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Sulfide Interferences on the Determination of
Inorganic Phosphate in Anoxic Waters.

by

Tom Almgren and Torgny Johansson

August 1972

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Introduction

The determination of inorganic phosphate in this work follows the method by Murphy and Riley, as presented in New Baltic Manual. The orthophosphate dissolved in sea water is complexed by ammonium molybdate. The rate of reaction is increased by antimonyl tartrate. The compound thus formed is reduced by ascorbic acid, and a blue colored complex is obtained. The complexation is carried out at about pH 0.5. The absorption maximum of this blue complex, at 882 nm, is also the most suitable wavelength for the analytical determination.

The term mixed reagent, used below in the text, alludes to a mixture of ammonium molybdate, antimonyl tartrate and sulfuric acid. The ascorbic acid is kept as a single reagent.

Using this method in anoxic sulfide containing sea water samples, serious disturbances have been observed. The mixed reagent has in such cases caused an intensive yellow color to develop in the samples. Furthermore a precipitation is formed; the turbidity increases with time. Thus anomalous values of the phosphate content have been obtained in these samples.

Theory

Both the antimony (III) - and the molybdate ions are known to form yellow to brown compounds with sulfide (3.4). The sulfides Sb_2S_3 and MoS_3 are not soluble in water. In excess sulfide, however, soluble thiocompounds are formed, which in turn decompose in acids and the sulfides precipitate again. Thus a number of compounds are likely to be formed between the antimony (III) - and the molybdate ions on one hand and the sulfide ion on the other, among which the two sulfides will precipitate.

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Experimental

The mixed reagent was put into a solution containing 500 μM sodium sulfide. The absorption spectrum was scanned automatically between 290 and 600 nm with a Beckman DB instrument and manually between 600 and 900 nm with an Unicam SP 500 spectrophotometer.

Two series of standard samples were made with phosphate concentrations between 1 and 10 μM . One of the series was also made 200 μM with sodium sulfide. Following the analytical procedure recommended the absorbances were measured against distilled water in 4 cm kyvettes at 882 nm with the Unicam instrument. To minor parts of the sulfide samples containing 6 and 10 μM phosphate, double portions of reagents were used.

Another duplicate sets of phosphate standards were made one of which contained 200 μM sulfide. These sulfide containing samples were acidified with 1 drop of 1M sulfuric acid. Nitrogen gas was then allowed to pass through them for 5 minutes. The absorbances were measured after complexation as described above.

The phosphate content in three samples from different depths, 20, 30 and 40 m, in the Byfjord was determined. Three different approaches to the determination were made;

1. The normal procedure, i.e. no bubbling with nitrogen gas. The mixed reagent was put into the sea water reference.
2. Same as 1. but no reagents in the sea water reference.
3. Both sample and sea water reference were acidified with 1 drop 1M sulfuric acid and bubbled for 5 min. with nitrogen gas. The mixed reagent was used in the sea water reference.

Results

The absorption spectrum shows no maxima in the interval scanned (Figure 1.). The absorbance increases, however, towards lower wave-lengths. At the wave-lengths between about 500 to 900 nm the absorbance is fairly constant and low.

The standard samples containing sulfide have in general higher absorbances, than those without sulfide (Figure 2.). For the 10 μM

samples, however, the opposite conditions are shown. By using double reagent portions to minor parts of the 6 and 10 μM samples, containing sulfide, the absorbance decreases in the former sample and increases in the latter one.

The absorbances of the sulfide containing phosphate standards, acidified and bubbled with nitrogen gas, and of the sulfide-free phosphate standards differ only slightly from each other (Figure 3.). The differences are at the same level as the scatter between duplicate samples.

In Figure 4 the results of the phosphate determinations in anoxic waters from the Byfjord are presented. At 20 m, where the sulfide concentration is rather low, the differences between the three values given, are very small, 0.2 μM . At 30 m, however, the normal analytical procedure gives a result about 1.5 μM lower, and the second procedure about 1 μM higher than the value of the acidified and nitrogen gas bubbled sample. At 40 m the second procedure gives nearly the same value as the nitrogen gas treated sample about 2.7 μM higher than the phosphate value obtained by using the normal way of analysis.

Discussion

It is obvious that the absorbances due to the yellow compounds formed in anoxic samples, cause no serious interference on the phosphate determination. Furthermore the slight increase in absorbance is canceled out by using the mixed reagent in the reference.

More serious, however, are the two other phenomena occurring in anoxic samples, namely the increasing turbidity caused by the molybdate- and the antimony (III) sulfides, and the fact that the formation of the sulfide compounds diminished the amount of available reagents for the complexation of phosphate. The effects of these two phenomena are clearly shown in Figure 2. In the range between 1 to 6 μM phosphate the reagents are still sufficient for the formation of the phosphate complex in the sulfide containing standards. The increase in turbidity is shown by the higher absorbances in these samples. The difference in absorbances between the

sulfide containing standards and the other ones are, however, in general diminishing towards higher concentration of phosphate. This fact could perhaps point out that the lack of reagents already occurs at lower phosphate concentrations than $6 \mu\text{M}$ in $200 \mu\text{M}$ sulfide. The turbidity dependent absorbance is in that case overlapping the decrease in absorbance due to the diminishing phosphate complex-formation. At $10 \mu\text{M}$ phosphate, however, the absorbance decrease is so great that the turbidity effect can no longer cancel it out. By using double portions of reagents to a minor part of the sample the absorbance decreases in the $6 \mu\text{M}$ standard with sulfide due to dilutions effects. The $10 \mu\text{M}$ sulfide containing standard shows, however, an increase in absorbance in spite of these dilution effects, i.e. more reagents are available for the complexation of phosphate.

The turbidity increase can be compensated for by using the mixed reagent in the reference. But we are here dealing with such a great turbidity that it might be hazardous to rely on this compensation since the samples easily get a heterogeneous character. The decrease in absorbance due to lack of reagents is, however, an effect impossible to correct for in this way. It would be possible to use stronger reagents, but then it would be necessary to use separate solutions or greater portions of the reagents and in both cases separate calibration curves must be used. Furthermore the amount of reagents required is a function of both the sulfide and phosphate concentrations. Since this problem concerns only a few samples at the west-coast area of Sweden we regarded it more convenient to blow off the sulfide as dihydrogen sulfide with nitrogen gas. This procedure has not shown any effect on the phosphate determination (c.f. Figure 3.).

In order to compare the results obtained by this procedure with the values obtained by the normal procedure some determinations were made in the anoxic water of the Byfjord (c.f. Figure 4.). The values are close to each other at low sulfide concentrations (20 m). As expected the sulfide containing samples (curve 1) fall below the nitrogen treated samples (curve 3) as the sulfide content increases. The difference between curve 2 and curve 1 is a measure of the turbidity effect due to sulfide precipitation. As can be seen this

difference increases with increasing sulfide content. The fact that the two curves 2 and 3 interact near 40 m is the result of the absorbance-increasing turbidity effect canceling out the decrease in effect of insufficient reagents.

As the interferences on the phosphate determination in anoxic waters of high total sulfide concentration ($> 100 \mu\text{M}$) seem to be very serious we suggest the following procedure for the analyses of phosphate;

Acidify the sample and the sea-water reference with 1 drop 1M sulfuric acid. Let a stream of nitrogen gas (or any inert gas) pass through them for 5 minutes. This can be done directly in the test tubes. Then go on with the normal analytical procedure for inorganic phosphate.

References

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- Vogel, A.J. 1953: A Textbook of Macro and Semimicro Qualitative Inorganic Analysis, 4:th Ed. Longmans (1953)
- Hägg, G., 1966: Allmän och Organisk Kemi, 4:e uppl. Almqvist och Wiksell (1966).

Figure 1 Absorptionspectrum for the antimony and molybdate thio-compounds.

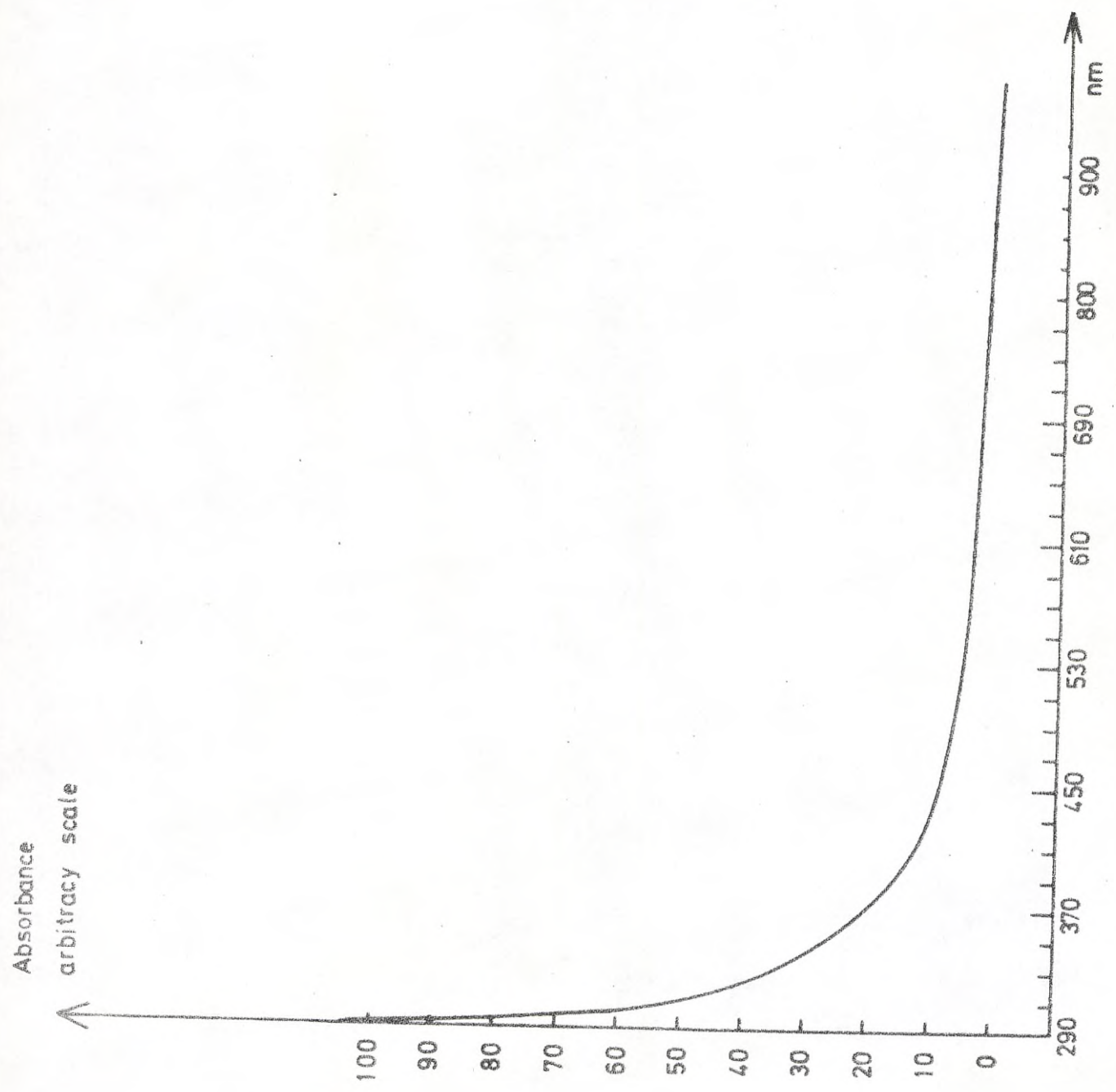


Figure 2 ○ Standard phosphate samples
 × Standard phosphate samples containing
 200 μM sulfide
 ▽ Standard phosphate samples containing
 200 μM sulfide, double reagents

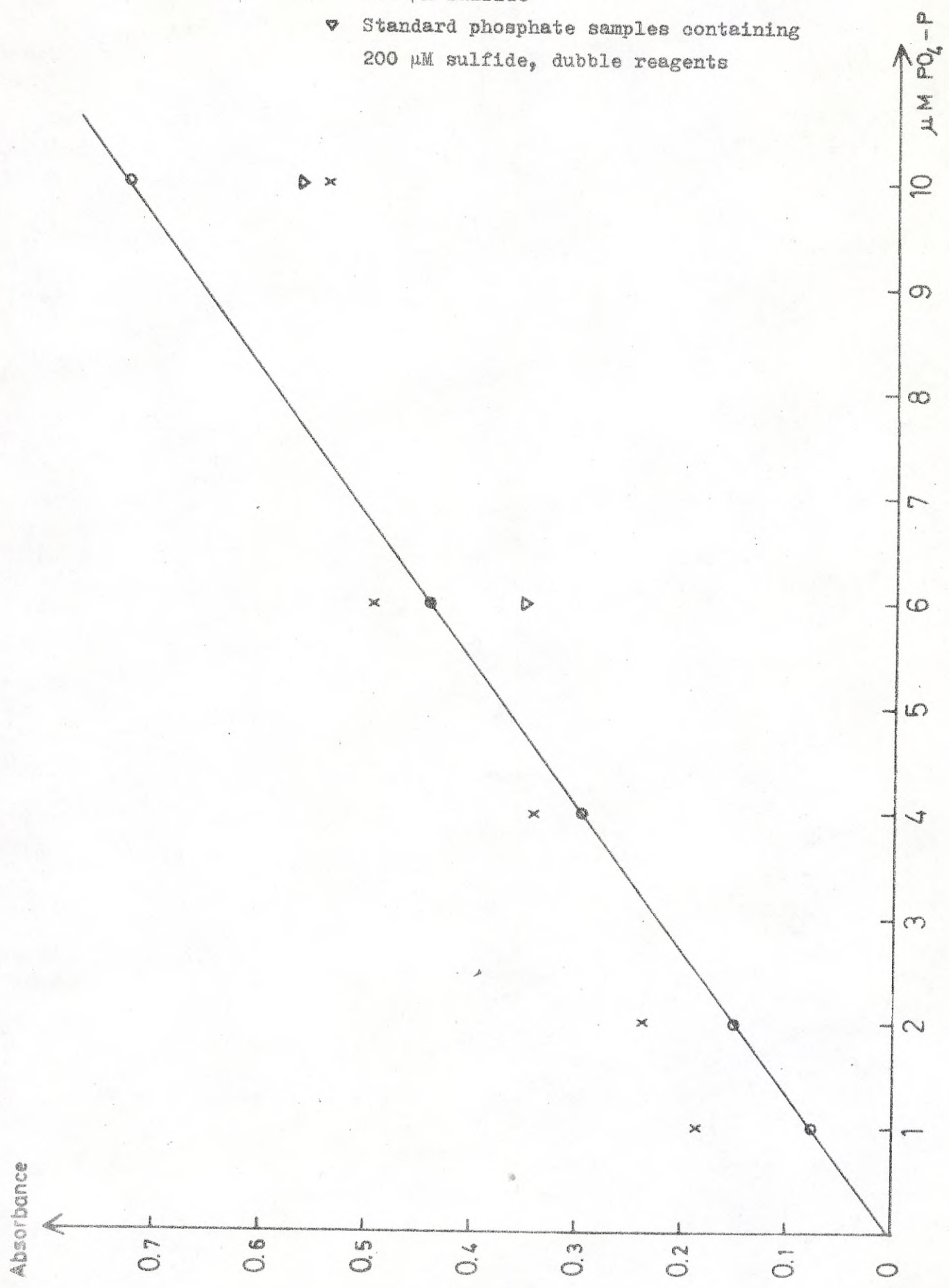


Figure 3 ○ Standard phosphate samples
X Standard phosphate samples made in 200 μM sulfide, acidified and bubbled with nitrogen gas

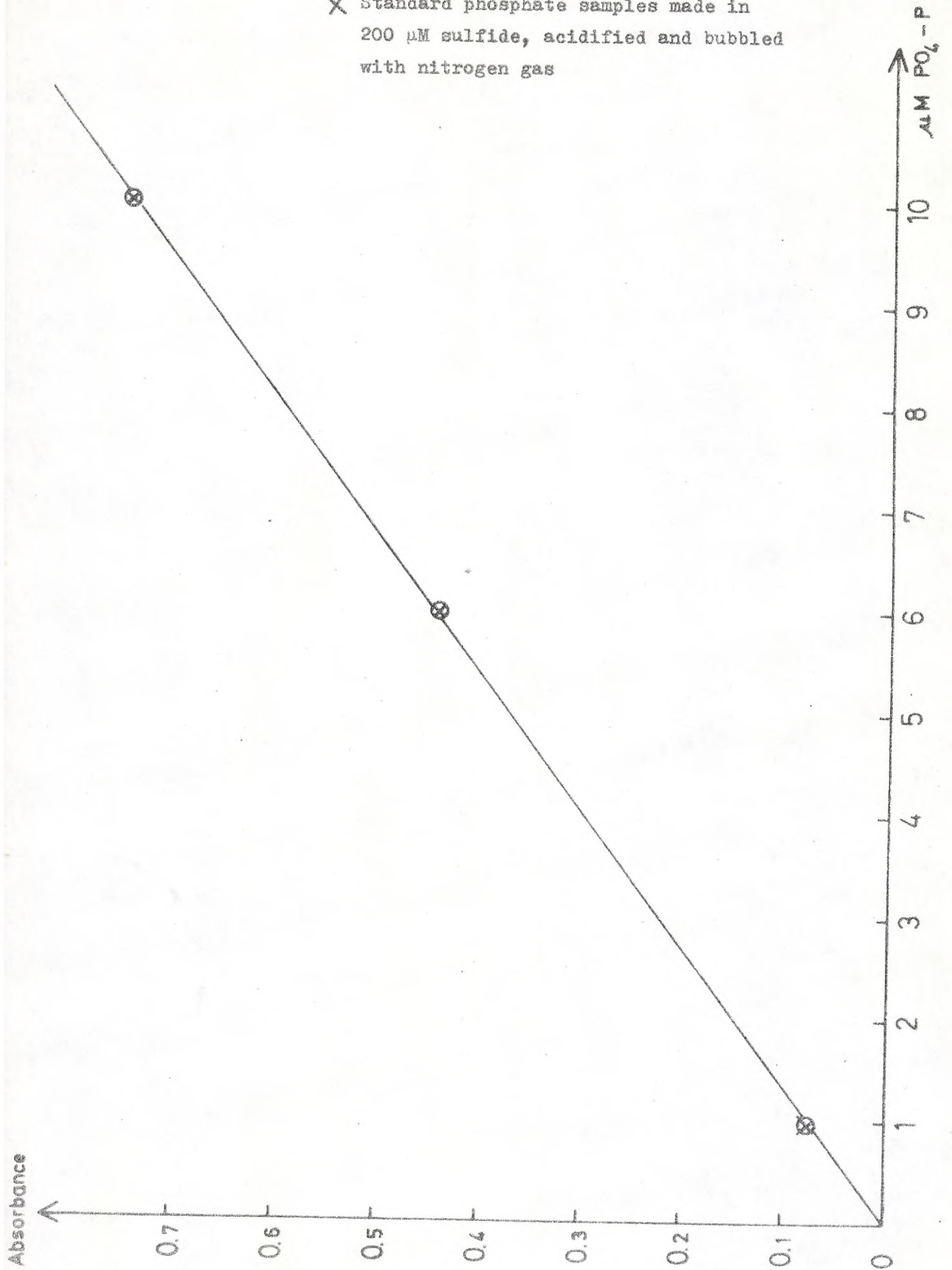


Figure 4 1) Samples measured against sea water references containing the mixed reagent
 2) Samples measured against pure sea water references
 3) Samples against sea water references, both samples and references acidified and nitrogen gas treated

