

TECHNICAL NOTE

A MODIFICATION OF THE HYDROGEN PEROXIDE METHOD OF DETERMINATION OF TOTAL PHOSPHORUS IN NATURAL WATERS

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Abstract—A modification is suggested of the H_2O_2 - H_2SO_4 digestion method for determining total dissolved and suspended P in natural waters in order to avoid loss of P by adsorption on hydrous Fe and Al oxides formed during neutralization prior to filtration. The modification consists in adding an extra volume of sulfuric acid after neutralization so that such oxides are dissolved and hence the adsorbed P can pass into solution.

INTRODUCTION

Phosphorus occurs in different forms in natural waters and in waste waters, all of which can be in soluble state (as inorganic as well as organic P), in particulate detritus, or in the bodies of aquatic organisms. Following the APHA (1971), "total dissolved and suspended phosphate" (from now on referred to as P_T) is the fraction of P determined by various digestion methods in order to rupture both C—P and C—O—P bonds, and solubilize suspended material releasing the phosphorus as soluble orthophosphate. On the other hand, "filtrable (dissolved) orthophosphate" (P_D) is the fraction determined directly in the filtrate which passes a $0.45 \mu m$ membrane.

There are several methods in the literature for determining P_T in natural waters. Harwood *et al.* (1969) tested five different methods of digestion to fulfill the oxidation of P-organic compounds and concluded the oxidation with 50% hydrogen peroxide to be the quickest and easiest technique. Nicholls (1975) proposed this method for simultaneous determination of total phosphorus and Kjeldahl nitrogen in natural waters.

Nevertheless, when the referred method was applied to the analysis of P_T in waters from the Guadamar river and from the Guadalquivir marshes (Sevilla, Spain), some results were lower than those for P_D , which seems to be in contradiction with the above definitions. The reason for this should be looked for in the digestion method, since the P_D determination does not involve any manipulation and is not expected to have large errors.

The present paper studies the possible origin of such anomalous results and suggests a simple modification of the referred method in order to improve its reliability.

EXPERIMENTAL

Triplicates of 50 ml-samples of water were placed in Kjeldahl flasks, and 1 ml of conc. H_2SO_4 and 1 or 2 anti-bumping granules were added to them. The flasks were heated on a hotplate in a fume hood until fumes of SO_3 appeared. After allowing to cool down, 1 ml of 30% H_2O_2 was added, and the flasks were again gently heated to fumes of SO_3 . If the digest is not clear the H_2O_2 treatment must be repeated. After the digest is clear, heating was prolonged up to accomplishing the H_2O_2 decomposition. When cool, 50 ml of distilled water and 3 drops of phenolphthalein solution (0.5% in 1:1 water-ethanol) were added, the mixture brought to pink colour with 12% NaOH solution and back to colourless with 5 N H_2SO_4 (Procedure A).

The present paper proposes a modification of procedure A (Procedure B), consisting in an extra addition of 0.5 ml of 5 N H_2SO_4 to the solution obtained by procedure A, and intermittent swirling for the next 30 min before proceeding as described below.

Samples from both procedures A and B were filtered into 100 ml volumetric flasks and made up to the marks with distilled water. The resulting solutions were analysed for P, Fe and Al. Phosphorus was analysed by the method of Murphy & Riley (1962). Atomic absorption spectrometry was used for analysis of Fe and Al, except when Al was less than 1 ppm, in which case it was determined by Hsu's method (1963) using thioglycolic acid to suppress Fe interferences.

It has been reported (Jenkin, 1968) that incomplete P recoveries have been observed when 30% H_2O_2 is used. Nevertheless, previous experiments of the authors with solutions of phosphoglyceric acid (calcium salt) have shown a recovering power for 30% H_2O_2 similar to a mixture of $HClO_4$ - H_2SO_4 (400 ml conc. H_2SO_4 + 20 ml 70% $HClO_4$), which recovers about 100% of total P (Harwood *et al.*, 1969).

Solid residues at 525°C were determined according to Rodier (1971) and P_D following the APHA (1971).

RESULTS AND DISCUSSION

Digestion and analysis of natural waters

Table 1 shows that when procedure A is applied to

Table 1. Composition of undigested natural waters and of filtrates after digestion

Sample No. and date	Undigested waters				*	Filtrates from digestion			
	P _D (ppm)	Al (ppm)	Fe (ppm)	Solid residues at 525°C (ppm)		pH†	P _T † (ppm)	Al (ppm)	Fe (ppm)
M-4 (29 June 1979)	0.00	ND	Traces	0.0	A	3.8 ± 0.2	0.04 ± 0.01	ND	ND
					B	2.3 ± 0.0	0.05 ± 0.01	ND	ND
M-7 (29 June 1979)	0.03	ND	Traces	17.0	A	6.0 ± 0.0	0.04 ± 0.04	ND	ND
					B	2.3 ± 0.0	0.18 ± 0.00	ND	ND
M-11 (29 June 1979)	0.33	ND	Traces	17.5	A	4.5 ± 1.3	0.15 ± 0.12	ND	ND
					B	2.1 ± 0.1	0.50 ± 0.01	ND	ND
M-4 (7 Nov. 1979)	0.00	ND	0.1	13.0	A	7.3 ± 0.3	0.00 ± 0.00	ND	ND
					B	2.2 ± 0.1	0.12 ± 0.01	ND	0.6
M-7 (7 Nov 1979)	0.24	ND	0.4	0.5	A	4.6 ± 1.9	0.55 ± 0.22	ND	ND
					B	2.3 ± 0.1	0.72 ± 0.01	ND	5.2
M-4 (12 Dec. 1979)	0.00	0.0	Traces	20.0	A	3.6 ± 0.1	0.08 ± 0.01	0.6	0.8
					B	2.3 ± 0.1	0.13 ± 0.02	0.8	1.4
M-7 (12 Dec. 1979)	0.52	0.0	0.1	5.8	A	3.4 ± 0.3	0.62 ± 0.14	0.4	0.6
					B	2.2 ± 0.1	0.68 ± 0.05	0.4	0.8
M-9 (12 Dec. 1979)	0.17	0.0	Traces	158.0	A	8.1 ± 0.4	0.07 ± 0.02	0.6	0.2
					B	2.2 ± 0.0	0.64 ± 0.01	8.2	6.6
M-11 (12 Dec. 1979)	0.28	0.0	Traces	140.0	A	6.2 ± 0.4	0.03 ± 0.01	0.0	0.4
					B	2.2 ± 0.4	0.61 ± 0.03	5.8	5.0

*Procedure (see text).

†Mean values ± SD.

natural waters, some results for P_T are lower than the corresponding P_D, as stated above. It can also be observed that P_T and pH values of filtrates are widely dispersed within replicates as shown by standard deviations. This table does not show the individual values of the replicates, but it was observed that there is a definite inverse relationship between the pH of filtrates and P_T.

Concentrations of Fe and Al in untreated waters filtered through a 0.45 μm membrane were smaller than those in the filtrates from digestion (Table 1). In most samples the formation of a precipitate was observed during the addition of 12% NaOH. Such a precipitate was partially dissolved when the samples were neutralized with 5 N H₂SO₄ (Procedure A) and

was noticeable when filtering as a brownish shade on the filter paper. When 0.5 ml of 5 N H₂SO₄ were added after neutralization and the sample was swirled for about 30 min (Procedure B), the precipitate disappeared and the pH of the filtrate decreased to approx. 2.2. At the same time the values of P_T and the concentration of Fe and Al in solution increased, and dispersion of the P_T values within replicates decreased (Table 1).

Generally, the higher the amounts of solid residues at 525°C, the higher were Fe and Al concentrations in solution after treatment by procedure B (Table 1). Linear correlations between the solid residues at 525°C and Fe and Al concentrations, were significant at the level of $P < 0.01$ and $P < 0.02$ respectively.

Table 2. Results of analysis of phosphoglyceric acid solutions

Solution	*	Dose P ₁		Dose P ₂	
		Filtrate pH†	Total P μg†	Filtrate pH†	Total P μg†
I	A	2.7 ± 0.3	3.11 ± 0.21	2.6 ± 0.2	5.55 ± 0.16
	B	2.1 ± 0.1	3.13 ± 0.37	2.1 ± 0.1	5.74 ± 0.28
II	A	3.1 ± 0.3	2.85 ± 0.03	3.8 ± 0.2	5.30 ± 0.05
	B	2.3 ± 0.1	2.96 ± 0.10	2.3 ± 0.1	5.40 ± 0.18
III	A	4.8 ± 1.7	2.77 ± 0.10	4.9 ± 1.8	5.23 ± 0.06
	B	2.2 ± 0.0	2.78 ± 0.16	2.2 ± 0.0	5.42 ± 0.03

Solution I: C₃O₇H₃PCa in water.Solution II: C₃O₇H₃PCa in 100 ppm Ca solution.Solution III: C₃O₇H₃PCa in 100 ppm Ca, 50 ppm Mg, 5 ppm K and 5 ppm Na solution.

*Procedures (see text).

†Mean values ± SD.

Table 3. Influence of Fe and Al contents upon P recovery

Group	*	P† (μg)	pH†	Fe† (μg)	Al† (μg)
a	A	25.9 ± 2.6	3.9 ± 0.5	238 ± 38	327 ± 15
	B	29.8 ± 0.1	2.2 ± 0.0	287 ± 19	313 ± 15
b	A	17.5 ± 11.7	5.7 ± 3.3	153 ± 127	0
	B	29.6 ± 0.4	2.2 ± 0.06	313 ± 6	0
c	A	17.1 ± 14.2	5.6 ± 0.4	0	137 ± 118
	B	29.5 ± 0.3	2.2 ± 0.06	0	323 ± 15

*Procedures (see text).

†Mean values ± SD.

Digestion and analysis of solutions of phosphoglyceric acid

Digestion of solutions of phosphoglyceric acid (calcium salt) with two different P levels, P₁ and P₂ (see Table 2), led to values of P in solution which were in good agreement with the known contents. Results were unaffected by addition of Ca alone or Ca, Mg, K and Na together in concentrations of the same order as the natural waters studied in this paper, even though pH values were higher (Table 2). Recovery of P was equally good by procedure B, except that standard deviations were somewhat higher.

Therefore it seems that alkaline and alkaline earth cations were not responsible for the anomalous results found for P_T in natural waters.

Influence of Fe and Al content upon P recovery

From the preceding section it seems likely that there is a connexion between the Fe and Al compounds present in natural waters and the incomplete recovery of P_T.

Measurable amounts of Fe and Al must be brought into solution by the H₂O₂-H₂SO₄ treatment, and they will be precipitated as hydrous oxides (brown Fe₂O₃·xH₂O and white Al₂O₃·xH₂O) when the pH is raised up to pink colour of phenolphthalein (pH 8.2-10) with 12% NaOH. It is reckoned that Fe and Al hydrous oxides have a great sorption capacity of anions (e.g. Cabrera *et al.*, 1977), and hence they can retire important amounts of P from the solution. When the suspension is brought back to colourless with 5 N H₂SO₄ the final pH much depends upon the buffer power of the suspension and the drop error. The former is related to the H₃O⁺ consuming nature of the hydrous oxides when dissolving and the latter may be great due to the high concentration of the acid. The final pH determines the fraction of the precipitate which is dissolved and accordingly the fraction of adsorbed P which passes into solution.

In order to test the above hypothesis, 3 groups, (a), (b) and (c) of 6 samples each were made up to simulate the composition of the solution resulting from the H₂O₂-H₂SO₄ treatments of natural waters. All samples contained 30 μg P as KH₂PO₄, 5000 μg Ca, 2500 μg Mg, 250 μg K and 250 μg Na in 50 ml of distilled water. Samples of group (a) contained 290 μg

Fe and 320 μg Al; group (b) 290 μg Fe; and group (c) 320 μg Al. One ml of conc. H₂SO₄ was added to all samples and three samples out of each group were processed by procedure A and the rest by procedure B.

Table 3 shows that P recovery by procedure A ranged from 57 to 86% of added P and standard deviations were high, yielding coefficients of variation of approx. 67%. On the other hand, P recovery by procedure B was always about 98-99% and coefficients of variation were 1% or less. The amount of P recovered for individual samples was function of final pH and Fe and Al concentrations of the filtrates, so that the more acid the pH the higher is the P recovered. The same can be said for Fe and Al recoveries, so that procedure A recovered 53-82% of Fe and 43-100% of Al added, and procedure B recovered about 100% of both.

The above findings suggest that most of the hydrous oxides precipitated when 12% NaOH is added are dissolved by procedure B, making possible for P adsorbed on them to be determined.

CONCLUSIONS

From the present results it may be concluded that the presence of Fe and/or Al materials in natural waters as those sampled from the Guadiamar river and Guadalquivir marshes, may cause a loss of P when determined by digestion with H₂O₂-H₂SO₄ mixture if the procedure given by Harwood *et al.* (1969) and Nicholls (1975) is followed. That loss of P depends upon the final pH of the digestion liquor filtrate, and it is overcome if the pH is acid enough as to dissolve the hydrous oxide precipitated by neutralization with NaOH.

In this paper a minor modification to that procedure is suggested, consisting in adding 0.5 ml of 5 N H₂SO₄ and waiting long enough as to dissolve the precipitate before filtering. It has been proved here that 30 min are sufficient for complete dissolution of the Fe and Al precipitate.

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