

## Analytical Determination of Inorganic Bound Phosphorus in the Presence of Alkylated Phosphorus

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A method has been worked out for the determination of P(III) and P(V) separately from alkylated phosphorus. This analysis makes it possible to follow the degree of conversion in syntheses of alkylated phosphorus compounds from  $\text{PCl}_3$ ,  $\text{POCl}_3$ , or other phosphorus compounds and, *e.g.*, halogenated hydrocarbons.

In the preparation of alkylated phosphorus compounds *via* the Clay-Kinnear-Perren complexes  $\text{RPCl}_3\text{AlCl}_4$ , we have used as starting materials  $\text{AlCl}_3$ ,  $\text{PCl}_3$ , and  $\text{CH}_3\text{Cl}$  or  $\text{C}_2\text{H}_5\text{Cl}$ , forming  $\text{RPCl}_3\cdot\text{AlCl}_4$  and  $\text{RPCl}_3\text{Al}_2\text{Cl}_7$ .<sup>1</sup> In these complex reaction mixtures, there are at least five different compounds made up of five elements. Ordinarily, slightly modified analytical methods may be used to estimate the composition of the mixture and the degree of conversion, but the errors are relatively high and make the results uncertain. A method of measuring the degree of conversion may be based on the determination of phosphorus in  $\text{PCl}_3$  separately from the phosphorus in the alkylated phosphorus complexes.

The alkylated phosphorus complexes with one or two moles of  $\text{AlCl}_3$  when hydrolyzed in water form an alkylsubstituted phosphoric acid while  $\text{PCl}_3$  gives  $\text{H}_3\text{PO}_3$ . Experiments with such alkylphosphoric acids formed by hydrolysis of pure phosphorus complexes and pure  $\text{RPOCl}_2$  have shown that it is possible to keep these acids unchanged when oxidizing  $\text{H}_3\text{PO}_3$  quantitatively to  $\text{H}_3\text{PO}_4$ . Therefore one can determine both the total phosphorus in the reaction mixtures and, in an aliquot sample, the phosphorus in  $\text{PCl}_3$  as phosphate, and so obtain a good estimate of the degree of conversion.

### METHODS

*Preparation of samples.* With these compounds all work must be done in a box with a perfectly dry atmosphere. The samples are filled into microbottles with tight lids and weighed. All samples which are not analyzed immediately must be kept in sealed ampoules.

The sample is treated with 50 ml water in a 300 ml flask with a ground glass stopper in the following manner. The flask with the water is cooled with ice, and the weighing

bottle together with the sample and the lid are placed in the flask, which is immediately sealed with the stopper. The flask is shaken for some minutes and then cooled in an ice bath. It is placed in the bath for one hour and shaken occasionally during that period. The sample solution may now be diluted and handled without special precautions.

1. Determination of the total amount of phosphorus.

a) Catalytic oxidation to phosphoric acid.

*Reagents:* Sulphuric acid,  $d = 1.84$ , analytical grade; nitric acid,  $d = 1.40$ , analytical grade; perchloric acid,  $d = 1.67$ , analytical grade.

*Catalyst:* 35 g sodium molybdate ( $2H_2O$ ) are dissolved in 150 ml water, 150 ml of the sulphuric acid is added, the mixture cooled and finally 200 ml of the perchloric acid is added.

*Procedure:* The sample containing about 10–50 mg phosphorus is transferred to a 100 ml Kjeldahl flask, 5–15 ml sulphuric acid is added and the mixture boiled until fumes of sulphur trioxide begin to be evolved. The sample is then cooled, 5 ml catalyst added together with 10 ml nitric acid and the mixture boiled until all perchloric acid is used up (white fume disappears) and then continued until fumes of sulphur trioxide are again evolved. The oxidation is repeated. The phosphate sample is then cooled, diluted, ready for the determination.

b) Colorimetric determination.

*Reagents:* I, Nitric acid:  $d = 1.40$ , analytical grade, dilution 1:2; II, ammonium vanadate: 2.5 g ammonium vanadate is dissolved in 500 ml warm water, the solution cooled and 20 ml nitric acid ( $d = 1.40$ ), added and the whole diluted to 1000 ml; III, ammonium molybdate: 50 g ammonium molybdate is dissolved in 500 ml water, filtered if necessary, and then diluted with water to 1000 ml. Standard phosphorus solution: 0.4393 g analytical grade sodium dihydrogen phosphate is dissolved and diluted to 1000 ml; this standard solution has 0.1 mg phosphorus/ml.

*Procedure:* A part of the sample containing 0.3–1 mg phosphorus is transferred to a 50 ml graduated flask, neutralized with ammonia and acidified to pH 3–4 with nitric acid (1:2). 5 ml of each of the solutions I, II, and III are added in this order, and the whole diluted to 50 ml and well mixed. 10 min later the absorbance is measured at 445 nm. A blank determination is made and a standard curve determined with 1, 2, 5, and 10 ml of the standard solution.

2. Determination of inorganic bound phosphorus.

a) High concentrations.

*Reagents:* Sulphuric acid,  $d = 1.84$ , analytical grade, dilution 1:1; potassium permanganate, 2 % solution; ammonium vanadate: 2.5 g ammonium vanadate is dissolved in water and the solution diluted to 1000 ml; ammonium molybdate: 100 g ammonium molybdate is dissolved in warm water. The solution filtered if necessary, and then made up to 1000 ml. Standard phosphorus solution: As before.

*Procedure:* A suitable quantity containing 0.1–0.5 mg phosphorus/50 ml. 5–10 ml is measured in to a 50 ml flask and 2 ml sulphuric acid and 1 ml potassium permanganate solution is added. The sample is then boiled for one minute and, after cooling to room temperature, the excess of potassium permanganate is eliminated with 3 % hydrogen peroxide (no excess of hydrogen peroxide).

10 ml ammonium vanadate is added the mixture and boiled until a yellow-green colour develops and then for a further half-minute, after which it is cooled and 10 ml molybdate added. 10 min later the well mixed sample is extracted with two portions of 10 ml amyl alcohol, each extraction being continued for 1 min. The extracts are filtered and combined and 25 ml amyl alcohol added. Finally the absorbance is measured at 425 nm, using a 1 cm cell with lid. A blank determination and a standard curve are made.

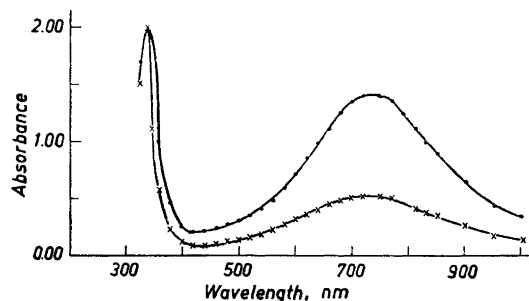
b) Low concentrations.

*Reagents:* Perchloric acid,  $d = 1.67$ , analytical grade; sulphuric acid, analytical grade, 20 %; potassium permanganate, 2 % water solution; ammonium molybdate: 2.5 g ammonium molybdate are dissolved in 100 ml water; sodium pyrosulphite: 10 g analytical grade, sodium pyrosulphite are dissolved in 100 ml water; reduction solution: 0.5 g 1-amino-2-naphthol-4-sulphonic acid, 29.3 g sodium pyrosulphite, and 1 g sodium sulphite are dissolved in 200 ml water, and the solution heated and then filtered. A fresh solution must be made every week.

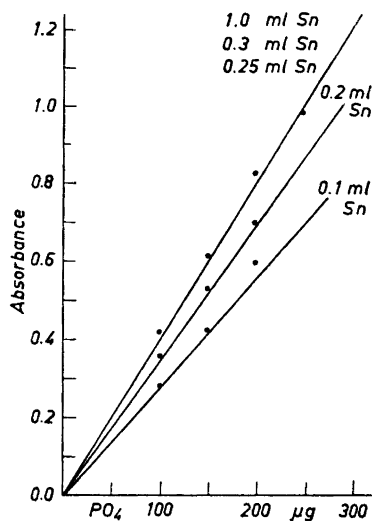
*Procedure:* The sample containing about 10–100  $\mu\text{g}$  phosphorus is transferred to a 50 ml flask and 1 ml sulphuric acid and 4–5 drops potassium permanganate solution added. The mixture is warmed for 10 min on a water bath and then 2 ml molybdate added. 10–15 min later when the sample is rendered colourless by adding more drops pyrosulphite, 1 ml reduction solution is added and the whole diluted to 25 ml. The flask is finally placed in water at 20°C for 15 min, and then the absorption is measured at 660 nm, using a 1 cm cell. A standard curve with 0, 0.02, 0.04, 0.06, and 0.08 mg phosphorus/25 ml is made.

## DISCUSSION OF RESULTS

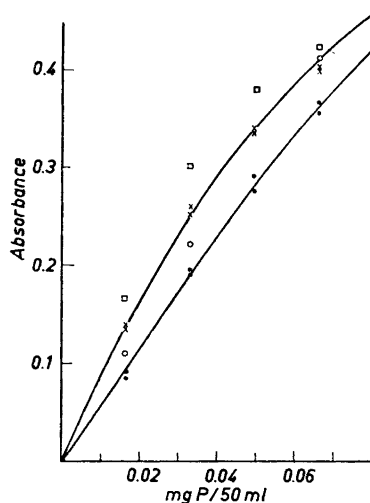
The molybdenum blue method for small quantities of phosphorus has been modified, the reduction being made with  $\text{Sn}^{2+}$  and with 1-amino-2-naphthol-4-sulphonic acid.



*Fig. 1.* Determination of phosphate (molybdenum blue). Reduction with  $\text{SnCl}_2$ .  $\times$  Blank against  $\text{H}_2\text{O}$ ,  $\bullet$  0.5 mg  $\text{PCl}_3$  against  $\text{H}_2\text{O}$ .



*Fig. 2.* Absorbance in  $\text{PO}_4$ -determination. Various quantities of 1%  $\text{Sn}^{2+}$  solution. 675 nm.



*Fig. 3.* Standard curve in  $\text{PO}_4$ -determination. 675 nm. Reduction with  $\text{SnCl}_2$ .  $\bullet$  New  $\text{SnCl}_2$ -solution,  $\times$  5 h old  $\text{SnCl}_2$ -solution,  $\circ$  24 h old  $\text{SnCl}_2$ -solution.

Table 1. Reduction with  $\text{Sn}^{2+}$ , 675 nm, 1 cm cell.

Sample mg $\text{CH}_3\text{POCl}_2$	mg $\text{PCl}_3$	Result $\text{PCl}_3$ mg	Difference %
260.9	—	0.1	—
—	168.8	170.0	+0.7
—	189.2	190.0	+0.4
102.9	78.4	77.4	-1.3
307.1	168.7	167.0	-1.0
83.2	176.6	167.8	-5.0

Table 2. Reduction with 1-amino-2-naphthol-4-sulphonic acid. Dilution 50 ml, 660 nm, 1 cm cell.

$\text{PCl}_3$ weight mg P	Result mg P	Difference %
0.0226	0.0230	+1.8
0.0226	0.0225	-0.4
0.0339	0.0355	+4.7
0.0339	0.0345	+1.8
0.0432	0.0435	+0.7
0.0432	0.0415	-3.9

In the presence of $\text{CH}_3\text{POCl}_2$ $\text{CH}_3\text{POCl}_2$ mg P	$\text{PCl}_3$ mg P	Result $\text{PCl}_3$ mg P	Difference %
0.260	—	0.0005	—
0.520	—	0.0008	—
0.106	0.0210	0.0205	-2.4
0.106	0.0210	0.0216	+2.9
0.212	0.0419	0.0405	-3.3
0.212	0.0419	0.0428	+2.1

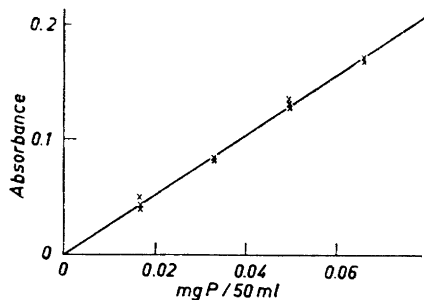


Fig. 4. Standard curve in  $\text{PO}_4$ -determination. 660 nm. Reduction with amino-naphthol-sulphonic acid.

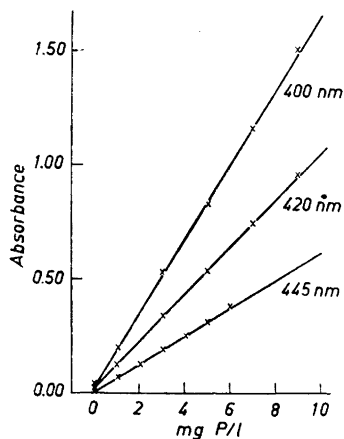


Fig. 5. Molybdovanadophosphoric acid. Absorbance at different wavelengths determined against  $\text{H}_2\text{O}$ .

The absorbance as function of the wavelength with  $\text{Sn}^{2+}$  reduction is shown in Fig. 1 and the influence of concentration and time on the  $\text{Sn}^{2+}$  solution in Figs. 2 and 3. The alternative method is illustrated in Fig. 4 at 660 nm. It eliminates the problems arising with  $\text{Sn}^{2+}$ . This method for the determination of small quantities of  $\text{PO}_4$  in hydrogen peroxide has been developed at Laporte Chemical, Ltd., England, and modified at this Institute. Results in Tables 1–2 are the same, but the new method is much more simple to handle.

Table 3. Determination with molybdate + vanadate.

Sample mg $\text{CH}_3\text{POCl}_2$	mg $\text{PCl}_3$	Result $\text{PCl}_3$ mg	Difference %
—	500.0	498.1	−0.4
—	500.0	503.4	+0.7
530.3	457.1	463.6	+1.4
530.3	457.1	472.5	+3.4
1060.6	914.2	909.5	−0.5

With large quantities of phosphorus, reduction to molybdenum blue is unnecessary and the phosphorus can most appropriately be determined as molybdovanadophosphoric acid at 425 nm (Fig. 5). This is extracted from the solution with amyl alcohol. The extraction is necessary to eliminate interference from  $\text{Mn}^{2+}$  ions which yield a dark green compound with vanadate, that is

Table 4.

Sample weight as mg P CH <sub>3</sub> POCl <sub>2</sub>	mg P PCl <sub>3</sub>	Result total P mg P	Result inorganic P mg P	Result organic P mg P	Difference in organic P %	Difference in inorganic P %
23.3	40.6	63.7	40.7	23.0	-1.3	+0.2
23.3	40.6	64.4	40.7	23.7	+1.7	+0.2
69.9	42.8	112.2	43.4	68.8	-1.6	+1.4
69.9	42.8	114.2	42.8	71.4	+2.1	±0.0

Table 5.

Quantity PCl <sub>3</sub> g	Theoretical excess PCl <sub>3</sub> g	Total P as PCl <sub>3</sub> g	Inorganic P as PCl <sub>3</sub> g	Organic P as PCl <sub>3</sub> g	Degree of conversion %
3.1348	+0.4463	3.0724	0.4121	2.6603	99.0
4.0484	+0.3648	3.9768	0.5531	3.4237	92.9
3.6285	+0.1068	3.5379	1.0050	2.5329	71.9
2.1760	—	2.1901	0.3273	1.8628	85.6
1.9012	—	1.8656	0.3001	1.5655	82.3
1.9793	+0.0646	1.9685	0.3796	1.5889	83.0
9.2459	+4.9019	9.1386	4.9903	4.1483	95.5

not extracted with this alcohol. Results are reported in Table 3. The method is developed at this Institute. In the second determination, *i.e.*, of total phosphorus, arises the problem of oxidizing the stable bond between carbon and phosphorus. Oxidation with sodium peroxide in Parr-bomb or Schöninger-bottle has given good results, but we have found the best method to be that of Simmons and Robertsson,<sup>2</sup> involving oxidation with nitric acid and perchloric acid in the presence of molybdate. The use of molybdate as catalyst has also been studied by Rechnitz and Laitinen.<sup>3</sup>

The determination of the phosphate formed may be made gravimetrically or colorimetrically. Here we have made use of ammonium vanadate and ammonium molybdate to give the yellow colour of molybdovanadophosphoric acid in an acid solution, this time according to Quinland and DeSessa.<sup>4</sup> The colour is fully developed within 10 min, and it is stable for more than 4 h. Measurements are made at 445 nm (Fig. 5). If molybdate is present from the beginning, it is necessary to work at a given pH-value, if a phosphorus molybdate is not

to be formed. This substance also gives a yellow solution and is formed in an irreversible reaction, so that the addition of vanadate will not give correct values.

Table 4 shows results from the analyses of mixtures of  $\text{CH}_3\text{POCl}_2$  and  $\text{PCl}_3$  by the molybdenum blue reaction and the total phosphorus method.

The analytical method has been used for the estimation of the yield from some syntheses of Clay-Kinnear-Perren complexes with various reaction times and temperatures. The results, which are summarized in Table 5 show good agreement with those from previous investigations at this Institute.

#### REFERENCES

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