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GEOLOGICAL SURVEY

THE MOLYBDENUM BLUE REACTION AND THE DETERMINATION
OF PHOSPHORUS IN WATERS CONTAINING
ARSENIC, SILICON, AND GERMANIUM*

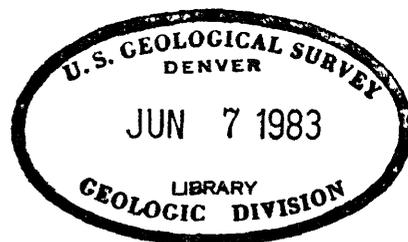
By

Harry Levine, J. J. Rowe, and F. S. Grimaldi

November 1953

Trace Elements Investigations Report 379

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CONTENTS

	Page
Abstract	4
Introduction	5
Studies of molybdenum blue reaction	6
The determination of phosphorus in waters containing arsenic, germanium, and silicon	12
Experimental data	13
Optimum conditions	13
Behavior of arsenic, germanium and silicon	17
Recovery of phosphate by coprecipitation with aluminum hydroxide	17
Removal of arsenic, germanium, and silicon by volatilization	19
Procedure	20
Reagents and apparatus	20
Determination of phosphorus	22
Test of procedure	23
The phosphate content of samples of sea water from the Gulf of Mexico	25
References	26

ILLUSTRATIONS

Figure 1. Conditions studied for the molybdenum blue reaction .	8
2. Field of reactivity of germanium and silicon with 1-amino-2-naphthol-4-sulfonic acid as the reducing agent	9
3. Field of reactivity of phosphorus and arsenic with 1-amino-2-naphthol-4-sulfonic acid as the reducing agent	9
4. Field of reactivity of phosphorus and arsenic with stannous chloride as the reducing agent	10
5. Field of reactivity of germanium and silicon with stannous chloride as the reducing agent	10
6. Effect of stannous chloride concentration on the absorbancy of the phosphate solution	14
7. Effect of molybdate concentration on the absorbancy of the phosphate solution	14
8. Effect of acidity on the absorbancy of the phosphate solution	15
9. Working curve for the determination of phosphorus ...	16
10. Absorption curve	18

TABLES

Table 1. Recoveries of phosphate after volatilization of AsCl ₃ , GeCl ₄ , and SiF ₄	21
2. Test of procedure to determine phosphorus	24
3. The phosphate content of sea water from the Gulf of Mexico	25

THE MOLYBDENUM BLUE REACTION AND THE DETERMINATION
OF PHOSPHORUS IN WATERS CONTAINING
ARSENIC, SILICON AND GERMANIUM

By Harry Levine, J. J. Rowe, and F. S. Grimaldi

ABSTRACT

A study was made of the various conditions under which it is possible to obtain the molybdenum blue reaction for Si, As, P, and Ge, using stannous chloride or 1-amino-2-naphthol-4-sulfonic acid as the reducing agents. For each reducing agent no conditions could be found where silicon could be distinguished from germanium and where phosphorus could be distinguished from arsenic (V). 1-Amino-2-naphthol-4-sulfonic acid seems to be superior to stannous chloride for differentiating Si and Ge from As and P.

The procedure described for the determination of phosphorus in waters makes provision for the separation of microgram amounts of phosphorus from at least 1 mg each of As_2O_5 , GeO_2 , and SiO_2 . The phosphate in waters is concentrated by precipitating $\text{Al}(\text{OH})_3$ which serves as a carrier for the AlPO_4 formed. The small precipitate is treated with a small volume of solution containing HF, HBr, HCl, and H_2SO_4 to volatilize any coprecipitated As, Ge, or Si. The phosphate is determined by the molybdenum blue reaction according to optimum conditions developed in this report. The total P_2O_5 content of several samples of sea water collected from the Gulf of Mexico ranged from 1.8 to 5.9×10^{-6} percent.

INTRODUCTION

The literature on the determination of phosphorus by the molybdenum blue reaction is voluminous. The methods are based on the formation of phosphomolybdic acid and its subsequent reduction to a blue compound. The original method (Denigés, 1920) has been modified for the determination of phosphorus in sea water. Important papers include those of Zinzadze (1935), Kalle (1935), Redfield et al. (1937), Woods et al. (1941), and Harvey (1948).

The molybdenum blue reaction is not specific for phosphorus as arsenic (V), germanium, and silicon also form heteropoly acids with molybdenum which also yield blue compounds on reduction. Some selectivity for phosphorus may be obtained by control of acidity. For example, at high acidity the heteropoly acids of phosphorus and arsenic may be reduced without interference from small amounts of silicon and germanium. The interference of arsenate in sea water may be eliminated by reducing the arsenate to arsenite before the addition of ammonium molybdate. Various agents, such as NaHSO_3 , have been proposed for the reduction of arsenic but the literature contains conflicting statements as to their effectiveness. It is also reported that arsenite may enhance the intensity of the blue color of the reduced phosphomolybdic acid.

Various reducing agents have been employed for the reduction of phosphomolybdic acid both to increase the stability of the resulting molybdenum blue complex and to make the reaction less sensitive to disturbing ions. No purpose is served in enumerating these reagents and it is doubtful whether any one of them is so far superior as to deserve special merit; usually the gains are made at the expense of some other desirable consideration such as sensitivity.

The aims of this research were, first, to study the molybdenum blue reaction to establish the range of conditions under which this reaction occurs for each of the elements, P, As, Ge, and Si and, second, to develop a method for the determination of microgram amounts of P applicable to waters containing As, Si, and Ge. This work was done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

STUDIES ON THE MOLYBDENUM BLUE REACTION

The variables studied were the acidity, the molybdate concentration, and the concentration of the reducing agent. Two series of experiments were made. Stannous chloride was used as the reducing agent in one series and 1-amino-2-naphthol-4-sulfonic acid, introduced by Fiske and Subbarow (1925), in the other. The experiments sought to establish the conditions under which P, As, Si, and Ge give the molybdenum blue reaction. The data should fill some gaps in our knowledge of the chemistry of the heteropoly acids of these elements and should reveal any differences in behavior that may be of analytical significance.

The general procedure used in this study follows: 5 ml of a solution of the element under study (10% P_2O_5 , 25% As_2O_5 , 25% SiO_2 , or 25% GeO_2) was added to a 100-ml beaker. A known amount of HCl was next added and the solution diluted with distilled water to 25 ml. The molybdate solution in known amounts was then added and the volume adjusted to 45 ml with water. Finally, a known amount of reducing agent was added and the volume adjusted to 50 ml. In the experiment where stannous chloride was used as the reducing agent, the absorbancy of the resulting solution was measured at 735 $m\mu$ after 3 minutes at room temperature using 1-cm

cells, slit at 0.06 mm, and water as reference. The same procedure was used for 1-amino-2-naphthol-4-sulfonic acid when silicon and germanium test solutions were used. The test solutions containing phosphorus and arsenic, however, were heated just to boiling and then cooled before measuring the absorbancy. This heating was found necessary in the cases of phosphorus and arsenic because the reduction of the heteropoly acids proceeded too slowly at room temperature with the organic reductant. All stock solutions were stored in polyethylene bottles and solutions of the reducing agents were freshly prepared each day. The solutions of P, As, Ge, and Si were prepared by dissolving the sodium or potassium salts in water redistilled in glass. The ammonium molybdate and stannous chloride solutions were prepared as directed under reagents. The 1-amino-2-naphthol-4-sulfonic acid solution was prepared by first adding 1.5 g of the reagent to 200 ml of water containing 7 g of anhydrous sodium sulfite and mixing the resulting solution with another solution made by dissolving 40 g of sodium metabisulfite in 800 ml of water.

The conditions studied are illustrated by the various points in figure 1. The total amount of concentrated HCl in the solution is plotted on the abscissa and thus includes that derived from the stannous chloride reagent when this reductant is used. In addition to the points in figure 1 several points at 0.02 ml HCl were selected in the cases of Si and Ge.

Following the representation used by Harvey (1948) the conditions under which the molybdenum blue reactions take place are given in figures 2, 3, 4, and 5. The data for Si and Ge are plotted together because the same data hold for both. This is also true for As and P. The

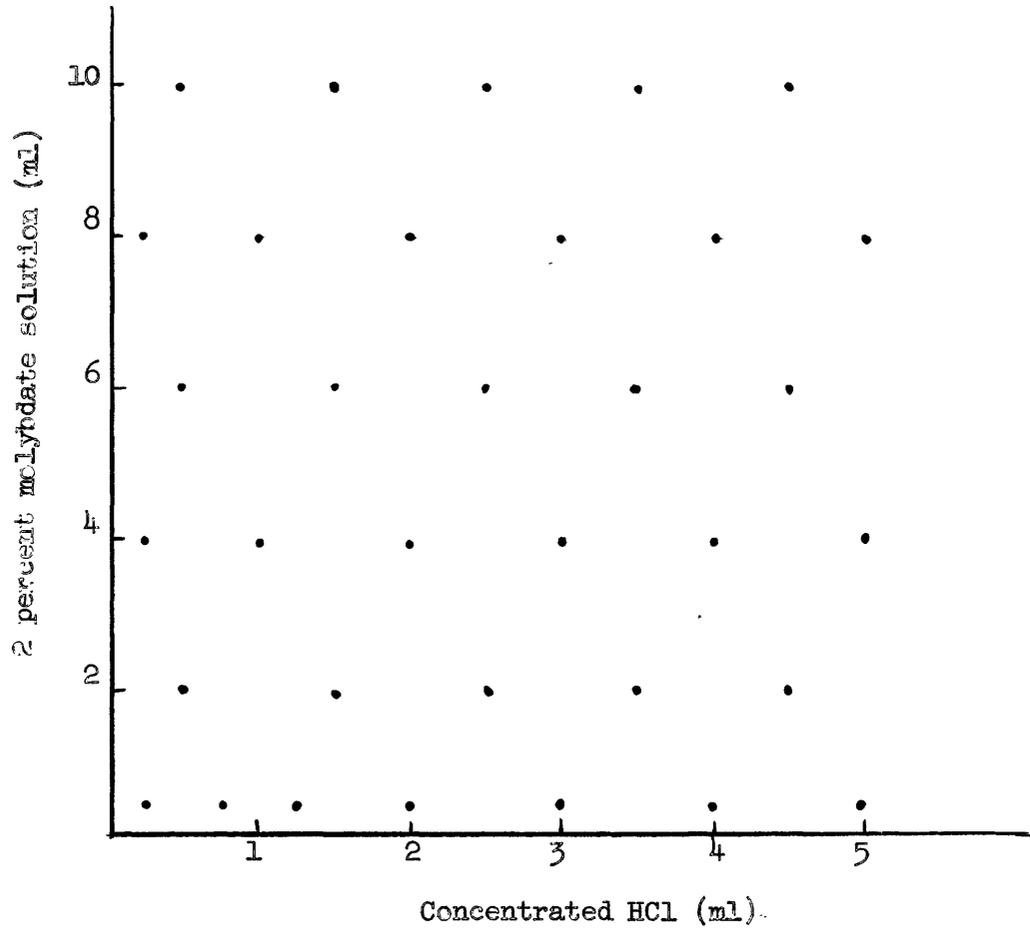


Figure 1.--Conditions studied for the molybdenum
blue reaction

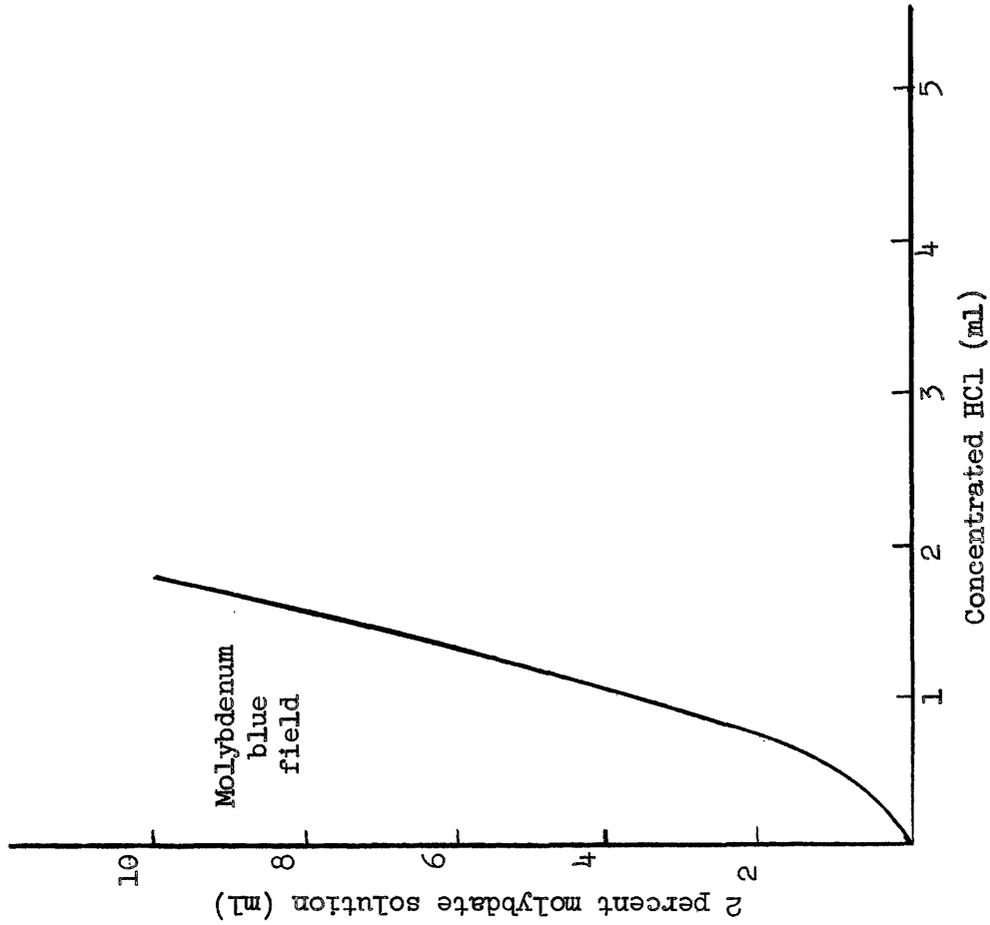


Figure 2.--Field of reactivity of germanium and silicon with 1-amino-2-naphthol-4-sulfonic acid as the reducing agent

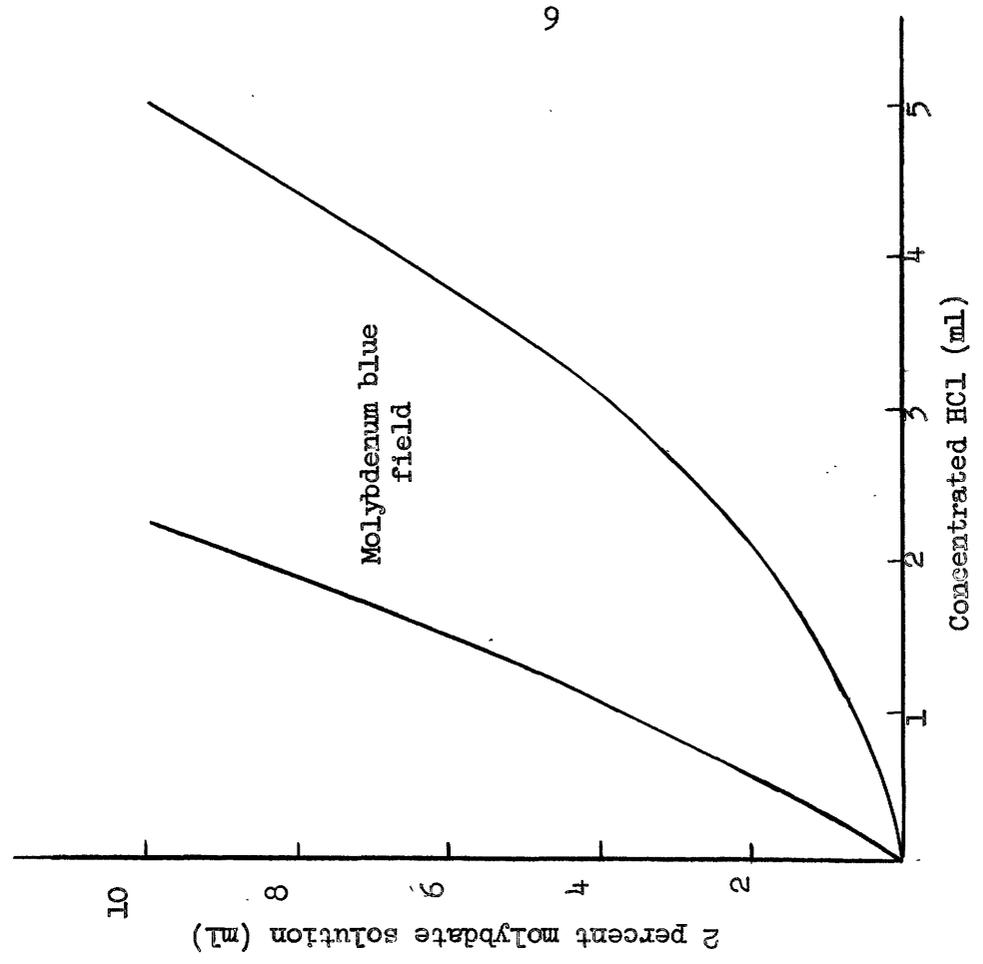


Figure 3.--Field of reactivity of phosphorus and arsenic with 1-amino-2-naphthol-4-sulfonic acid as the reducing agent

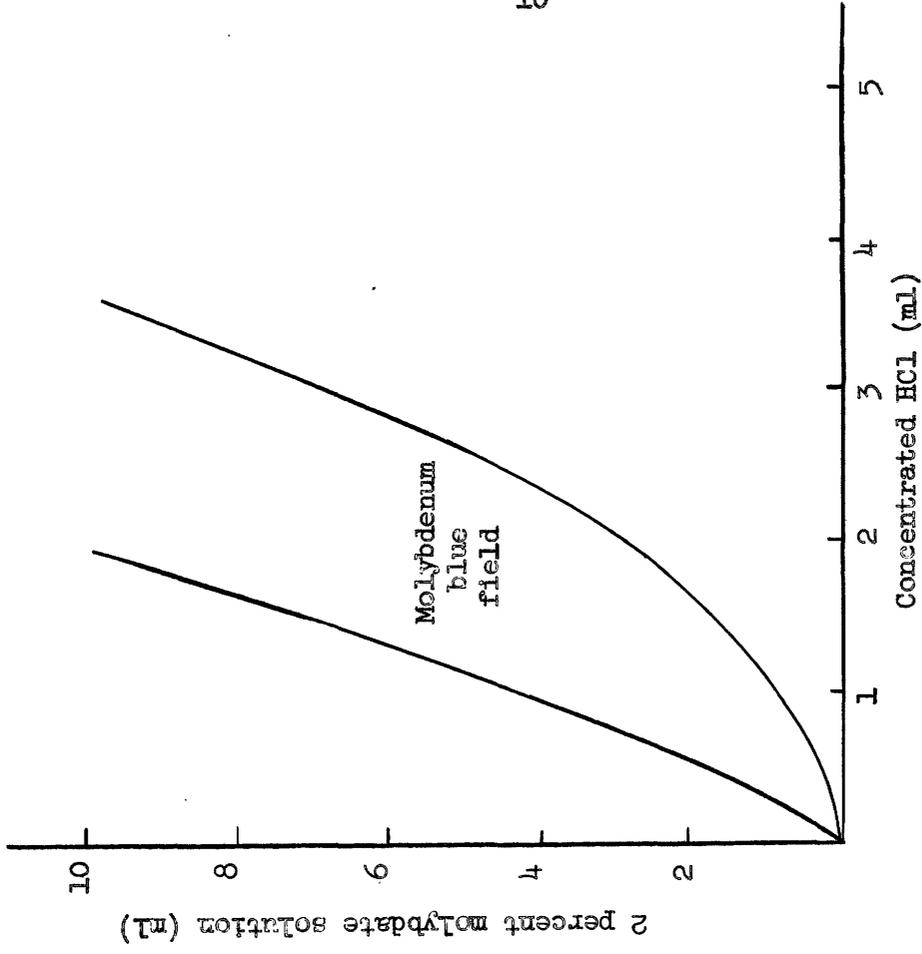


Figure 5.--Field of reactivity of germanium and silicon with stannous chloride as the reducing agent

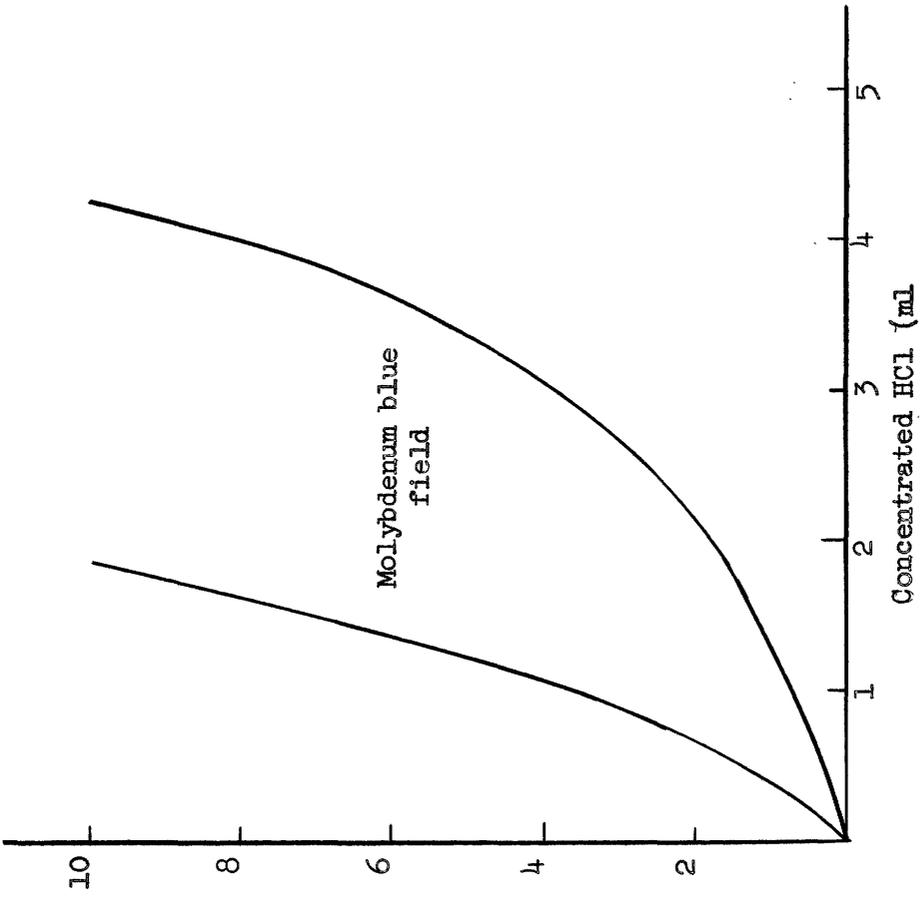


Figure 4.--Field of reactivity of phosphorus and arsenic with stannous chloride as the reducing agent

molybdenum blue reaction is assumed to have occurred only if the blank shows a very small absorbancy (<0.01) and the sample shows a visible blue and a greater absorbancy than the blank. The reactions obtained were dependent on the amount of reducing agent used. The figures represent a composite of the data obtained for several concentration levels of each reducing agent. The amount of the aminonaphtholsulfonic acid reductant used ranged from 0.1 ml to 2 ml, tests being made with 0.1, 0.5, 1, and 2 ml of the reductant for each test condition. The stannous chloride was varied from 0.1 ml to 3 ml, tests being made with 0.1, 0.3, 1, and 3 ml of stannous chloride solution for each test condition.

The concentration of the organic reductant is relatively unimportant in the germanium reaction, the same field of reactivity being obtained for the various concentrations of reductant tested. The concentration of the reductant is slightly more important for As, 0.1 ml of reductant being more nearly optimum. The fields of reactivity for Si and P are spotty and the concentration of reductant is more critical for both. The optimum amount of organic reductant for Si should be between 1 and 2 ml, and for P between 0.5 and 1 ml.

The molybdenum blue reactions for Si and Ge were found to be especially sensitive to changes in concentration of the stannous chloride and for this reason this reagent is not an ideal one for these two elements. The field of reactivity was exceptionally spotty, and only under a few of the conditions did a reaction occur at all. If this reagent is used, about 0.1 ml of the SnCl_2 solution should be nearly optimum for either element. Arsenate is least sensitive to stannous chloride concentration and the optimum amount of the reductant should be between 0.1 and 1 ml

of reagent. Stannous chloride seems to be better than the aminonaphtholsulfonic acid for the reduction of phosphomolybdic acid. The field of reactivity is again somewhat spotty unless the amount of SnCl_2 is limited to from 0.1 to 0.5 ml of reagent.

A few other observations should be noted. The conditions for which the molybdenum blue reactions take place depend on the particular reducing agent chosen; for the reducing agents tested Si cannot be differentiated from Ge nor can P be differentiated from As. It seems unlikely that such differentiations can be made by the selection of some other reducing agent. However, one reductant may be better than another for purposes of differentiating the pair As and P from the pair Ge and Si. In this respect the aminonaphtholsulfonic acid is better than the stannous chloride.

THE DETERMINATION OF PHOSPHORUS IN WATERS CONTAINING ARSENIC, GERMANIUM, AND SILICON

The procedure to be described makes provision for the separation of phosphorus from at least 1 mg each of As_2O_5 , GeO_2 and SiO_2 prior to the determination of phosphorus by the molybdenum blue reaction using stannous chloride as the reducing agent. Although it may be possible to determine phosphorus without separation from the above elements it is best that such separation be made where highest accuracy is sought. The separations are sufficiently simple so as not to increase unduly the time for an analysis. The need for the more or less uncertain salt correction when analyzing sea water samples is at the same time eliminated.

The phosphate in sea water is concentrated by precipitating $\text{Al}(\text{OH})_3$ which serves as a carrier for the AlPO_4 formed. The small precipitate

is treated with a small volume of solution containing HF, HBr, HCl, and H₂SO₄ to volatilize any coprecipitated arsenic, germanium, and silicon. The phosphate is then determined by the molybdenum blue reaction under the conditions developed in this report.

Experimental data

Optimum conditions

The molybdenum blue color should be most stable and the reaction least sensitive to small changes in conditions for concentration of reagents represented by some point near the center of the field of reactivity (fig. 4). Accordingly, this region was investigated in greater detail to establish optimum working conditions. The general procedure described previously was used to obtain the data. In each experiment 5γ P₂O₅ was taken and the final volume of each solution was made to 50 ml. Figure 6 illustrates the effects produced by varying the stannous chloride concentration in the solution containing 2 1/2 ml of HCl and 5 ml of molybdate reagent. The optimum amount of SnCl₂ solution was taken as 0.3 ml. The data plotted in figure 7 illustrate the effect of varying the molybdate concentration keeping the total amount of acid fixed at 2 1/2 ml HCl and stannous chloride solution fixed at 0.3 ml. Five milliliters of molybdate reagent was taken as optimum. In figure 8 the acidity was varied in solutions at optimum concentrations of stannous chloride and ammonium molybdate. The optimum amount of HCl is taken as 2 1/2 ml or a concentration of 5 percent by volume. Figure 9 is the working curve for different amounts of phosphorus using the optimum conditions developed above.

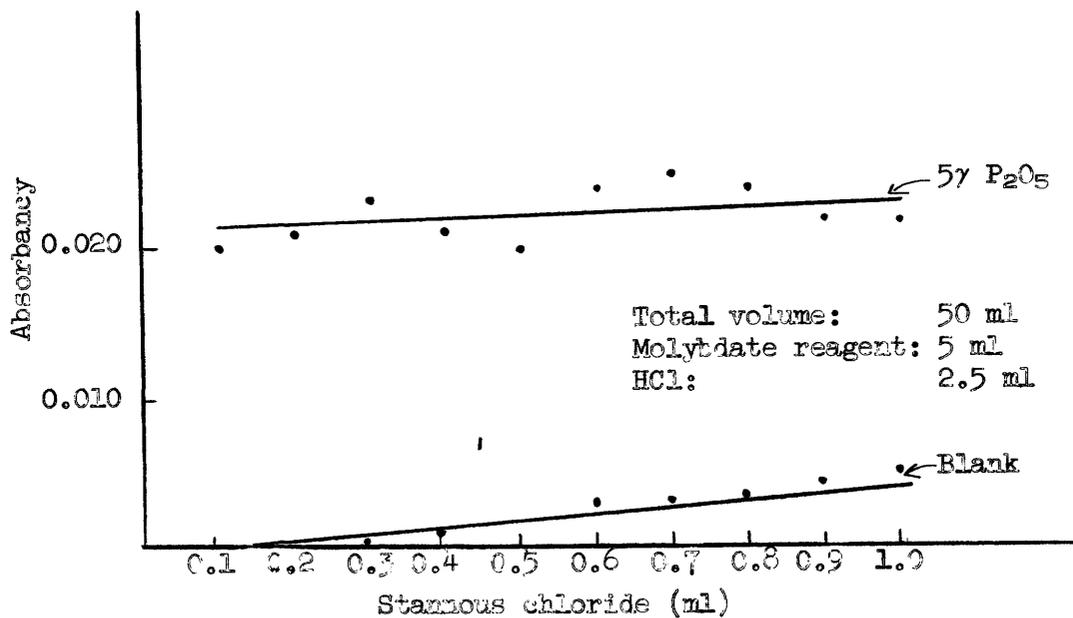


Figure 6.--Effect of stannous chloride concentration on the absorbance of the phosphate solution

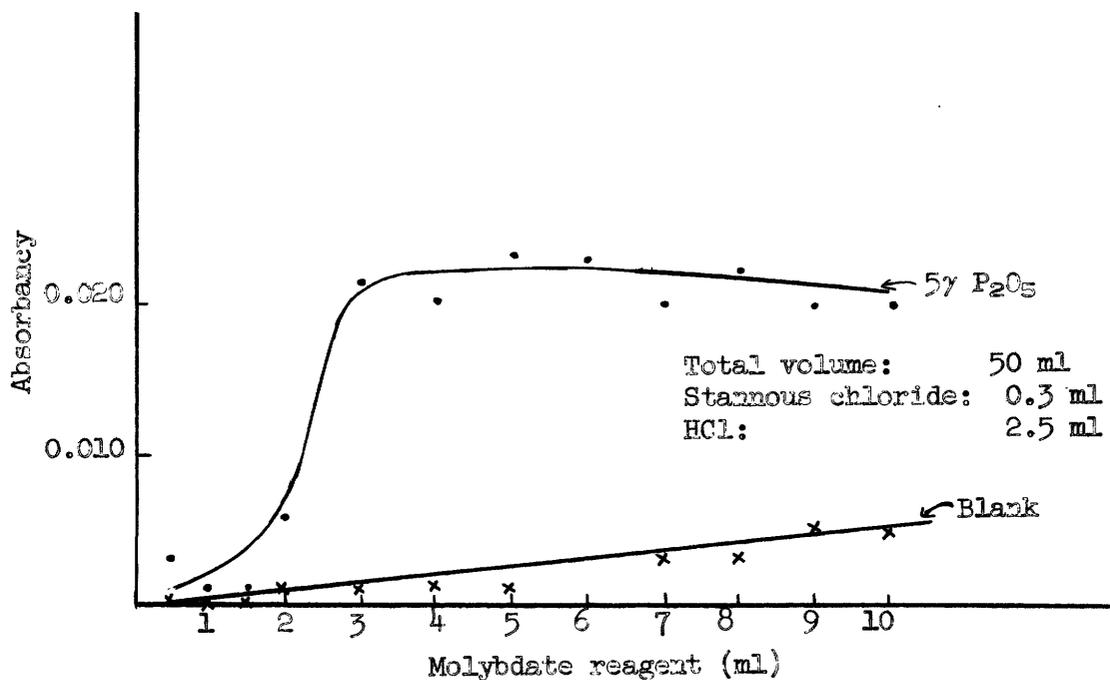


Figure 7.--Effect of molybdate concentration on the absorbance of the phosphate solution

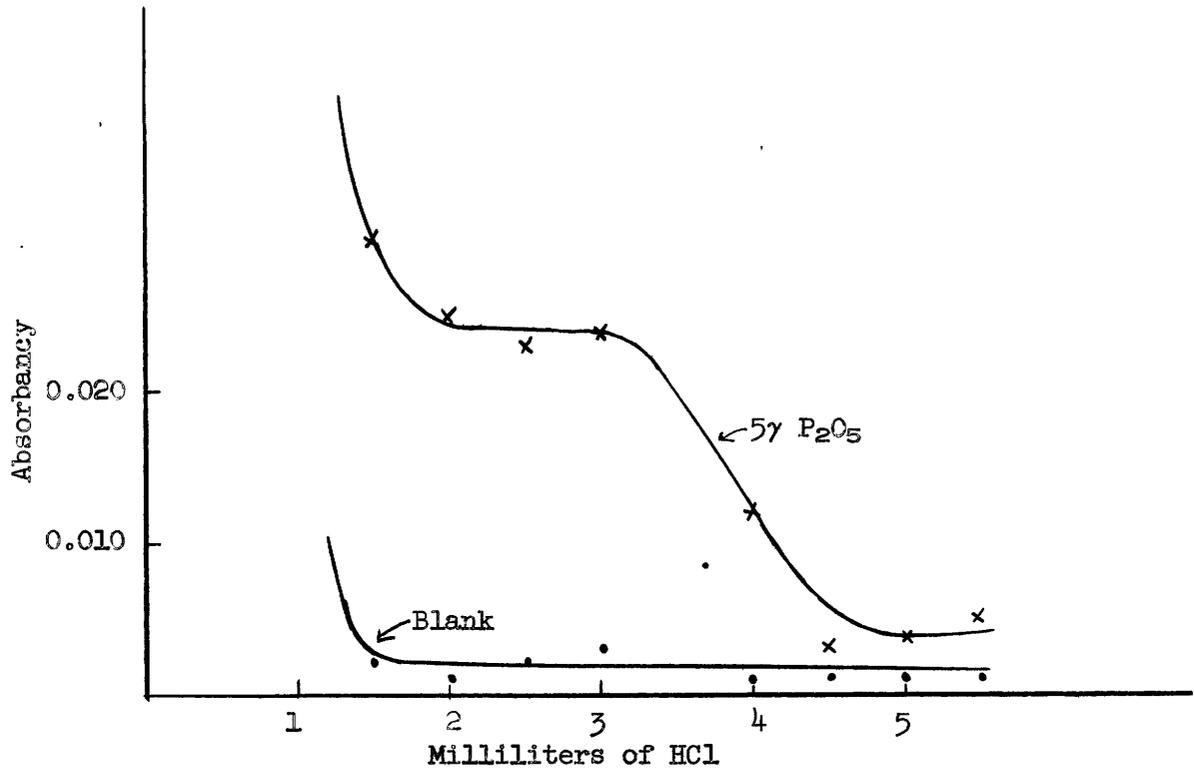


Figure 8.--Effect of acidity on the absorbancy of the phosphate solution.

Total volume: 50 ml

Stannous chloride: 0.3 ml

Molybdate reagent: 5 ml

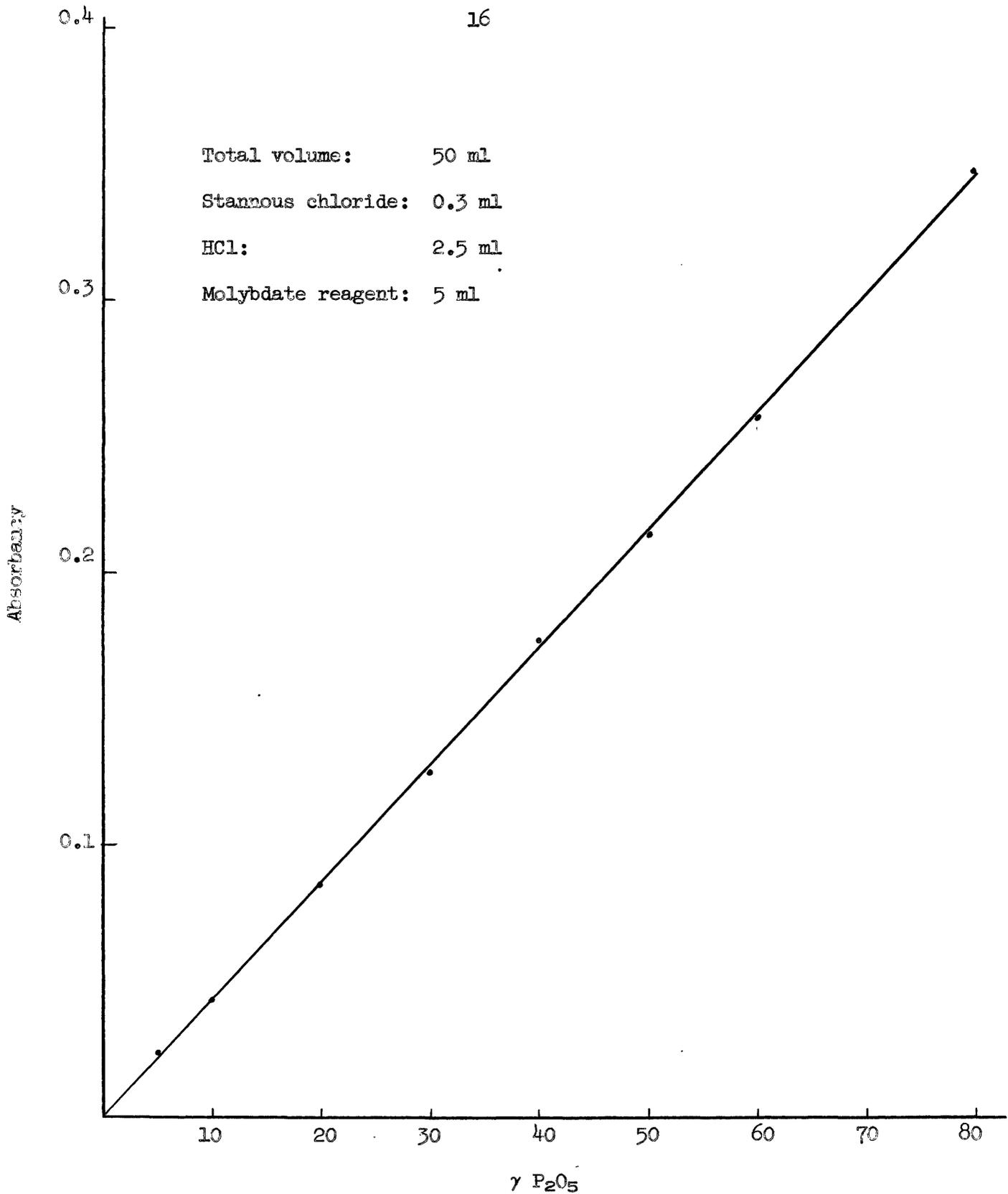


Figure 9.--Working curve for the determination
of phosphorus

The absorbancies of the standards were redetermined after allowing the solutions to stand for 1 hour; the change in absorbancy averaged a decrease of 5 percent. The absorption curve, figure 10, shows optimum wave length at 735 m μ .

Behavior of arsenic, germanium and silicon

The interference of As (III), As (V), Ge, and Si were checked, under optimum conditions for phosphate, by determining the absorbancy of 25 γ of each of the oxides of these elements alone and in the presence of 5 γ P₂O₅. The absorbancies were additive. The extent of interference of these elements is summarized as follows:

25 γ As₂O₅ equivalent to 8 γ P₂O₅

25 γ As₂O₃ equivalent to <1 γ P₂O₅

25 γ GeO₂ equivalent to 2.5 γ P₂O₅

25 γ SiO₂ equivalent to 2 γ P₂O₅

Recovery of phosphate by coprecipitation with aluminum hydroxide

The following procedure was used to test the recovery of microgram amounts of P₂O₅ by coprecipitation with aluminum hydroxide. Ammonium hydroxide was added dropwise to a hot solution containing known amounts of P₂O₅, 3 ml of HCl, and 10 ml of aluminum chloride solution (1 ml = 0.002 g Al₂O₃) all in a total volume of 60 ml, until methyl red was just yellow. The precipitate was digested and the solution cooled. The sample was then transferred to a 100-ml centrifuge tube and centrifuged for 10 minutes at about 1700 rpm. This technique was used instead of filtration because it was found that filter paper ash contained appreciable

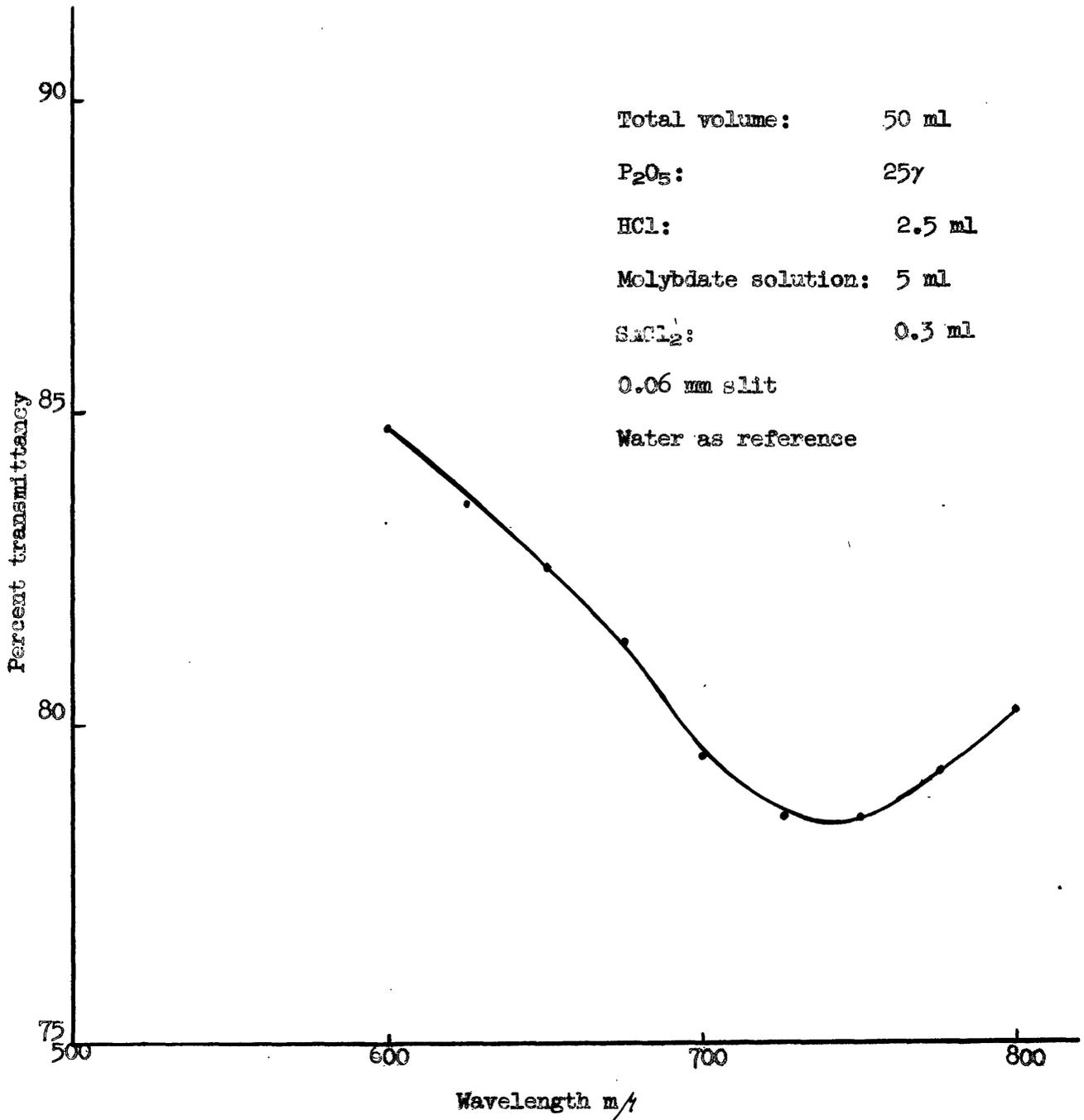


Figure 10.--Absorption curve

amounts of phosphate. The supernatant solution was decanted and the precipitate washed several times by centrifuging after the addition of 15-ml portions of 0.1 percent NH_4Cl solution. The precipitate was then transferred to a platinum dish, 1 ml of HF was added, and the solution evaporated to dryness. The residue was treated twice with 3-ml portions of HCl, evaporating each time to dryness. The residue was then dissolved in (1 + 1) HCl and the phosphorus determined colorimetrically. The listed recoveries corrected for a blank of 47 P_2O_5 are good:

P_2O_5	
<u>Taken</u>	<u>Recovered</u>
5	5.0
10	9.8
20	19.8
50	49.3

Removal of arsenic, germanium, and silicon
by volatilization

Mixtures of phosphate and arsenate, phosphate and germanate, and phosphate and silicate were treated according to the above-described procedure (coprecipitation with aluminum hydroxide). After the final evaporation with HCl the residues were digested with 5 ml of HCl and the solutions then transferred to 50-ml Erlenmeyer flasks. One milliliter of HBr (to reduce arsenate), and 0.2 ml H_2SO_4 were added to each test solution and the samples evaporated to fumes of H_2SO_4 . The solutions were then gently and carefully fumed for an additional two minutes and cooled. Four milliliters of (1 + 1) HCl was added to each sample and the solutions warmed to dissolve the soluble salts. The solutions were then transferred to 50-ml volumetric flasks and the phosphorus determined

according to the standard procedure. The results, corrected for a blank of 4γ P_2O_5 , are given in table 1.

Procedure

Reagents and apparatus

HCl and HBr: Reagent grade, redistill if P_2O_5 blank is high

H_2SO_4 : Reagent grade

HF : Use reagent with low phosphate blank. Preferably the reagent should be redistilled from a platinum still.

H_2O : Doubly distilled from Pyrex glass

NH_4OH : Prepare by bubbling tank NH_3 into doubly distilled water.

$AlCl_3$: Solution, 1 ml = 0.002 g Al_2O_3 . Dissolve 0.95 g $AlCl_3 \cdot 6H_2O$ in 100 ml of H_2O .

Standard phosphate solution A, 1 ml = 0.0001 g P_2O_5 : Dissolve 0.1917 g KH_2PO_4 in 1000 ml water.

Standard phosphate solution B, 1 ml = 2γ P_2O_5 : Take 10 ml of solution A and make to 1000 ml with water.

Stannous chloride solution A, 5%: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 10 ml of hot (1 + 1) HCl and dilute to 100 ml with water. This solution may be kept for about a week.

Stannous chloride solution B, 0.5%: Take 10 ml of solution A and dilute to 100 ml with water. Prepare a fresh solution daily.

Ammonium molybdate solution, 2%: Dissolve 2 g $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ in 100 ml of water.

Spectrophotometer: The Beckman Model DU, with 1-cm corex cells.

Centrifuge.

Table 1.--Recoveries of phosphate after volatilization of
 AsCl_3 , GeCl_4 , and SiF_4 .

P_2O_5 taken (γ)	As_2O_5 taken (mg)	GeO_2 taken (mg)	SiO_2 taken (mg)	P_2O_5 found (γ)
10.0	0.01	--	--	10.2
30.0	0.01	--	--	30.4
10.0	0.10	--	--	10.0
30.0	0.10	--	--	30.0
10.0	1.0	--	--	10.7
30.0	1.0	--	--	30.9
10.0	--	--	0.01	10.2
30.0	--	--	0.01	31.0
10.0	--	--	0.10	9.8
30.0	--	--	0.10	30.5
10.0	--	--	1.0	11.0
30.0	--	--	1.0	31.5
10.0	--	0.01	--	10.5
30.0	--	0.01	--	31.6
10.0	--	0.10	--	10.6
30.0	--	0.10	--	30.5
10.0	--	1.0	--	10.7
30.0	--	1.0	--	32.0

Determination of phosphorus

1. Pipet 100 ml of sea water into a clean porcelain dish and evaporate the solution to dryness on the steam bath.
2. Destroy organic matter by placing the dish in a furnace and heating for about 30 minutes at 600 C. Cool.
3. Add 6 ml of (1 + 1) HCl and digest the solution. Add 35 ml of water and digest again to dissolve salts.
4. Add 10 ml of AlCl_3 solution, heat to gentle boil, and add NH_4OH until methyl red is just yellow. Digest the solution on the bath for a few minutes. Cool.
5. Transfer the contents to a centrifuge tube and centrifuge for 10 minutes at 1500-2000 rpm. Decant clear solution. Wash the precipitate twice by centrifuging with two 15-ml portions of 0.1 percent NH_4Cl , discarding the clear solutions.
6. Transfer the precipitate to a small platinum dish. Add several drops of HCl, 1 ml of HF, and evaporate to dryness on the steam bath.
7. Add 5 ml of HCl and take to dryness.
8. Add 1 to 2 ml of HCl and 5 ml of water, digest to dissolve salts, and transfer the solution to a small Erlenmeyer flask. Add 1 ml HBr and 0.2 ml H_2SO_4 and evaporate to fumes of H_2SO_4 .
9. Fume gently for a few minutes to remove any HBr and bromine. Cool.
10. Add 2.00 ml of HCl and wash sides of flask down with water. Add water to make to 30 ml and digest the solution a few minutes to obtain a clear solution. Cool.

11. Transfer the solution to a 50-ml volumetric flask. Add 5 ml of ammonium molybdate solution. Adjust volume to 45 ml and mix.
12. Add 0.3 ml of stannous chloride solution B. Make to volume and mix.
13. Measure the absorbancy of the solution within 30 minutes on a spectrophotometer at 735 *m μ* . Use 0.06 mm slit, setting water at 100 percent transmission.
14. Obtain phosphorus content by reference to a standard curve. A blank should be run along with the samples and its value deducted.

Test of procedure

Two series of experiments were made to test the procedure. In the first series distilled water was used to which various amounts of P, As (V), Si, and Ge were added. In the second series a sample of sea water from the Gulf of Mexico was used to which was added various amounts of the same elements. The total phosphorus content of the sea water was first established by running quintuplet determinations. The values found in 100 ml of sea water were 1.9 γ , 1.5 γ , 1.6 γ , 1.9 γ , and 1.6 γ after subtracting an average blank of 4 γ . The results given in table 2 indicate good recoveries of added phosphate.

Table 2.--Test of procedure to determine phosphorus

	<u>1</u> P ₂ O ₅ in sample (γ)	<u>2</u> P ₂ O ₅ added (γ)	<u>3</u> As ₂ O ₅ taken (mg)	<u>4</u> GeO ₂ taken (mg)	<u>5</u> SiO ₂ taken (mg)	Total P ₂ O ₅ (cols 1 + 2) (γ)	Total P ₂ O ₅ found (γ)
Series 1	--	5.0	0.01	0.01	0.01	5.0	5.0
	--	20.0	0.01	0.01	0.01	20.0	18.8
	--	5.0	0.10	0.10	0.10	5.0	5.3
	--	20.0	0.10	0.10	0.10	20.0	19.0
	--	5.0	1.0	1.0	1.0	5.0	5.2
	--	20.0	1.0	1.0	1.0	20.0	20.0
Series 2	1.7	3.3	0.01	0.01	0.01	5.0	5.3
	1.7	18.3	0.01	0.01	0.01	20.0	18.5
	1.7	3.3	0.02	0.02	0.02	5.0	4.5
	1.7	18.3	0.02	0.02	0.02	20.0	19.2
	1.7	3.3	0.03	0.03	0.03	5.0	5.0
	1.7	18.3	0.03	0.03	0.03	20.0	20.1
	1.7	3.3	0.05	0.05	0.05	5.0	5.3
	1.7	18.3	0.05	0.05	0.05	20.0	19.8
	1.7	3.3	0.10	0.10	0.10	5.0	5.5
	1.7	18.3	0.10	0.10	0.10	20.0	19.3
	1.7	3.3	1.0	1.0	1.0	5.0	6.8
	1.7	18.3	1.0	1.0	1.0	20.0	19.5

THE PHOSPHATE CONTENT OF SAMPLES OF SEA WATER FROM
THE GULF OF MEXICO

Total phosphorus was determined in duplicate on five samples of sea water collected off the Gulf of Mexico. The values found, table 3, ranged from 1.8 to 5.9×10^{-6} percent P_2O_5 .

Table 3.--The phosphate content of sea water from the Gulf of Mexico. (All water samples taken on June 12, 1952)

Sample no.	Location	Sample depth (meters)	Percent P_2O_5 $\times 10^{-6}$
55	Station 15: (Water depth 100 fathoms) Lat. $26^{\circ}08'$ Long. $84^{\circ}19'$	50	2.0 2.2
57	Station 15: Lat. $26^{\circ}08'$ Long. $84^{\circ}19'$	140	2.2 2.4
58	Station 15: Lat. $26^{\circ}08'$ Long. $84^{\circ}19'$	182	5.5 6.3
59	Station 16: (Water depth 100 fathoms) Lat. $26^{\circ}47'$ Long. $84^{\circ}33'$	0	1.7 1.9
60	Station 16: Lat. $26^{\circ}47'$ Long. $84^{\circ}33'$	25	1.8 1.9

REFERENCES

- Denigés, G., 1920, Reaction de coloration extrêmement sensible des phosphates et des arseniates: Acad. Sci. Paris Comptes rendus 171, pp. 802-804.
- Fiske, C. H., and Subbarow, Y., 1925, Colorimetric determination of phosphorus: Jour. Biol. Chemistry, vol. 66, pp. 375-400.
- Harvey, H. W., 1948, The estimation of phosphate and total phosphorus in sea waters: Jour. Marine Biol. Assoc., vol. 27, pp. 337-359.
- Kalle, K., 1935, Meereskundliche Chemische Untersuchungen mit Hilfe des Zeisschen Pulfrich-Photometers. V. Die Bestimmung des Gesamt-Phosphorgehaltes, des Plankton-Phosphorgehaltes (lebende Substanz) und Trübungsmessungen: Annalen der Hydrographie, Jahrg. 63, pp. 195-204.
- Redfield, A. C., Smith, H. P., and Ketchum, B., 1937, The cycle of organic phosphorus in the Gulf of Maine: Woods Hole Biol. Bull. 73, pp. 421-443.
- Woods, J. T., and Mellon, M. G., 1941, The molybdenum blue reaction: Ind. and Eng. Chemistry, Anal. Ed. 13, pp. 760-764.
- Zinzadze, C., 1935, Colorimetric methods for the determination of phosphorus in presence of silica, arsenic, iron and nitrate: Ind. and Eng. Chemistry, Anal. Ed. 7, pp. 227-230.