total H<sub>2</sub>O %.</u> <u>Azeotropic distillation.</u>	<u>Difference.</u>
2.6	21.0	23.6	24.0	± 0.4
9.2	21.4	30.6	30.6	- 0
13.7	21.3	35.0	35.3	± 0.3
14.0	21.2	35.2	35.2	- 0
15.2	20.8	36.0	36.2	+ 0.2
20.2	21.1	41.3	41.6	+ 0.3
20.7	21.6	42.3	42.4	+ 0.1
21.2	20.8	42.0	42.2	± 0.2
21.7	20.7	42.4	42.4	- 0
24.2	21.1	45.3	45.4	+ 0.1
25.2	20.9	46.1	45.8	- 0.3

As can be seen from the table above free water was found to vary from 2.6% to 25.2% in the samples examined. Hydrate water contents of all samples were close to the theoretical of 20.93% ranging, from 20.7% to 21.6% with an average of 21.08%. The results for hydrate water content were considered sufficient evidence to support the assumption of complete removal of free water by the isopropanol/ether extraction procedure.

4.2.3. Extension of the proposed method to the determination of dihydrate and hemihydrate in phosphoric acid slurry.

The extension of the method to be described was found applicable to the determination of dihydrate and hemihydrate in wet process phosphoric acid slurry.

Under certain conditions it is well known that calcium sulphate dihydrate and hemihydrate will coexist in strong phosphoric acid solution. The amounts of the individual hydrates are determined as follows:-

About 6 g. of the slurry is transferred to a sintered silica crucible of average pore size 20-30 microns and excess phosphoric acid is removed under suction. The residue in the crucible is washed with three successive 15 ml. portions of isopropanol followed by three successive 15 ml. portions of ether. The ether is removed by sucking air through the crucible and residue for about 10 minutes and the residue is weighed. The crucible and its contents are ignited for a period of thirty minutes at 500° C. and then cooled in a desiccator and reweighed. Complete dehydration to anhydrous calcium sulphate takes place and the hemihydrate content is calculated from the following expression

$$100 - \frac{((\% \text{ combined H}_2\text{O} - 6.2) 100)}{14.72} = \% \text{ hemihydrate}$$

It follows that 100 - % hemihydrate = % dihydrate.

4.3. Conclusions.

The method developed for the determination of free moisture in gypsum filter cake is both rapid and accurate, a complete determination requiring only 20 minutes. Filtration efficiency is readily checked by this method. The accuracy of the method is considered to be sufficiently satisfactory to enable it to be used for plant control purposes.

4. THE DETERMINATION OF FREE WATER AND COMBINED WATER IN GYPSUM FILTER CAKE (Contd.)

4.3. Conclusions (Contd.)

The method has been in use in our Laboratories for nearly two years and has been found to give good results in the hands of Control Laboratory Assistants.

4.4. Summary.

Most of the methods described for the determination of free water in gypsum suffer from some disadvantage. Some are of doubtful accuracy while others require a long period of time for completion.

In an effort to overcome these disadvantages and to obtain an accurate and rapid method suitable for routine control the method of extraction of free water with isopropanol and ether was investigated.

The method has been found to be very suitable for routine control and is both rapid and accurate; in addition it requires very little manipulative work. The reliability and accuracy of the method was not determined by comparison with a standard method since previous experience indicated that other methods available were of variable reliability.

Experience with the proposed method shows it to be the most satisfactory of the rapid control methods available for the determination of free water in gypsum filter cake.

6. GENERAL SUMMARY.

For the adequate control of wet process phosphoric acid plants rapid and accurate methods of analysis are required. Of importance in process control are the sulphate content of phosphoric acid, the dilution ratio of phosphoric acid-gypsum slurry, the water soluble phosphate content of phosphoric acid and the free water content of gypsum filter cake.

A critical examination of the traditional analytical procedures was considered to be desirable and the results of this work are described in the present paper.

Methods for the determination of sulphate in phosphoric acid, free water in gypsum filter cake and the dilution ratio of phosphoric acid-gypsum slurries have been examined and more rapid and accurate methods have been developed than those previously employed. Where accurate methods exist they have been used as standards for assessing the accuracy or value of the more rapid methods evolved. A statistical interpretation of results and comparisons has been given where applicable and statistically the methods developed and applied to routine control analysis have been shown to be satisfactory.

6. ACKNOWLEDGMENT.

Acknowledgment is made to the Directors of West Norfolk Fertilisers for permission to present this Paper. Also to Assistants who carried out much of the experimental work and without whose care and interest the work could not have been concluded successfully.

7. REFERENCES.

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## APPENDIX 1.

### DETERMINATION OF TOTAL SULPHATE IN PHOSPHORIC ACID.

#### PRINCIPLE.

Sulphate is determined turbidimetrically as barium sulphate by means of the Unicam Spectrophotometer. Optical density is measured at a wavelength of 470m $\mu$  using the blue filter.

#### REAGENTS.

Nonex 501 B.D.H.	0.1% solution in distilled water.
Barium chloride dihydrate.	Analar Solid, Particle size 60-100 mesh B.S.S.

#### PROCEDURE.

Accurately weigh 10g. of the previously filtered phosphoric acid and transfer to a 100ml. graduated flask. Dilute to 100ml. with distilled water, mix well and transfer an aliquot of 10mls. to a 100ml. graduated flask, dilute to 100ml. with distilled water and mix well. Transfer 1ml. of Nonex solution followed by 10mls. of the dilute sample solution to a 100ml. graduated flask, dilute to 100mls. with distilled water and mix well. Add exactly 0.2g. of the solid barium chloride to the prepared solution and mix well until all the barium chloride is dissolved. Determine the optical density of the suspension on the Unicam SP.600 at 470m $\mu$  with the blue filter in position using as blank 1ml. of Nonex solution diluted to 100mls. with distilled water and 0.2g. of solid barium chloride. Calculate the sulphate content by reference to the standard graph.

#### NOTE 1.

The temperature of the blank and test solutions should be constant and the same as the solutions used in the preparation of the standard graph. A temperature of 20°C. is recommended.

#### NOTE 2.

Shaking for approximately one minute is sufficient to dissolve the solid barium chloride. The optical density reading should be taken as soon as possible after solution of the barium chloride in order to minimise precipitation of barium sulphate.

#### NOTE 3.

It is essential to use absolutely clean flasks for the development of the final turbidity. The flasks should be cleaned after use using a 0.1N. solution of E.D.T.A. containing a slight excess of ammonia. The flasks should be thoroughly washed with distilled water prior to use.

## APPENDIX 2.

### DETERMINATION OF FREE AND COMBINED WATER IN GYPSUM FILTER CAKE.

#### PRINCIPLE.

Free water in the sample is determined gravimetrically by the loss in weight on leaching with isopropanol and ether.

#### REAGENTS.

Isopropanol.  
Ether (Note 1).

#### PROCEDURE.

Prepare a No. 3. porosity sintered glass crucible (Note 2) by washing with distilled water, three 15ml. portions of isopropanol and three 15ml. portions of ether. Suck air through the crucible, by means of the vacuum pump, for five minutes, remove the crucible from the vacuum system and wipe with a clean dry cloth.

Accurately weigh the prepared crucible and transfer to it 5g. of gypsum filter cake. Pass three 15ml. portions of isopropanol through the sample under slight suction, sucking dry between additions. Remove isopropanol by washing with three 15ml. portions of ether, sucking dry between additions and then remove ether under full suction for fifteen minutes. Remove the crucible and its contents from the vacuum system, wipe with a clean dry cloth and reweigh.

#### CALCULATION.

$$\frac{\text{Loss in weight} \times 100}{\text{Weight of sample}} = \% \text{ free water.}$$

Accurately weigh 1-3g. of the cake previously dried with isopropanol and ether into a previously weighed platinum or silica crucible. Transfer the crucible to a suitable muffle furnace and ignite at a temperature between 500 C. and 800 C. for one hour. Remove from the furnace, cool in a desiccator and reweigh.

#### CALCULATION.

$$\frac{\text{Loss in weight} \times 100}{\text{Weight of sample}} = \% \text{ combined water.}$$

#### NOTE 1.

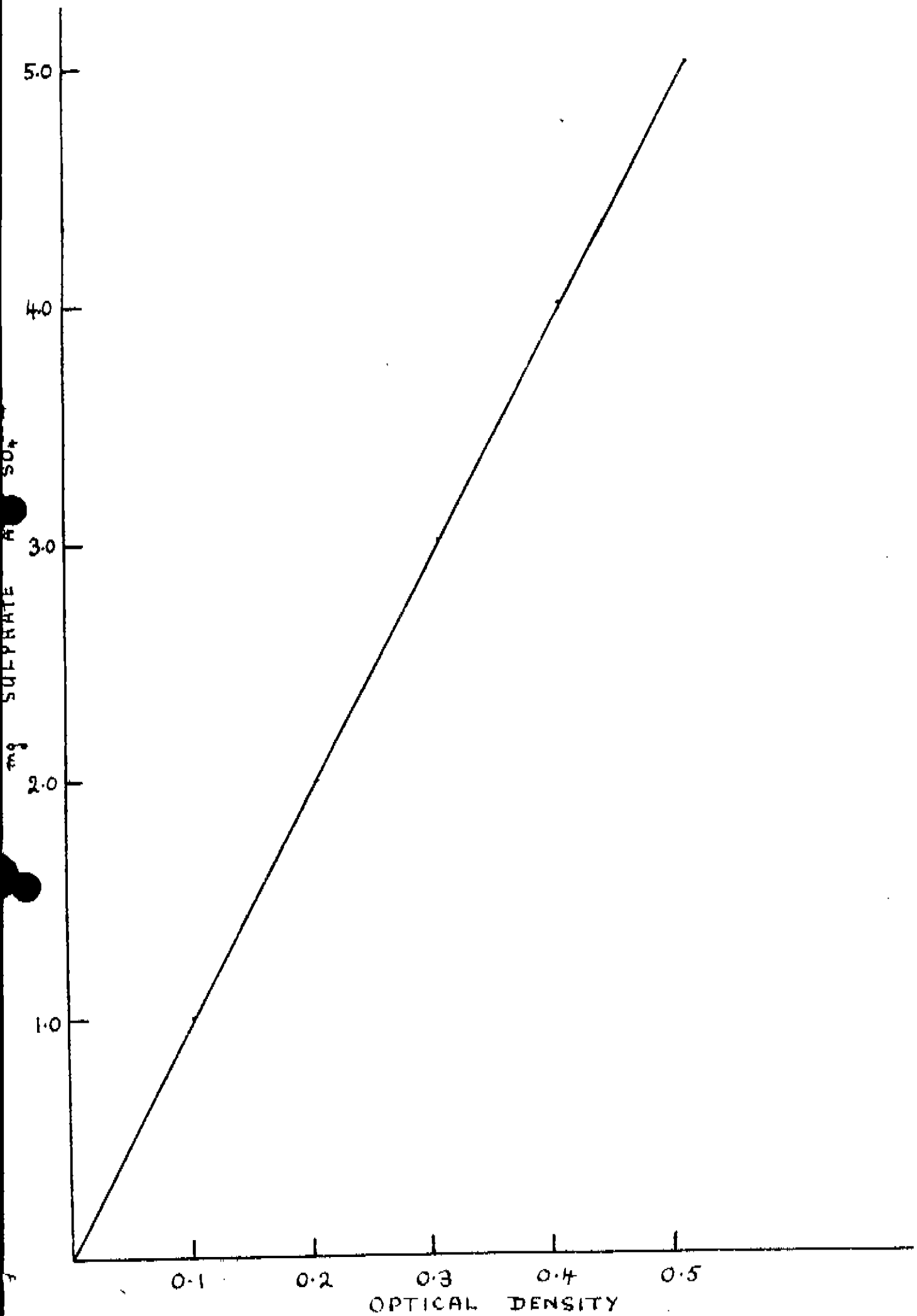
Care must be taken when using ether in the Laboratory. All naked lights should be extinguished.

#### NOTE 2.

Alternatively a sintered silica crucible may be used in which case the combined water is then determined by igniting the contents of the crucible instead of transferring to a platinum crucible.

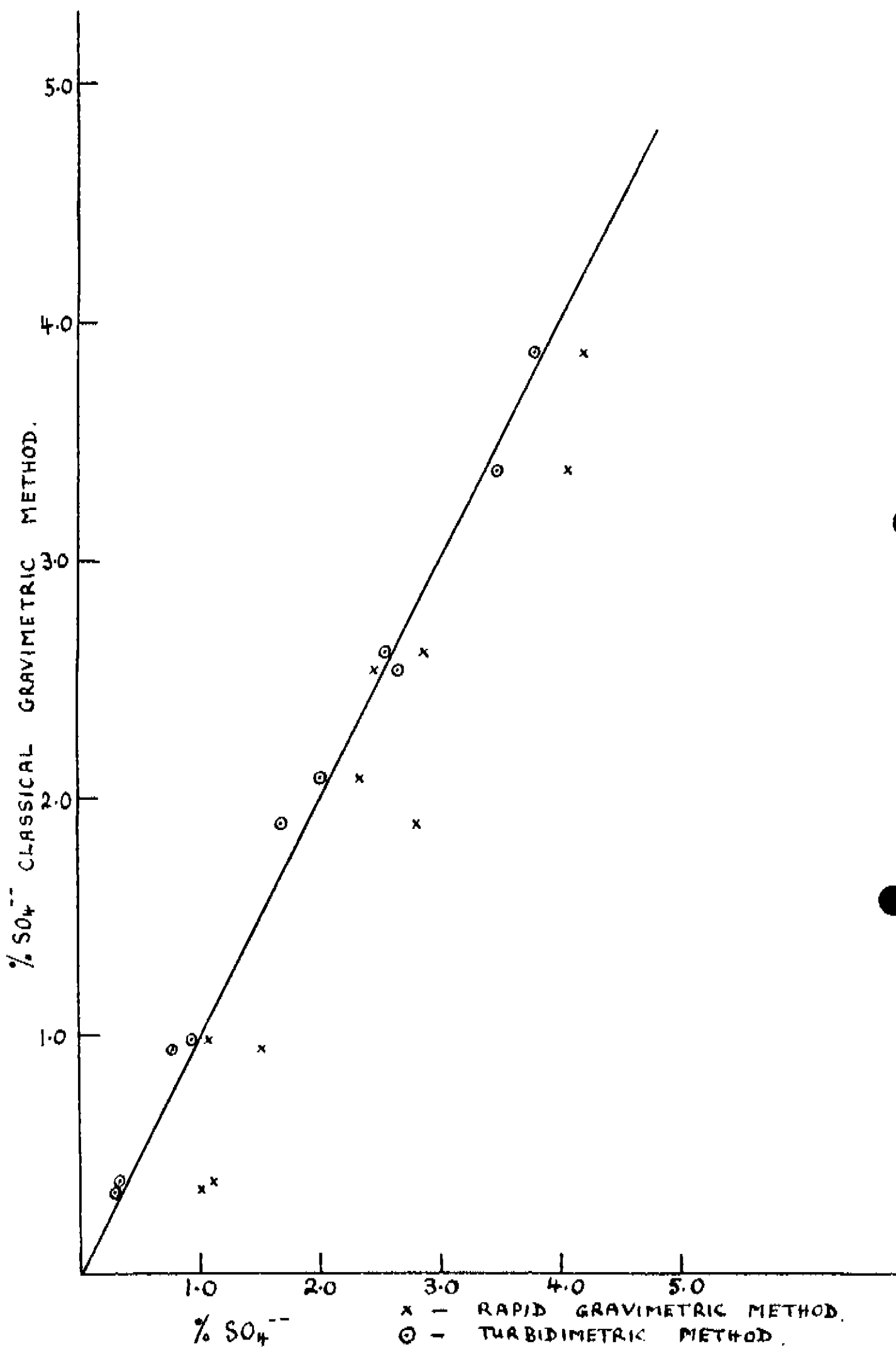
# FIGURE 1.

DETERMINATION OF TOTAL SULPHATE IN PHOSPHORIC ACID.  
CALIBRATION GRAPH.



# FIGURE 2.

DETERMINATION OF TOTAL SULPHATE IN PHOSPHORIC ACID.  
COMPARISON OF METHODS.



# FIGURE 3.

DETERMINATION OF THE DILUTION RATIO OF PHOSPHORIC  
ACID SLURRIES.  
CALIBRATION GRAPH.

