

12-TUNGSTOPHOSPHORIC ACID AND THE DETERMINATION OF PHOSPHATE

STUDIES ON THE FORMATION OF 12-TUNGSTOPHOSPHORIC ACID:
APPLICATION TO THE DETERMINATION OF PHOSPHATE

BY

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ABSTRACT

A new extraction-spectrophotometric method has been developed for the determination of phosphorus as orthophosphate. The method is based on the chemistry of the 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ (TPA). In the method, the TPA is formed in aqueous solution from tungstate, phosphate and acid and is subsequently extracted into n-amyl alcohol. The formation of TPA was studied as a function of reagent concentration (e.g., tungstate and phosphate), pH, time and temperature. For particular molar ratios of tungstate and phosphate, quantitative formation of TPA occurred instantly when the pH was 1.3-1.9 and the solution heated to 60-100°C. Under the conditions, Beer's law was found to be valid over the entire range of phosphate concentrations studied (0-25 ppm P). The method was successfully applied to a wide variety of phosphorus-containing materials and was found to be less prone to solution conditions and interfering species [especially As(V) and Si(IV)] than the widely used molybdenum-blue and molybdovanado-phosphate methods. The accuracy, precision and sensitivity of the TPA method is at least competitive with these methods.

Under similar conditions, TPA was found to form from paratungstate Z and freshly-precipitated white tungstic oxide. From the metatungstate, TPA could be formed only in very acidic solution. It was not formed at all from yellow tungstic oxide.

Since the formation of isopolytungstates is very relevant to the

IPA method for the determination of phosphorus, appropriate studies of these species were made. These studies resulted in a re-interpretation of the point-titration curve of tungstate solutions, and in the discovery that a poorly-defined species called polytungstate Y is stable in n-amyl alcohol, from which it can perhaps be characterized. The extractability of isopoly species into n-amyl alcohol was studied as a function of pH. The results of this study were important with regard to the analytical application of TPA.

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I. INTRODUCTION

I. A. OCCURRENCE OF PHOSPHORUS

The abundance of phosphorus on earth is not large (TABLE I). The element occurs in nature* almost exclusively as orthophosphate. (1,2) In addition, soil contains several organic non-orthophosphate compounds derived mainly from residues of plant materials and dead or living micro- and macro- organisms. These constitute about 30-70% of the total phosphorus in soil. (4) In natural waters, phosphorus exists as dissolved inorganic or organic phosphates, as insoluble or adsorbed phosphates or as organically-combined phosphorus in suspended matter (5,6) (TABLES IIA and IIB). Dissolved phosphate results from natural weathering and dissolution of phosphate minerals, soil erosion, biological transfer and man-made pollution. Organic phosphorus compounds in natural waters, which account for 30-60% of the total phosphorus, are the products of biological growth.

* A large number of inorganic and organic phosphorus compounds unknown in nature have also been synthesized and these, together with the naturally-occurring compounds, have been used extensively in industry (e.g., as plasticizers, oil and gasoline additives, detergents, flame-proofing materials, toothpaste, polishing agents, pesticides, pyrotechnics and fertilizers). (1,3)

TABLE I

Abundance of Phosphorus

| Location | Mean weight. (%P) |
|---------------|---|
| Earth's crust | 0.12 |
| Ocean | 7×10^{-6} (0.07 ppm; <0.03 ppm in upper layers)* |
| Meteorites | 0.19 |
| Moon | 0.06 |

* <0.03 ppm as dissolved P

TABLE IIA

Forms of Dissolved Phosphorus in Natural-Water

Systems. (6)

| Form | Representative species |
|---------------------------------|--|
| Orthophosphate | $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , $FeHPO_4^+$ $CaH_2PO_4^+$ |
| Inorganic Condensed Phosphates: | |
| Pyrophosphates | $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$ $CaP_2O_7^{2-}$, $MnP_2O_7^{2-}$ |
| Triphosphates | $H_2P_3O_{10}^{3-}$, $HP_3O_{10}^{4-}$, $P_3O_{10}^{5-}$ $CaP_3O_{10}^{3-}$ |
| Metaphosphates | $HP_3O_9^{2-}$, $P_3O_9^{3-}$, $CaP_3O_9^-$ |
| Organic orthophosphates | Sugar phosphates, inositol phosphates, phospholipids, phosphoamides and phosphoproteins. |
| Organic condensed phosphates | Adenosine-5'-triphosphate |
| Pesticides | $O_2N-C_6H_4-OPS(OCH_3)_2$, etc. |

TABLE IIB

Solid-phase Forms of Phosphorus in Natural Water Systems. (6)

| Form | Representative groups or species |
|--|---|
| Solid and rock mineral phases | $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ (hydroxyapatite) |
| Mixed phases, solid solutions, sorbed phases, etc. | Clay phosphate, clay organo-phosphate, metal hydroxide- inositol phosphate |
| Suspended or insoluble organic phosphorus | bacterial cell material, plankton material, plant debris and proteins |

Phosphorus is an important constituent of protoplasm. Every form of energy exchange within the living cell involves phosphorus-containing compounds such as adenosine triphosphate. (7,8)

Phosphorus is one of the essential nutrients sustaining aquatic life. Luxuriant growth of algae and other aquatic plants is reported to occur at a phosphate-phosphorus concentration of 0.02 ppm. (9-11) In the upper layers of the oceans, the mean phosphate-phosphorus concentration is less than 0.03 ppm, (12) while in the upper levels of unpolluted fresh-water bodies, it is of the order of 10^{-2} to 10^{-4} ppm. (13) However, the phosphate concentration in waste waters from municipal sewage effluents, industrial drainage and agricultural run-off is higher by 3 to 4 orders of magnitude. Municipal sewage, for example, contains 1 to 25 ppm of phosphorus,* derived mainly from polyphosphate detergents. (15,16) The release of waste water into rivers and lakes may increase the phosphate concentration to ppm levels and cause excessive growth of algae (eutrophication) and depletion of dissolved oxygen in the water. This action, in turn, leads to fish kills and the development of anaerobic zones in which bacterial action produces foul odours and undesirable tastes, resulting in the deterioration of fresh-water quality. (16) It is, therefore, important to limit the amount of phosphorus released into the water environment. The Canada Water Act (17,18) and the Water Quality Act in the U.S.A. (16) set the

* In Ontario, the total concentration of phosphorus in sewage is found to vary from 2.3 to 18 ppm. (14)

critical concentration of total phosphorus in lakes at 0.017 ppm and 0.015 ppm, respectively. Above these values, algae blooms could be expected.

An understanding of the role of phosphorus compounds in areas such as the environmental and biological sciences could not progress to an advanced state without suitable methods for the quantitative determination of organic and inorganic phosphate.⁽¹⁹⁾ The currently accepted methods for the determination of trace amounts of phosphate are beset with certain drawbacks and these are discussed below.

I. B. ANALYTICAL CHEMISTRY OF ORTHOPHOSPHATE

1: General

The separation, identification, characterization and the quantitative estimation of phosphorus-containing species have required the use of virtually all the available techniques of analytical chemistry. These range from the classical methods of chromatography, gravimetry, titrimetry and spectrophotometry to the sophisticated techniques of X-ray, high resolution mass- and nmr spectroscopy.

This thesis is concerned with the development of an analytical method for the determination of phosphorus based on the chemistry of the orthophosphate ion, PO_4^{-3} . Methods which allow the estimation of phosphorus as PO_4^{-3} are of particular importance in studies relating to natural waters, biological systems, soils, minerals, ores, alloys, fertilizers, food stuffs, pesticides and other products.⁽¹⁹⁾ In these systems and materials, the total phosphorus content is obtained by converting all bound phosphorus not already in the orthophosphate form

to PO_4^{-3} . For example, inorganic polyphosphates are acid-hydrolyzed to PO_4^{-3} ; organophosphorus compounds are oxidized either by wet digestion or by oxygen-flask combustion. A discussion of the methods that deal with the determination of orthophosphate follows. Particular emphasis is given to spectrophotometric procedures involving the formation of the molybdophosphate complexes.

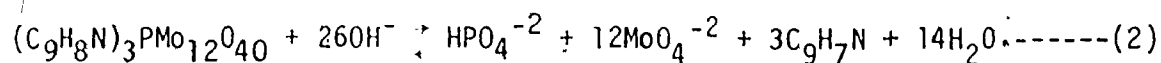
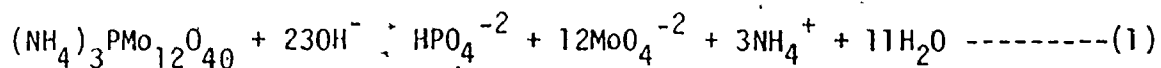
2. Determination of Orthophosphate

(a) Gravimetric methods

According to Boltz⁽²⁰⁾, the three important gravimetric methods are based on the precipitation of magnesium ammonium phosphate hexahydrate $[\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}]$, ammonium molybdophosphate $[(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}]$ and quinolinium molybdophosphate $[(\text{C}_9\text{H}_8\text{N})_3\text{PMo}_{12}\text{O}_{40}]$. Each method suffers from several cationic and anionic interferences and from unstable weighing forms. (20,21) In addition, gravimetric procedures are slow and tedious, particularly in situations where a large number of determinations are required.

(b) Titrimetric methods

Of the several titrimetric methods available, those based on the determination of total acidity associated with either the ammonium- or quinolinium molybdophosphate are the most popular. The following equations represent the stoichiometry involved.



Since precipitation of phosphorus as ammonium- or quinolinium molybdophosphate precedes the actual titration, these methods are susceptible to the same interferences as in the gravimetric procedures.

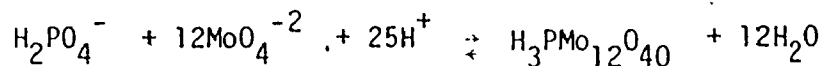
Apart from problems of interference, both the gravimetric and titrimetric methods are not as sensitive as spectrophotometric methods for materials containing less than 0.1% phosphorus. (20,21)

(c) Spectrophotometric methods

These are by far the most widely used methods, particularly the procedures based on molybdophosphoric acid and its subsequent reduction to the heteropoly blue species. Although faster and more sensitive than the gravimetric and titrimetric methods referred to above, these methods suffer other disadvantages as discussed below. The better known spectrophotometric procedures are summarized in TABLE III. (22-37)

The 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$ or MPA), which is formed in aqueous solution from molybdate, phosphate and acid*, has a low molar extinction coefficient (TABLE III). (22,23) In addition, while a heptapoly molybdate ($Mo_7O_{24}^{-6}$) is formed in the sample solution, the reference solution contains an octapoly molybdate ($Mo_8O_{26}^{-4}$). (38) The resulting difference spectrum overlaps with the desired MPA spectrum and causes a systematic error. Arsenic, silicon, germanium and vanadium also interfere by forming the corresponding heteropoly molybdates which absorb in the same uv region as MPA. Attempts have been made to

* Formally, the reaction may be represented as:



The actual mechanism is not known.

TABLE III

Summary of Spectrophotometric Methods for the Trace Determination of Phosphate*

| Method | Medium | Preferred wavelength of measurement (nm) | Molar absorptivity (litre/mol/cm) | Optimum range (ppm) | Reference |
|--|--|--|-----------------------------------|---------------------|-----------|
| 1. 12-Molybdophosphoric Acid (MPA) | i. Aqueous | 380-400 | $(1.0-1.2) \times 10^3$ | 2-15 | 22,23 |
| | ii. Organic (20% isobutanol in chloroform) | 310-315 | 2.4×10^4 | 0.1-1.2 | 24 |
| 2. MPA-extraction, decomposition and subsequent determination of P by the indirect determination of Mo as: | | | | | |
| | a. MoO_4^{-2} | in aqueous ammonia (pH 9) | 230 | 5.7×10^4 | 0.1-0.5 |
| b. thiocyanate complex of Mo (V) | aqueous and SnCl_2 | 475 | 1.9×10^5 | 0.02-1.0 | 27 |

TABLE III (Continued)

| Method | Medium | Preferred wavelength of measurement (nm) | Molar absorptivity (litre/mol/cm) | Optimum range (ppm) | Reference |
|---|--|--|--|----------------------|-------------|
| c. 2-amino naphthol-4-chloro-benzenethiol complex of Mo(VI) | organic (CHCl ₃) | 710-720 | 9.7X10 ⁴ | 0.4-1.6 | 28 |
| d. phenylfluorone complex of Mo(VI) | organic (60% alcohol) | 523 | 5.2X10 ⁵ | 2-10 | 29 |
| e. acid chrome violet complex of Mo(VI) | organic | 570 | 5.3X10 ⁴ | 0.6-16.0 | 30 |
| 3. MPA-reduction to blue | i. aqueous ii. organic (isobutanol) | 820-830 720-735 | 2.7X10 ⁴ 2.3X10 ⁴ | 0.1-1.0** 0.2-1.5 | 31 32,33 |
| 4. Molybdovanado-phosphate | i. aqueous ii. organic (1-pentanol) | 400 308 | 5.6X10 ² 2.5X10 ⁴ | 0.75-5.5 0.2-1.1 | 34,35 36 |

* Many publications, each with slight modifications, exist for each of the methods listed in TABLE III. The data quoted in the TABLE are those reported by the authors who first developed the method for analytical use.

** Although it is usual to use the molybdenum blue method in the range 0.1-1.0 ppm, the method can apparently be used down to the level of 7 ppb P. (37)

overcome these interferences and to increase the sensitivity by extraction of the MPA and measurement of its absorbance in the organic extract. (24) The most selective solvent for MPA (i.e., butyl acetate) however, does not lead to a good phase separation and is not ideal for use. Another solvent (20% isobutanol in chloroform) yields a good phase separation, but is not as selective; it extracts the corresponding heteropolymolybdates of arsenic and silicon, and thus fails to overcome the interference from these elements. (24) In both extraction procedures, the concentration of molybdate in the aqueous phase is critical. It should be high enough to form the MPA but low enough to avoid appreciable formation of isopolymolybdates which subsequently are extracted.

Boltz et al (25,26) modified the method by decomposing the extracted MPA with $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer in a back-extraction and measuring the absorbance of the resultant molybdate ion at 230 nm. In this manner, advantage could be taken of the 12:1 stoichiometric ratio and of the higher molar absorptivity of the MoO_4^{-2} to increase the sensitivity. For reasons unknown, no significant increase in sensitivity over the direct extraction procedure is achieved. Furthermore, the method has serious shortcomings. A 20% mixture of isobutanol in ether is used as the extracting solvent. During the process of back-extraction, some isobutanol is carried into the aqueous buffer system. (39) At the same time, the extracted isopoly species undergo decomposition to give MoO_4^{-2} . Thus, the observed absorbance is made up of contributions from the absorption of isobutanol and from the absorption of MoO_4^{-2} derived from MPA and isopolymolybdates.

The difficulties associated with the absorption of isopoly-molybdates and organic solvents in the uv region can be avoided by shifting the analytical wavelength to the visible region. Thus, MoO_4^{-2} has been complexed with 2-aminonaphthol-4-chlorobenzenethiol hydrochloride,⁽²⁸⁾ phenyl fluorone,⁽²⁹⁾ or acid-chrome violet.⁽³⁰⁾ In each case, the colour development is slow (> 15 minutes) and the complexes are unstable (lifetime < 30 minutes). Experimental conditions such as pH, reagent concentration and time of extraction are critical. Fe(III), Sn(II), W(VI), Cr(III), Sb(V) and Ge(IV) interfere by giving coloured compounds.

In a slightly different approach, Mo(V) obtained by reduction of MoO_4^{-2} with stannous chloride and ferrous ammonium sulphate has been complexed with thiocyanate ion.⁽²⁷⁾ Serious interference can arise, however, from arsenate, silicate, tungstate, vanadate and from the complexation of ferric ion with thiocyanate. The colour of the Mo(V) thiocyanate complex is not stable.

The molybdovanadophosphate (MVP) method, first introduced by Nilsson,⁽⁴⁰⁾ involves measurement of the heteropoly acid formed from molybdate, dihydrogen phosphate, vanadate and acid under appropriate conditions. The absorption in the visible region is measured either in the aqueous phase^(34,35) or in the organic phase after extraction.⁽³⁶⁾ Whereas some investigators^(34,41-44) recommend the use of a mixed

reagent containing both the molybdate and vanadate, others⁽⁴⁵⁾ prefer the use of separate reagents, since the colour is developed quickly only if the reagents are added in the order: acid, vanadate, molybdate and phosphate.⁽⁴⁵⁾ Any variation from this order of addition results in other complexes and/or precipitates which are only slowly converted into the desired form. The complex is of uncertain composition and is stable only for two hours.⁽⁴⁵⁾ The exact wavelength chosen for measurement ranges from 310 nm⁽³⁵⁾ to 400 nm,^(41,45) depending on the particular experimental conditions employed. Measurements beyond 400 nm are not uncommon when Fe(III) and Cr(VI) interfere.⁽²¹⁾

The molybdenum blue method is the most popular of all the existing analytical methods for the determination of phosphate. It is widely used, for example, in the analysis of natural waters.^(12,46) The method is based on the measurement, either in the aqueous phase or in the organic phase after extraction, of the blue colour which develops when MPA is reduced under appropriate conditions.

The numerous publications on the method clearly indicate that the intensity and the stability of colour, the position of the peak maxima and the extent of interference, are all sensitive to the choice and concentration of the reductant, the concentration of molybdate and acid, standing time, temperature and even the nature of the organic solvent used for the extraction of MPA.⁽⁴⁷⁻⁵³⁾ If stannous chloride, for example, is used as the reducing agent, the acid to molybdate ratio is very critical.⁽⁵⁴⁾ When the molybdate concentration is greater than $5 \times 10^{-3} M$ and the acidity is less than 0.7M, reduction of condensed isopolymolybdate occurs to give a blue colour even when no phosphate is

present.⁽⁵⁴⁾ At acid concentrations greater than 1M, the intensity of the heteropoly blue is diminished. Measurements should be made quickly since the colour intensity varies with time.^(54,55) Thus, conditions must be found in which maximum sensitivity in the presence of phosphate is combined with minimum absorbance in its absence.⁽⁵⁶⁾

The difficulty of the stannous chloride procedure has led to the development of methods involving other reductants such as hydrazine sulphate,⁽⁵⁰⁾ sodium bisulphite,^(57,58) ascorbic acid⁽⁵⁹⁻⁶¹⁾ and 1-amino-2-naphthol-4-sulphonic acid.^(49,62-64) With the possible exception of ascorbic acid, these reductants are no better than stannous chloride. As originally developed, the reduction with ascorbic acid took twelve hours for completion.⁽⁶¹⁾ But Murphy and Riley⁽⁶⁵⁾ found that in the presence of Sb(III),* the colour develops within ten minutes and is stable for at least a day.

According to Burton,⁽⁶⁶⁾ the Murphy-Riley method is now used in more than 90% of the phosphate analyses in marine work. At least two manuals on sea-water analysis^(5,67) strongly recommend its use. The method has been accepted by the Canadian Centre for Inland Waters.⁽⁶⁸⁾ The American Public Health Association has tentatively adopted the

* Presumably, Sb(III) reacts with MPA to form a mixed heteropoly species called molybdoantimonyl phosphate in which the phosphorus to antimony ratio is 1:1. This species is then reduced by ascorbic acid to give the blue species which absorbs at 882 nm. The molybdenum blue formed by reduction of MPA with ascorbic acid in the absence of Sb absorbs at ~ 800 nm.⁽⁶⁵⁾

procedure as one of the standard methods in its latest edition dealing with the analysis of water and waste water.⁽³⁷⁾

The procedure of Murphy and Riley is simpler, faster and more sensitive than the stannous chloride method. Nevertheless, the method is not without serious difficulties. At one ppm phosphorus, no more than 0.01 ppm As, 50 ppm Fe and 10 ppm each of Si and Cu can be tolerated.⁽⁶⁵⁾ Arsenate is returned as its equivalent amount of phosphate (i.e., 75 ppb As = 31 ppb P). Indeed, Levine et al⁽⁶⁹⁾ could find no conditions by which to distinguish phosphate from arsenate with any of the proposed reductants. In most bodies of natural water, the concentration of arsenic is only about 2-3 ppb⁽⁷⁰⁾ and is not a serious interference. But appreciable quantities of the element have been found in the Sargasso sea⁽⁷¹⁾ and in areas where arsenic herbicides have been used for weed control.⁽⁷²⁾ Efforts to overcome the interference of arsenic (as arsenate) by reduction to arsenite* have not been successful, either because of incomplete reduction^(73,74), or because of the instability of the reducing solutions⁽⁷⁵⁻⁷⁷⁾ employed under the conditions of the experiment. Removal of arsenic by volatilization with perchloric acid and bromide is tedious.⁽³²⁾ Finally, a recent study⁽⁷⁸⁾ indicates that Hg(II) which is used as a preservative for water samples, causes a significant positive interference in the determination of phosphate in the range 0-0.08 ppm by the method of Murphy and Riley. The recovery

* Arsenite does not react with molybdate in acid medium to form a heteropoly compound.

of added phosphate is found to range from 135 to 265 percent when the concentration of $Hg(II)$ is increased from 9 to 26 ppm. (78)

In a study of the Murphy-Riley method and its several modifications (see TABLE IV), (4,72,79/81) Hosokawa et al (82) observed two peaks: one at 720 nm due to the molybdoantimonate species (MAA) and the other at 880 nm due to the molybdoantimonyl phosphate species (MAPA). The peak at 720 nm was found to decrease gradually while the peak at 880 nm increased gradually. Thus, although Murphy and Riley claim that the colour develops in 10 minutes and is stable for at least a day, quantitative conversion to MAPA may take several days. Indeed, Strickland and Parsons (5) in their manual recommend that measurement be made within two hours. It is doubtful whether the Murphy-Riley method can be extended* to the determination of more than 2 ppm P since the absorption due to MAPA is reported to shift from 880 nm at one ppm P to 820 nm at 2.6 ppm P. This shift with increasing phosphorus concentration is indicative of a structural change. (81) Also, MAA is reported to precipitate in sea water at a phosphorus concentration greater than 1.2 ppm. (72) The role of Sb(III) (e.g., as a possible catalyst) in the reduction of MPA to the blue is yet to be studied. Finally, in all of the molybdenum blue methods, the chemical nature of the blue species is not entirely known. It has been assumed that the blue species contains the same number of molybdenum atoms as the unreduced MPA and "blues" have been proposed in which Mo is in some combination of either +4 and +5 or +5 and +6 oxidation states. (83-90)

* In the original Murphy-Riley procedure, the range is set between 0.02 to 0.2 ppm P. (65)

TABLE IV

Final Concentrations of Reagents in the Murphy-Riley Method and its Various

Modifications

| Ammonium molybdate tetrahydrate (mg/100 ml) | Ascorbic acid (mg/100 ml) | Antimony (mg/100 ml) | Sulphuric acid (N) | Reference |
|---|---------------------------|----------------------|--------------------|--|
| 96 | 84.5 | 0.80 | 0.40 | Murphy and Riley (1962) ⁶⁵ |
| 55 | 98 | 0.23 | 0.23 | Stephens (1963) ⁷⁹ |
| 27 | 24 | 1.80 | 0.11 | Edwards et al. (1965) ⁷² |
| 48 | 95 | 0.48 | 0.20 | Vogler (1965) ⁸⁰ |
| 55 | 98 | 0.46 | 0.23 | Strickland and Parsons (1968) ⁵ |
| 996 | 400 | 4.0 | 0.40 | Harwood et al. (1969) ⁸¹ |

(d) Miscellaneous methods

A number of instrumental techniques other than spectrophotometry have been used for the determination of phosphorus in the form of phosphate. These include flame photometry,⁽⁹¹⁻⁹⁴⁾ direct and indirect atomic absorption methods,⁽⁹⁵⁻⁹⁷⁾ neutron activation,⁽⁹⁸⁻¹⁰⁰⁾ cathodic stripping chronopotentiometry,⁽¹⁰⁰⁾ x-ray fluorescence spectrometry⁽¹⁰²⁾ and phosphorus-31 fourier transform nmr spectrometry.⁽¹⁰³⁾ In general, they are less sensitive and more tedious than spectrophotometric methods and have not met with popular acceptance. No further discussion of these methods is given here.

Conspicuous by their absence in the above discussion are methods based on the formation of the heteropoly species, 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, (TPA). As the basis of analytical procedures for phosphate-phosphorus, this compound has received little attention. To date, studies on TPA have been superficial and fragmentary. (The extractive behaviour of TPA in a number of oxygenated organic solvents has been examined,^(104,105) but these studies have been concerned primarily with the equilibria involved in the extraction process.) Any hint that TPA might be useful for the trace determination of phosphorus is contained only in one communication by Jean⁽¹⁰⁶⁾ but this worker made no attempts to develop a method for phosphate based on the formation of TPA in solution by combination of tungstate, phosphate and acid.

This thesis presents a study of the tungstophosphate complex as a potential analytical system. The study was deemed justified on the basis of the following points:

- (i) Jean reports⁽¹⁰⁶⁾ the molar absorptivity, ϵ , of TPA to be 4×10^4 litre mol⁻¹ cm⁻¹ at 265-270 nm. If the absorbance can be measured with care to 0.01 units, then the sensitivity attainable in the final measured solution would be 8 ppb P for a one-cm cell. Thus, methods based on TPA for the trace determination of phosphorus would be potentially more sensitive than those based on MPA, molybdenum blue and molybdovanado-phosphate (TABLE III);
- (ii) the possibility exists of less critical control of conditions for the quantitative formation and measurement of TPA than for some of the other procedures;
- (iii) the stability of TPA in aqueous and organic solvents could prove to be superior to that of the heteropoly blue species;
- (iv) the system based on TPA might be subject to fewer interferences, in general, than the existing systems based on the heteropoly molybdates.

I. C. THE SOLUTION CHEMISTRY OF THE ISOPOLYTUNGSTATES

Because of the formation of isopoly tungstates simultaneous to the formation of TPA, an understanding of the chemistry of the isopoly species was thought to be important. This section outlines briefly the chemistry of the isopolytungstates.

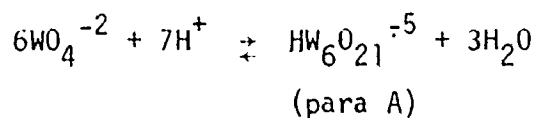
The weak acids formed by the amphoteric metals of group Vb (i.e., vanadium, niobium and tantalum) and group VIb (i.e., chromium, molybdenum and tungsten) of the Periodic Table condense to form anions containing several molecules of the corresponding acid anhydrides. Such condensed acids containing only one type of acid anhydride are called isopoly acids [e.g., $H_2Cr_2O_7$, $H_6Mo_7O_{24}$, $H_6(H_2W_{12}O_{40})$]. If more than one kind of acid anhydride is present, the condensed species are called heteropoly acids (e.g., $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$) and these are discussed in the next section. It is beyond the scope of this INTRODUCTION to deal, in general, with all of the isopoly acids. Their chemistry has been well documented in several reviews⁽¹⁰⁷⁻¹¹⁶⁾ and in chapters in textbooks.⁽¹¹⁷⁻¹²⁶⁾ What follows is a brief introduction to the aqueous solution chemistry of only the isopolytungstates as it pertains to this thesis. Details covering the nomenclature, preparation and solid-state structures of the isopolytungstates have been well reviewed.^(108,111,112,114)

Laurent⁽¹²⁷⁾ in 1847 and subsequently Gibbs⁽¹²⁸⁾ in 1879 classified the tungstates which crystallize from solutions under various conditions as normal, para and meta tungstates. Soon after,

studies by Miolati⁽¹²⁹⁾ and Rosenheim⁽¹³⁰⁾ provided some information on the degree of condensation and the charge of the complex ions formed in acidified solutions of tungstate ion.

Lately, more information on the formation, charge and degree of aggregation of the isopoly tungstates in solution has been obtained through the use of a large number of experimental techniques.⁽¹³¹⁻¹⁵²⁾ A number of reactions have been substantiated, with general agreement among workers as to their occurrence (Figure 1). These are briefly discussed below.

At pH > 8, W(VI) exists in solution as the normal tungstate ion, WO_4^{-2} .⁽¹⁵³⁻¹⁵⁶⁾ In acid solution, however, polymerization of WO_4^{-2} occurs.^(109,111,114,126) Thus at pH 6 and $\rho^{**} = 1.167$, the paratungstate A anion is formed:^(109,111,114)



The equilibrium constant for this reaction is reported to be 10^{54} at 25°C.^(111,148,160) Although paratungstate A is hexameric in solution,^(111,112,131,132,140,148,161-163) its exact composition and structure are unknown. In a slow reaction, paratungstate A comes into equilibrium with a dodecamer called paratungstate Z.^(109,111,112,140,164-166)

* The tetroxo anion, WO_4^{-2} is found in several crystal structures.^(153,155,157-159)

** $\rho = [H^+] / [WO_4^{-2}]$ where the concentrations represent analytical concentrations.

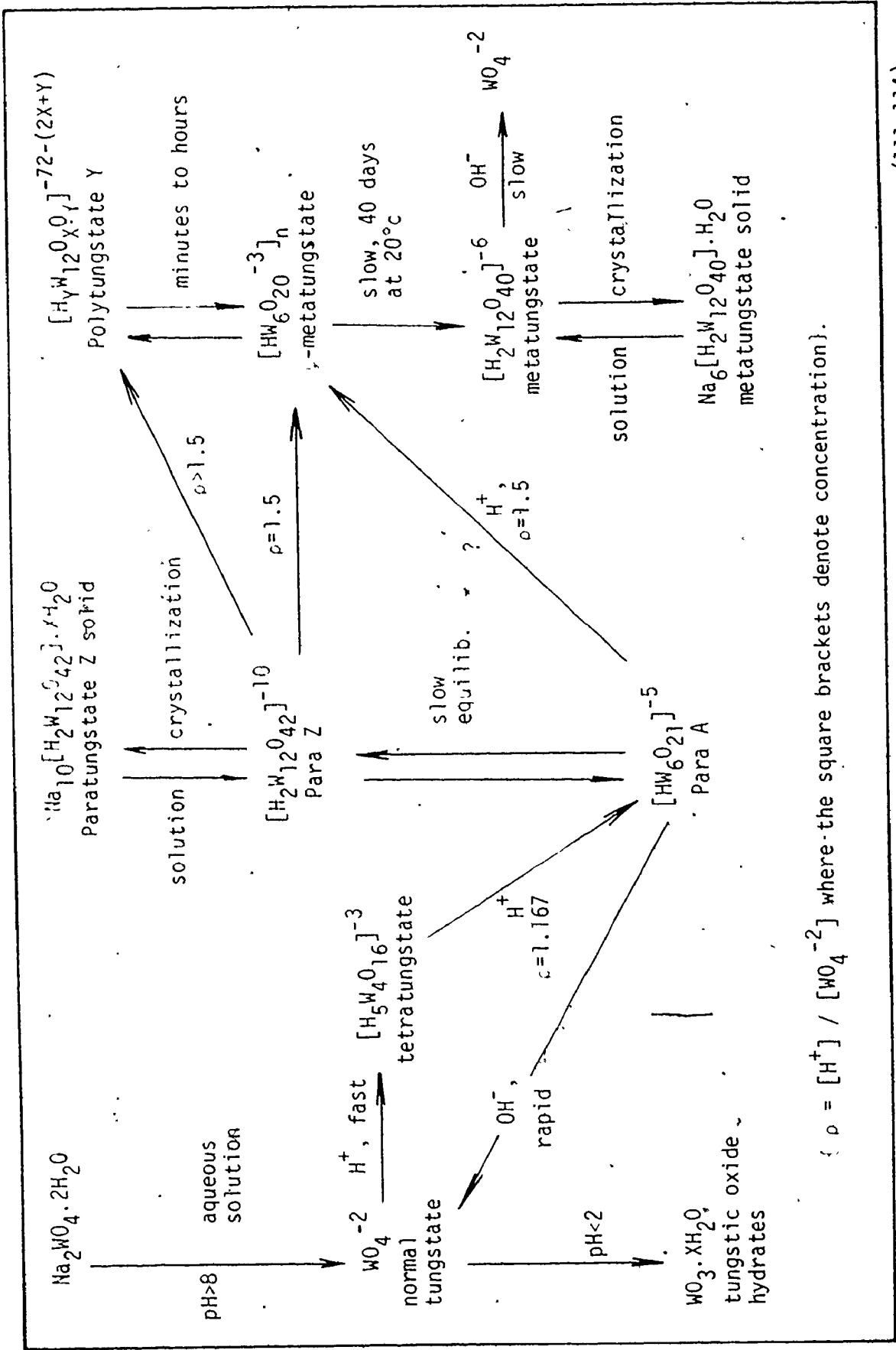
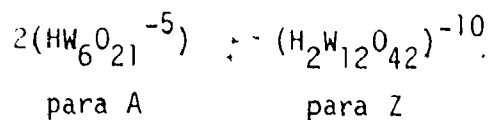


Figure 1. Processes and Species Resulting from Acidification of Tungstate Solutions. (111,114)

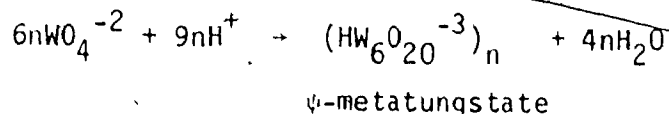
Thus,



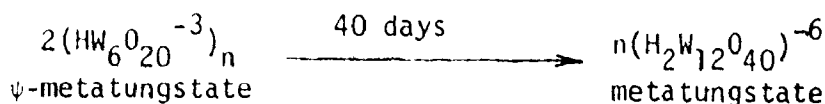
The equilibrium constant for this reaction is $10^{2.1}$ at 25°C . (111)

The dodecameric nature of paratungstate Z has been proved by cryoscopy (112,140) and ultracentrifugation. (148,167)

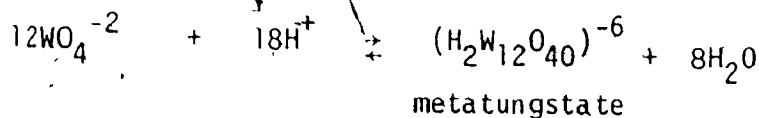
Acidification of a WO_4^{-2} solution to about pH 4 and $\rho=1.5$ yields the so-called ψ -metatungstate anion: (138,140,144)



This reaction appears to occur by the addition of two protons to the paratungstate A anion followed by loss of water. The structure of the ψ -metatungstate is not known and formulae containing 6 to 24 tungsten atoms have been proposed. (111,138,140,144) At room temperature, the ψ -metatungstate changes very slowly into a dodecamer called the metatungstate without change in pH: (141,144)



The metatungstate is formed rapidly, however, on boiling a solution of tungstate ion (WO_4^{-2}) acidified to pH below 4: (148)



The mechanism of this reaction is unknown. The overall equilibrium constant has been estimated to be about 10^{135} at room temperature. (111,148) The metatungstate ion is the most stable of all the isopolytungstates and exists in the pH region <0-10. (126)

Acidification of a solution of tungstate ion or paratungstate Z to about pH 2 at room temperature and $\rho = 2$ leads to the formation of a new dodecamer called the polytungstate Y which is stable only for about an hour. (111) It does not form when a solution of paratungstate or tungstate is boiled under the above conditions. The species is virtually uncharacterized. Above pH 2.5, the poly Y is said to transform into the ψ -metatungstate. (168,169)

A solution of tungstate ion at about pH 1 yields tungstic oxide hydrate ($WO_3 \cdot H_2O$), a creamy white precipitate. At higher acidities (pH < 1), a yellow-green dihydrate ($WO_3 \cdot 2H_2O$) is formed. These oxides appear to be structurally different. (170,171) The tungstate ion on saturation with concentrated acid yields a tungstic cation (WO_2^+). (149) Being unstable the species rapidly converts to the yellow tungstic oxide. (149) Interestingly enough, no isopolytungstates are formed at tungstate concentrations of $\leq 5 \times 10^{-5} M$. (172)

With regard to the above discussion, the interconversion of normal and isopolytungstates is believed to occur through intermediates. These include, for example, di-, (173,174) tri-, (146) and tetratungstates. (172,175,176) Of all the proposed intermediates, there is evidence only for the existence of the tetratungstate. (172,175,176)

Although, the literature on the isopolytungstates has been limited so far to the determination of the average composition and

charge of the polyions, attempts are now being made to elucidate the mechanism of their formation in solution. (177-179)

I. D. THE FORMATION OF THE HETEROPOLYTUNGSTATES

As early as 1826, Berzelius⁽¹⁸⁰⁾ found that molybdate ion reacted with the phosphate ion in acid medium to form a molybdophosphate compound, and in 1862, Marignac⁽¹⁸¹⁾ determined its composition. In 1872, Schiebler⁽¹⁸²⁾ discovered the corresponding tungstophosphate complex. By 1900, a number of these compounds had been reported. Rosenheim,⁽¹⁸³⁾ in 1912, recognized that they were not double salts but belonged to a distinct class and he classified them as heteropoly compounds. Although systematic formulae were soon proposed for these species,^(107,129) it was not until Keggin's X-ray work on tungstophosphoric acid in 1934⁽¹⁸⁴⁾ that structural knowledge became available. Today, heteropoly compounds and their salts form a unique group of polynuclear complexes in which vanadates, molybdates or tungstates condense with a heteroatom in acid medium. The heteroatoms include all elements excepting those of group IA, IIA (other than beryllium), the halogens (other than iodine) and the rare gases. The heteropoly compounds have been reviewed thoroughly.^(107,116-126,185-187) In this work only the chemistry of heteropolytungstates and, in particular, of the 12-tungstophosphate will be discussed:

An important property of the heteropolytungstates (in fact, of all heteropoly compounds) is the ratio of the condensed tungsten atom to the heteroatom. While all integral species from 1:12 to 1:1 have been claimed, only those heteropolytungstates with ratios of 1:12, 1:6 and 2:18 have been well characterized^(186,187) (TABLE V).

TABLE V

Principal Classes of Heteropolytungstates

| Ratio of atoms (X:W) | Central group | Principal heteroatoms (X) | Typical formula | Structure by X-ray | Reference |
|----------------------|-----------------|---|--|--------------------|--------------|
| 1:12 | XO ₄ | B(III); Si(IV), P(V), Al(III), Fe(III), Co(II), Co(III), Cu(I), Cu(II), Zn(II), [Cr(III), Mn(IV), Te(IV)]*, [Ga(III)]** | (X ⁺ⁿ W ₁₂ O ₄₀) ⁻⁽⁸⁻ⁿ⁾ | known | 116, 188-192 |
| 1:6 | XO ₆ | Te(VI), I(VII), Ni(IV) | (X ⁺ⁿ W ₆ O ₂₄) ⁻⁽¹²⁻ⁿ⁾ | known | 193-196 |
| 1:6 | XO ₆ | Ni(II), Ga(III) | (X ⁺ⁿ W ₆ O ₂₄ H ₆) ⁻⁽⁶⁻ⁿ⁾ | known | 192, 197-199 |
| 2:18 | XO ₄ | P(V), As(V) | (X ₂ ⁺ⁿ W ₁₈ O ₆₂) ⁻⁽¹²⁻ⁿ⁾ | known | 200 |

* existence of anion or membership of series requires confirmation.

** closely-related 11-tungstate.

As a class, the heteropolytungstates possess high molecular weight (> 3000 , unusual for an inorganic electrolyte) and extraordinary solubility in water and oxygenated organic solvents (e.g., alcohols, ethers and ketones).⁽²⁰¹⁾ They are more stable to the effects of temperature, acids and reducing agents than the corresponding heteropolymolybdates.^(186,202) Within specific ranges of pH and other experimental conditions, solutions of heteropolytungstates contain only one distinct species of the anion.^(186,203,204) The heteropolytungstates usually decompose above pH 4-5 to yield species with a W to P ratio < 12 to 1. Beyond pH 8, they decompose completely to yield the corresponding oxoanions (e.g., WO_4^{-2} and HPO_4^{-2} in the case of $PW_{12}O_{40}^{-3}$).

The 12-heteropolytungstates have been the most numerous and the most extensively studied. A typical member of this series is 12-tungstophosphoric acid (TPA, $H_3PW_{12}O_{40}$). Keggin⁽¹⁸⁴⁾ was the first to report its exact composition and structure by an X-ray powder analysis of the pentahydrate.* According to Keggin, the best expression for the compound is $H_3P(W_3O_{10})_4$ to indicate a modified PO_4 tetrahedral group in which each of the oxygen atoms has been replaced by a $(W_3O_{10})^{-2}$ group. Four such $(W_3O_{10})^{-2}$ groups are arranged round the central P atom in tetrahedral symmetry so that each oxygen is shared among the three WO_6 octahedra. In addition, each WO_6 octahedron has four of its remaining five oxygens in common with its four nearest neighbours while the

* A recent refinement of its structure shows it to be a hexahydrate, existing as a dioxonium salt, $[(H_5O_2^+)_3 (PW_{12}O_{40}^{-3})]$.⁽²⁰⁵⁾

remaining oxygen is free. The structure of the $\text{PW}_{12}\text{O}_{40}^{-3}$ anion is shown in Figure 2. The water of crystallization is packed in the interstices between the $\text{PW}_{12}\text{O}_{40}^{-3}$ anions. Infra-red studies⁽²⁰⁶⁻²¹²⁾ show that the three protons in TPA ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot\text{XH}_2\text{O}$) exist as oxonium ions. (This is at least in partial agreement with the recent X-ray work).⁽²⁰⁵⁾ The anhydrous compound (i.e., $\text{H}_3\text{PW}_{12}\text{O}_{40}$) exists in the temperature range 200-400°C, according to the results of DTA and TG experiments.⁽²¹³⁻²¹⁸⁾ Broad-line nmr spectra of the anhydrous acid reveals that the three protons are arranged on a triple axis within the sphere of the anion, $(\text{PW}_{12}\text{O}_{40})^{-3}$, and constitute an equilateral triangle to the anion.⁽²¹⁹⁾

The solution chemistry of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is not fully understood. Although in the solid state TPA is triprotic,⁽¹⁸⁴⁾ several physicochemical studies in aqueous solution seem to indicate that it is heptaprotic.⁽²²⁰⁻²²⁶⁾ Other studies suggest that the basicity of TPA is dependent on its concentration.⁽²²⁷⁻²³⁰⁾ Subsequent studies by polarographic and cryoscopic methods, however, suggest that heptabasicity is the result of hydrolysis of TPA to give species of higher charge (e.g., the unstable $\text{PW}_{11}\text{O}_{39}^{-7}$, for which there is little proof).^(231,232)

Hitherto, there has not been much evidence as to the mechanism of formation of the heteropolytungstates in general and TPA in particular. Jander⁽²³³⁾ and Souhay⁽²³⁴⁾ seem to believe that either the paratungstate A or the ψ -metatungstate is a precursor to the formation of the $\text{PW}_{12}\text{O}_{40}^{-3}$ anion. Spitsyn et al.⁽²³⁵⁾, on the contrary, are of the opinion that the isopolytungstates are not involved in the

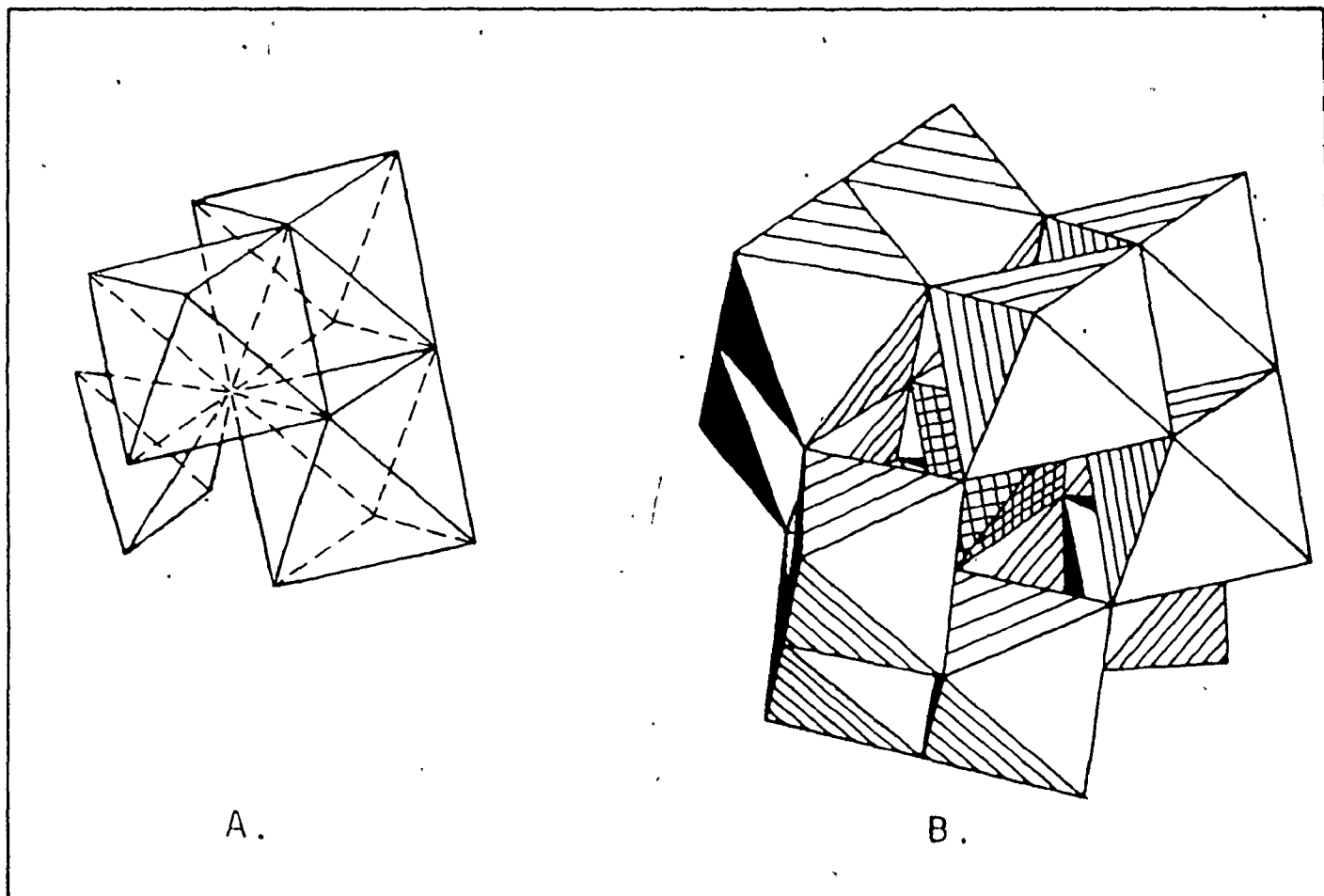


Figure 2. The structure of 12-tungstophosphate anion, $\text{PW}_{12}\text{O}_{40}^{-3}$
 A. One group of three WO_6 octahedra relative to central PO_4 tetrahedron
 B. Complete complex anion, $\text{PW}_{12}\text{O}_{40}^{-3}$

(D.L. Kepert, in "Comprehensive Inorganic Chemistry", J.C. Bailar, Ed.,
 p. 654, Pergamon Press, Oxford, 1973)⁽¹²⁶⁾

formation of TPA.

E. STATEMENT OF THE PROBLEM

This thesis is concerned with the development of an extraction-spectrophotometric method for the determination of phosphorus in the form of orthophosphate. The procedure is based on the chemistry of the 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$. Since the formation of TPA from tungstate, phosphate and acid is the basis for the trace determination of phosphate in the present work, the following aspects have been examined:

1. the optimum experimental conditions (viz., concentrations of tungstate, phosphate and acid, time and temperature) which lead to the quantitative formation of TPA and its subsequent extraction into an organic phase;
2. the pH region in which TPA remains stable without undergoing any hydrolytic decomposition or dissociation to the anion;
3. the concentration ranges in which Beer's law is obeyed;
4. the maximum permissible concentration of interfering elements;
5. the precision and accuracy of the method with respect to those of existing methods;
6. preliminary knowledge on the mechanism of formation of TPA through studies involving its formation from
 - (a) tungstic oxides, phosphate and acid,
 - (b) metatungstate, phosphate and acid, and
 - (c) paratungstate Z, phosphate and acid;
7. the potentiometric and spectrophotometric (uv) behaviour of the

normal tungstate ion in the absence of phosphate under conditions of varying pH, time, temperature and concentration.

II. EXPERIMENTAL SECTION

II. A. REAGENTS AND SOLUTIONS

Reagent-grade chemicals were used throughout the course of this work. Unless otherwise mentioned, these reagents, listed below, were used without further purification.

1. Sodium tungstate dihydrate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ('Baker Analysed' Reagent, J.T. Baker and Company, Phillipsburg, New Jersey). A stock solution of 0.1 M of the reagent was prepared by dissolution of the approximate amount in deionized water and transfer to a polythene bottle. Tungstate solutions less than 0.1 M were prepared by dilution of appropriate aliquots of the 0.1 M solution.

The tungstate stock solution was standardized gravimetrically through tungstyl oxinate, $\text{WO}_2(\text{C}_6\text{H}_7\text{NO})_2$, and barium tungstate, BaWO_4 .⁽²³⁶⁾ The grand average of six determinations was 0.102 ± 0.002 M.

2. Sodium paratungstate, $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot \text{XH}_2\text{O}$ (K & K Laboratories Incorporated, Plainview, New York). The water content of the compound, unspecified on the bottle label, was determined by thermogravimetry and isothermal dehydration. The results corresponded to the formula $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$.

Dilute solutions of the hydrate were prepared freshly as required in deionized water. Each solution was standardized through the determination of tungsten as tungstyl oxinate and of sodium by atomic absorption. The concentration range of the solutions was $(4.05 \pm 0.01) \times 10^{-4}$ M - $(3.99 \pm 0.02) \times 10^{-4}$ M.

3. Sodium metatungstate, $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot\text{XH}_2\text{O}$. The compound was synthesized and purified by the method of Freedman. (170) The water content of the compound, determined by thermogravimetry and isothermal dehydration, corresponded to the formula, $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot 29\text{H}_2\text{O}$.

A stock solution (10^{-3} M) of the metatungstate was prepared in deionized water and stored in a polyethylene bottles. The solution, standardized through the tungstyl oxinate, was $(9.87 \pm 0.02) \times 10^{-4}$ M.

4. 12-tungstophosphoric, -silicic and -germanic acids, $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot\text{XH}_2\text{O}$, $\text{H}_4\text{Si}(\text{Ge})\text{W}_{12}\text{O}_{40}\cdot\text{XH}_2\text{O}$ (Alfa Inorganics, Ventron corporation, Beverly, Massachusetts). $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (TPA) was further purified by four extractions with ether from 2M HClO_4 (aqueous) solution. (237) After evaporation of the ether, the compound was dried at $280\text{-}300^\circ\text{C}$ for 10 hours to yield the anhydrous product. (214-218) $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (TSA) and $\text{H}_4\text{GeW}_{12}\text{O}_{40}$ (TGA) were used without further purification but were obtained in the anhydrous state by heating to $330\text{-}340^\circ\text{C}$ (213,238) and $290\text{-}300^\circ\text{C}$, (239) respectively, for ten hours. All three anhydrous compounds were stored over concentrated sulphuric acid.

The purity of the anhydrous TPA, TSA and TGA was checked by the gravimetric determination of tungsten and the heteroatoms. Tungsten was determined as tungstyl oxinate, phosphorus as both $\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$, (236) silicon as quinolinium silicotungstate, (236) and germanium as GeO_2 through ignition of the tannin complex formed after prior distillation of Ge as GeCl_4 . (236)

Calcd. for $\text{H}_3\text{PW}_{12}\text{O}_{40}$: %W, 76.60; %P, 1.08. Found: %W, 76.57 ± 0.02 ; P, 1.08 ± 0.01 .

Calcd. for $H_4SiW_{12}O_{40}$: %W, 76.64; %Si, 0.98. Found: %W, 76.61 ± 0.02 ;
%Si, 0.97 ± 0.01 .

Calcd. for $H_4GeW_{12}O_{40}$: %W, 75.51; %Ge, 2.48. Found: %W, 75.53 ± 0.01 ;
%Ge, 2.48 ± 0.02 .

Stock solutions (1.0×10^{-3} M) of the anhydrous TPA, TSA and TGA were prepared in deionized water and stored in polyethylene bottles. The solutions were standardized through the determination of tungsten as tungstyl oxinate and found to be: TPA, $(1.01 \pm 0.01) \times 10^{-3}$ M; TSA, $(1.003 \pm 0.002) \times 10^{-3}$ M; and TGA, $(1.02 \pm 0.01) \times 10^{-3}$ M.

5. Tungstic oxide hydrates. Yellow and white tungstic oxide hydrates ($WO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$, respectively) were prepared, purified and dried by the method of Freedman.⁽¹⁷⁰⁾ The compositions were checked by determination of the water content by thermogravimetry and the tungsten content by tungstyl oxinate.

Calcd. for $WO_3 \cdot 2H_2O$: %W, 86.58; %H₂O, 13.42. Found: %W, 85.98 ± 0.04 ;
%H₂O, 13.76 ± 0.06 .

Calcd. for $WO_3 \cdot H_2O$: %W, 92.78; %H₂O, 7.22. Found: %W, 92.53 ± 0.03 ;
%H₂O, 7.44 ± 0.05 .

6. Potassium dihydrogen phosphate, KH_2PO_4 (Primary Standard, 'AnalaR', British Drug Houses Ltd., Poole, England). The compound was dried at 110°C for 6 hours and desiccated. A stock solution (5.0212×10^{-3} M, equivalent to 155.5 ppm P) was prepared with deionized water and stored in an amber glass bottle. Solutions of lower concentration of phosphate were obtained by appropriate dilution.

7. Disodium hydrogen arsenate, $Na_2HASO_4 \cdot 7H_2O$ (Certified ACS reagent, Matheson, Coleman and Bell Inc., Los Angeles, California).

A 0.1M aqueous stock solution of arsenate was prepared. Lower concentrations were obtained by suitable dilution. The stock solution was standardized gravimetrically by determination of the arsenate as $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$.⁽²³⁶⁾ The average of three determinations was 0.1012 ± 0.0003 M.

8. Sodium perchlorate monohydrate, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ('AnalaR', B.D.H.). This salt was used to adjust the ionic strength of the solution under study. The amount required for adjustment was dissolved directly into the solution.

9. Amberlite CG-120, cation exchange resin, $\text{RSO}_3^- \text{Na}^+$ (100-200 mesh, Chromatographic Grade, Mallinkrodt Chemical Works, Montreal). The polystyrene-type resin had a total exchange capacity of 4.5 meq/g of dry resin.

10. Tetra-n-butylammonium hydroxide, supplied as a 25% solution in methanol ('Baker Analysed' Reagent).

11. Methyl ethyl ketone (2-butanone), ('Baker Analysed' Reagent). The ketone was dried over potassium carbonate and then distilled. The fraction boiling between 79.6 - 80.2°C at atmospheric pressure was collected. Traces of water were removed by storage over type 4A Linde Molecular Sieves.⁽²⁴⁰⁾

12. n-Amyl alcohol (n-pentanol), (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin and Fisher Scientific). The solvent, which was more than 99% pure, was dried over K_2CO_3 and distilled. The fraction boiling between 138.0 - 138.2°C at atmospheric pressure was collected.⁽²⁴⁰⁾

13. Quinoline hydrochloride solution, 2%. To 400 ml of hot water containing 12.5 ml of concentrated HCl was added 10 ml of

redistilled quinoline (ACS Certified, Fisher Scientific). The solution was stirred, cooled to room temperature and then paper pulp added with stirring. The solution was filtered by suction through a paper pulp pad and diluted to 500 ml with distilled water. The solution was used in the determination of silicon. (236)

14. Standard perchloric acid solutions. Solutions (1 M and 0.1 M) of perchloric acid were prepared by dilution of appropriate volumes of 70% perchloric acid (ACS Certified, Mallinkrodt Chemical Works) and stored in polythene bottles. Concentrations lower than 0.1 M were obtained by appropriate dilution of the 1 M or 0.1 M solutions.

The stock solutions were standardized by titration with sodium hydroxide using phenolphthalein indicator.

15. Standard sodium hydroxide solutions. Appropriate volumes of a 50% W/V solution of carbonate-free⁽²⁴¹⁾ sodium hydroxide ('AnalaR', B.D.H.) were diluted with freshly boiled distilled water to give approximately 1.0 M and 0.1 M solutions. These solutions were standardized against primary-standard grade potassium hydrogen phthalate ('AnalaR', B.D.H.) using phenolphthalein indicator.

Several other reagents and solutions were used in this work but in a minor way. These were: oxalic acid (ACS certified, McArthur Chemical Co., Montreal); benzoic acid ('AnalaR', B.D.H.); sodium thiosulphate (ACS certified, Fisher Scientific); sodium metabisulphite $\text{Na}_2\text{S}_2\text{O}_5$ (ACS certified, Fisher Scientific); ascorbic acid ('AnalaR', B.D.H.); 8-hydroxyquinoline (Aldrich, recrystallized from petroleum ether); ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ('AnalaR', B.D.H.); ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (ACS certified, Merck & Co.,

Montreal); potassium pyrosulphate, $K_2S_2O_7$ ('AnalaR', B.D.H.); 6 M H_2SO_4 ; 6 M and 1 M NaOH; 1:1 V/V aqueous nitric acid and 30-32% W/W H_2O_2 .

II. B. APPARATUS

Certified volumetric ware was used when appropriate.

An ultra-precision digital micrometer syringe burette (Model S 3200, Gilmont Instruments Inc., New York) was used for dispensing volumes of solutions (e.g., phosphate and arsenate) less than one ml. The instrument is accurate to $\pm 0.02\%$ at full capacity (i.e., at 2.5 ml).

Weighings were made on conventional micro- or semi- micro analytical balances (Type M-5 and B-6, respectively, Mettler).

A Radiometer Model pHM4 meter (Radiometer, Copenhagen) or an Accumet Model 520 Digital pH/Ion Meter (Fisher Scientific Company), each equipped with a fibre-type saturated calomel electrode and a low sodium-ion error glass electrode (Type B-28 and E-2, respectively, Beckman Instruments, Fullerton, California) were used for measurements.

Spectra in the ultraviolet (uv) region were recorded with a Bausch and Lomb Spectronic 600 double-beam spectrophotometer, equipped with a Sargent Model SRL strip-chart recorder (E.H.Sargent and Company, Toronto). Quartz cells (Hellma Cells Inc., Jamaica, New York and 'Spectrosil' cells, Canadian Laboratory Supplies Ltd., Toronto) with path lengths ranging from 50 mm to 0.1 mm were used, depending on sample concentration. The cells were transparent over the range 170-2,500 nm, with transmission better than 80% at 200 nm.

Thermograms were recorded on a Stanton HT-D automatic-recording thermobalance (Stanton Instruments Ltd., London, England) with a sensitivity corresponding to ± 0.1 mg/div for weight loss.

X-ray diffraction powder photographs of 12-tungstophosphoric acid were obtained by radiation of samples in a 57.3-mm diameter Debye-Scherrer camera with nickel-filtered CuK_α radiation emitted by a Philips PW 1011 X-ray generator (Philips Scientific Equipment, Holland).

Atomic-absorption measurements of sodium ion were made with a dual-beam instrument (Model DCRI, Perkin-Elmer Corporation, Norwalk, Connecticut). A sodium hollow-cathode lamp was used (Type WL 23059A, Pyrex window, neon-gas filled, maximum current, 12 ma, Westinghouse, U.S.A.). Measurements were made at 5890 nm using a fuel-lean air/acetylene flame.

The potentiometric-titration apparatus for the study of the condensation reactions of tungstate ion in acid medium consisted of a titration cell, the Radiometer pH meter equipped with electrodes as described above, a constant-temperature water bath and 50- or 10- ml burettes. The titration cell was a jacketed 250-ml pyrex beaker fitted with a lucite cover having holes for the burettes, electrodes and a nitrogen gas inlet tube. Water from the constant temperature bath was circulated through the jacket to keep the temperature at $25.0 \pm 0.2^\circ\text{C}$.

For the filtration of certain water samples prior to the determination of their phosphate concentration, MF-Millipore filters were used (Type HA; plain, white, 90 mm diameter, 0.45μ pore size,

Millipore Ltd., Mississauga, Ontario). The filtration was carried out under suction by water-aspirator.

II. C. PROCEDURES FOR SOLUTION STUDIES

1. Isopolytungstate systems

(a) Potentiometric titration of tungstate (WO_4^{-2}) solutions

Fifty ml of a standard tungstate solution was pipetted into the titration cell and nitrogen gas (purified grade) was gently bubbled through and over the solution to maintain an atmosphere free of carbon dioxide. The tip of the burette was placed just below the surface of the solution, which was stirred magnetically after the addition of each increment of standard perchloric acid solution. The pH meter was standardized immediately before use with buffer solutions of pH 4.00 ± 0.02 , 7.00 ± 0.01 and 10.00 ± 0.02 .

The concentrations of the tungstate solutions titrated were 1.0, 0.1, 0.01 and 0.001 M. These solutions were titrated with standard perchloric acid solutions of 1.0, 0.01 and 0.001 M. The initial pH range of the solutions was 8.5-6.2 and the final pH range, after titration, was 3-0.

(b) Point-titration of WO_4^{-2} solutions

Fifty ml of a standard tungstate solution was placed in a series of 100-ml beakers. The pH of each solution was adjusted to a different value by the addition of $HClO_4$ (1.0 to 1.0×10^{-3} M). The pH range covered was 8-1.5. The pH values were measured immediately after the addition of perchloric acid and again after 1 hour, 5 hours, and 1, 3, 5, 10 and 15 days. The temperature was maintained at

25.0 ± 0.2°C by means of a thermostatted water bath. These point-titrations were done for 0.1, 0.01 and 0.001 M tungstate solutions.

The effect of ionic strength on the point-titrations was studied by addition of solid NaClO_4 to 0.1 M and 0.01 M tungstate solutions to give ionic strengths of 1.0 and 0.1, respectively. The conditions of measurement were exactly the same as before.

(c) Spectrophotometric-pH studies on tungstate solutions

(i) In aqueous solution. A known volume (24.0 ml) of standard tungstate solution (0.001 M) was pipetted into 50-ml volumetric flasks and measured volumes of standard perchloric acid or standard sodium hydroxide were then added to adjust the pH. The tungstate solutions were diluted to the mark with distilled water, their pH measured (pH 8-0) and their spectra taken immediately (0 time) over the range 200-400 nm. The spectra were also recorded at time = 0.5, 1, 5 hours and 1, 5, 10, 30 and 60 days. The pH was also recorded for each interval of time. The temperature of the standing solutions was maintained at 25.0 ± 0.2°C.

In a separate study, the solutions were prepared exactly as before except that the pH range was 0-2 and the solutions were brought to a boil and then cooled to room temperature in a water bath prior to the recording of spectra. For these experiments, 4.8, 2.4 and 1.2 ml of a 0.1 M solution, 4.8, 2.4 and 1.2 ml of a 0.01 M solution, and 6 ml of a 1.0×10^{-3} M solution of tungstate were pipetted into 10-ml volumetric flasks. After the solutions had been cooled to 25°C, their spectra were recorded. The solutions were then discarded. In all

cases, spectra were recorded using the corresponding blanks as references and cells of path length (from 0.1 mm to 5 mm) suitable to give absorbance values in the range 0.1-0.7 A units.

Spectra of the metatungstate species ($H_2W_{12}O_{40}^{-6}$) were also recorded. To exactly 1.00 ml of a 9.87×10^{-4} M sodium metatungstate solution placed in several 50-ml volumetric flasks, volumes of $HClO_4$ or NaOH solutions were added to adjust the pH. The solutions were diluted to the mark with distilled water. The acidity values ranged from 5 M H_3O^+ to pH 13. Spectra of the solutions were recorded over the range 200-350 nm under the following conditions: immediately after preparation of the solutions at room temperature; after the solutions had been allowed to stand at 25°C for one day and immediately after freshly prepared solutions were brought to a boil and cooled to 25°C. A cell with a 5-mm path length was used throughout and corresponding blanks were used as reference solutions.

Spectral studies of solutions of paratungstate Z ($H_2W_{12}O_{42}^{-10}$) were also made. Solutions containing exactly 1.00 ml of a 4.01×10^{-4} M solution of sodium paratungstate were adjusted from 5 M H_3O^+ to pH 13 as above. Spectra of the solutions were recorded over the range 200-350 nm using 5-mm cells and the corresponding blank as a reference under the following conditions: immediately after preparation of the solutions at room temperature; after the solutions had been allowed to stand at 25°C for 0.5, 2, 4, 6 and 10 hours and 1 and 40 days; and immediately after freshly prepared solutions were brought to a boil and cooled to 25°C.

(ii) In n-amyl alcohol. Solutions of tungstate were prepared as above from the 0.001 M stock tungstate solutions over the

pH range 0-2.2. The pH values were measured immediately and then the solutions were placed into 125-ml separatory funnels containing 25 ml of n-amyl alcohol. The flasks were shaken for two minutes and the organic phase was taken for spectral measurement over the range 200-350 nm. Equilibrated n-amyl alcohol (i.e., the n-amyl alcohol extract of distilled water treated under identical conditions as the test solutions) was used as the reference. These measurements were repeated for aqueous solutions that had been allowed to stand for 0.5 hours and 1 day. The temperature of the standing solutions was maintained at $25.0 \pm 0.2^\circ\text{C}$.

In another experiment, corresponding aqueous solutions were brought to a boil, cooled to room temperature and extracted for two minutes. The absorbance of the organic phase was measured as before.

Extraction studies were also made on paratungstate Z solutions. Three series of solutions were prepared containing 2, 4 and 8 ml of a 4.01×10^{-4} M solution of sodium paratungstate. The pH range of each series was 0-4. The final volume of each solution was 25 ml. The solutions were extracted as previously described and their spectra were recorded as before under the following conditions: immediately after preparation of the solutions at room temperature; after the solutions had been allowed to stand for one day at 25°C and after the freshly prepared solutions were brought to a boil and cooled to 25°C .

Solutions of metatungstate were prepared as above (analytical

concentration = 1.97×10^{-5} M). Volumes of perchloric acid were added to give acidities ranging from 7 M H_3O^+ to pH 2. The pH values were measured immediately and then the solutions were placed into 125-ml separatory funnels containing 25 ml of n-amyl alcohol. The flasks were shaken for two minutes and the spectra of the organic phases were recorded over the range 200-350 nm using equilibrated n-amyl alcohol as the reference and cells of 5-mm path length.

2. Heteropolytungstate systems

(a) Potentiometric titration of 12-tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (TPA)

Potentiometric titrations of TPA in aqueous and non-aqueous media were performed with the apparatus used in the study of the isopolytungstates.

For titrations in aqueous medium, 50 ml of a 10^{-3} M aqueous solution of TPA was titrated with 2.01×10^{-2} M and 9.90×10^{-2} M solutions of sodium hydroxide in the pH range 2-7 and 7-12, respectively. The ionic strength was maintained approximately at unity by the addition of sodium perchlorate.

For titrations in non-aqueous media, 0.153 and 0.144 g of anhydrous TPA were dissolved in 50 ml of n-amyl alcohol and 50 ml of methyl ethyl ketone, respectively, and the solutions titrated with a 0.101 M solution of tetra-n-butylammonium hydroxide. The base, obtained commercially as a 25% solution in methanol for use as a titrant, was standardized as follows: 0.770 g of benzoic acid

was dissolved in 25.0 ml of freshly-distilled dry pyridine and titrated with the 25% solution of base to the first permanent blue colour of thymol blue indicator (1.0% in CH_3OH).⁽²⁴²⁾ A blank titration yielded a correction of < 0.01 ml. The commercial solution of base was found to be 1.01 ± 0.01 M. A 0.101 M solution was obtained by dilution of 5.00 ml of the commercial solution with either n-amyl alcohol or with methyl ethyl ketone to 50.0 ml. All titrations were performed in duplicate.

(b) Spectrophotometric-pH studies on TPA

A series of solutions was prepared containing 12.0 ml of a 1.34×10^{-4} M solution of TPA and sufficient amounts of HClO_4 or NaOH to give acidities ranging from 4 M HClO_4 to pH 12 after dilution to 50 ml with distilled water. Sodium perchlorate was added to give an ionic strength of unity for all solutions > pH 0. Spectra were recorded in the range 200-400 nm using 5-cm cells and corresponding blanks as references at time = 0 (immediately after preparation of the solution), 1, 5, 10, 24 and 120 hours.

(c) Conformity of TPA to Beer's law

The conformity of TPA to Beer's law was tested in water and in n-amyl alcohol. For the aqueous solution, 1.4625 g of anhydrous TPA was dissolved in 250 ml of deionized water to give a stock solution containing 62.91 ppm P. Aliquots of this solution were suitably diluted to give amounts of phosphorus in the range 0-60 ppm. The absorbance values of the resulting solutions were measured at 267 nm, using deionized water as the reference. Beer's law was tested for the above series of solutions at pH 0, 1, 1.5 and 2. Cells with path lengths of

50 nm, 5 nm, 1 nm and 0.1 nm were used to cover the respective ranges 0-0.1, 0.1-1, 1-5 and 5-60 ppm P.

For solutions of TPA in n-amyl alcohol, a stock solution containing 58.78 ppm P (1.3660 g of anhydrous TPA dissolved in 250 ml n-amyl alcohol) was suitably diluted with n-amyl alcohol to give concentrations of phosphorus ranging from 0-55 ppm. The absorbance of each solution was measured at 267 nm in cells of appropriate path length. The reference was n-amyl alcohol.

Conformity to Beer's law was also tested by extraction of various amounts of TPA from the aqueous to the n-amyl alcohol phase. Aliquots of aqueous solution of TPA were pipetted into 10-ml volumetric flasks, adjusted to pH 0-3 and diluted to the mark with deionized water. The amounts of phosphorus ranged from 0-60 ppm after the final volume adjustment.

The solutions were transferred to 125-ml separatory funnels and extracted for two minutes with exactly 10 ml of n-amyl alcohol. After separation of the phases, the absorbance of the alcohol phase was measured at 267 nm in cells of appropriate path length, with the corresponding blanks as reference solutions. Absorbance measurements were also made after 1, 5 and 24 hours. The solutions were maintained at 25°C.

(d) Formation of TPA in solution from tungstate, phosphate and acid

(i) Measurement in aqueous solution. Preliminary studies on the formation of TPA in aqueous solution were carried out as follows. To 2 ml of a 1.0×10^{-3} M solution of KH_2PO_4 , contained in a 100-ml beaker, was added 24 ml of a 1.0×10^{-3} M solution of sodium tungstate from a 10-ml burette. Several such solutions were prepared and the

final volume in each beaker was adjusted to 50 ml with deionized water after addition of the required amounts of perchloric acid to give pH values ranging from 5.4 to 0. Spectra were then recorded at time = 0, 0.5, 1 and 5 hours and 1, 5, 10 and 15 days; 5-mm and 1-cm cells were used and corresponding blank solutions (i.e., solutions containing no phosphate but otherwise identical in composition and treatment) were used as references.

(ii) Measurement in the n-amyl alcohol phase after extraction from aqueous solution. The general method of studying the optimum conditions for the quantitative formation of TPA in solution from tungstate, phosphate and acid was as follows. A known amount of phosphate (e.g., 0.50 ml of 1.0×10^{-3} M KH_2PO_4 solution) was added from a micrometer syringe burette to a known volume of standard tungstate solution (e.g., 0.60 ml of 1.0×10^{-2} M tungstate solution) in a 100-ml beaker. Several such solutions were prepared and the final volume in each beaker was adjusted to 10 ml with deionized water after addition of the required amounts of perchloric acid to give pH values ranging from 0-3.

The solutions were then transferred to a series of 125-ml separatory funnels containing 25 ml of n-amyl alcohol and extracted for two minutes. The spectra of the alcohol phases were recorded over the range 200-400 nm. Both n-amyl alcohol (i.e., the solvent) and the n-amyl extracts of corresponding blank solutions were used as reference solutions.

The aqueous solutions were extracted under the following conditions: immediately after preparation of the solutions at room temperature; after bringing new corresponding solutions to a boil and

cooling to 25°C; after heating corresponding solutions to $60 \pm 2^\circ\text{C}$ and cooling to 25°C; after heating corresponding solutions to $45 \pm 2^\circ\text{C}$ and cooling to 25°C.

The above experiments were repeated at the same concentration of phosphate (0.50 ml of 1.0×10^{-3} M KH_2PO_4) but different concentrations of tungstate such that the tungstate to phosphate molar ratios were 24:1 (1.2 ml of 1.0×10^{-2} M WO_4^{-2}), 48:1 (2.4 ml), 96:1 (4.8 ml), 144:1 (7.2 ml) and 240:1 (1.2 ml of 0.10 M WO_4^{-2}). For each molar ratio, a set of solutions spanning the pH range 0-3 was prepared.

In another experiment, the phosphate concentration was varied. For example, in one set of solutions, the concentration of phosphate was increased ten-fold (i.e., 0.5 ml of 1.0×10^{-2} M H_2PO_4^-). To maintain the above tungstate to phosphate molar ratios, the tungstate concentrations were correspondingly raised by an order of magnitude (i.e., 1.2 ml, 2.4 ml, 4.8 ml and 7.2 ml of 0.10 M tungstate solution). Separate sets of solutions were prepared for each molar-ratio value. In another set of solutions, the concentration of phosphate was decreased by an order of magnitude (i.e., 0.50 ml of 1.0×10^{-4} M). The corresponding tungstate to phosphate molar ratios studied were 24:1, 48:1, 144:1, 240:1, 480:1, 960:1, 1440:1 and 2400:1.

In a final experiment, the effect on TPA formation of boiling the tungstate solutions (adjusted to desired pH values) prior to the addition of phosphate was investigated. Thus, a series of solutions containing 4.8 ml of 1.0×10^{-2} M WO_4^{-2} was adjusted to pH values in the range 0-2 and diluted to 9.5 ml with deionized water. The solutions were boiled and cooled to 25°C, and then 0.50 ml of 1.0×10^{-3} M KH_2PO_4

solution was added to each. Immediately after this addition, the solutions were extracted. In a repetition of this experiment, the final aqueous solution was allowed to stand for 10 hours before extraction and recording of the spectra.

(iii) X-ray powder diffraction analysis of TPA isolated after its formation in solution from tungstate, phosphate and acid. The following experiments were done to ensure that the compound formed in solution from tungstate, phosphate and acid and extracted into n-amy alcohol was TPA. Two ml of a 1.0×10^{-2} M solution of KH_2PO_4 solution was treated with 4.8 ml of a 0.1 M WO_4^{-2} solution. The pH of the solution was set between 1.5-1.9 with perchloric acid and the final volume was set to 10 ml with deionized water. The solution was boiled, cooled and extracted as before.

The organic phase was transferred to a porcelain dish and evaporated gently on a hot plate at 70-75°C. After most of the alcohol was evaporated, the dish was placed in an oven at 275-300°C for one hour. After cooling, the crystalline solid obtained was finely powdered to less than 200 mesh in an agate mortar. The powder was inserted into a thin-walled melting-point tube having an inside diameter of 0.5 mm. The tube was held in place at the centre of the X-ray camera with wax and was aligned to rotate without a wobble. A 5-hour exposure to nickel-filtered CuK_α radiation was used. The powder-diffraction pattern obtained with this sample of TPA formed in solution was then compared with that of commercially available TPA (dried to the anhydrous form at 300°C for one hour), taken in identical fashion.

(e) Formation of TPA in solution from paratungstate Z, phosphate and acid

A known amount of phosphate (0.50 ml of 1.0×10^{-3} M KH_2PO_4) was added to a series of 100-ml beakers, each containing a known concentration of paratungstate Z solution (e.g., 2.0 ml of 4.01×10^{-4} M solution, corresponding to a W:P molar ratio of 19:1). Amounts of perchloric acid were added such that after dilution to a final volume of 10 ml, the pH of the solutions ranged from 0-4. The solutions were extracted for 2 minutes with 25 ml of n-amyl alcohol under the following conditions: immediately after preparation of the solutions at room temperature; after freshly prepared, corresponding solutions were allowed to stand for one day at 25°C; and after corresponding solutions were brought to a boil and cooled to 25°C. The spectra of the organic phases were recorded. An n-amyl alcohol extract of the corresponding aqueous blank solutions (i.e., solutions containing the same amount of para Z and acid as in the test solution but no phosphate) was used as the reference.

The experiments were repeated at the same concentrations of phosphate but different concentrations of paratungstate (e.g., 4.0 and 8.0 ml of 4.01×10^{-4} M and 2.0 ml of 4.01×10^{-3} M, corresponding to W:P ratios of 38:1, 76:1 and 190:1, respectively).

(f) Formation of TPA in solution from metatungstate, phosphate and acid

A series of solutions was prepared containing metatungstate and phosphate in the W:P stoichiometric ratio 24:1 (0.50 ml of 1.0×10^{-3} M

KH_2PO_4 solution and 1.0 ml of 9.87×10^{-4} M metatungstate solution). The final volume was set to 50 ml with distilled water after adjustment of the pH of the solutions with perchloric acid to cover the range pH₂ to 4 M. The spectra of the solutions were then recorded under the following conditions: immediately after preparation of the aqueous solution at room temperature; after freshly prepared, corresponding solutions were brought to a boil and cooled to 25°C; after extraction of corresponding solutions into 25 ml of n-amyl alcohol for two minutes; and after extraction of the corresponding solutions for one hour.

Measurements under the above conditions were repeated at W:P molar ratios of 120:1 and 240:1 (respectively, 5.0 and 10.0 ml of 9.87×10^{-4} M metatungstate for 0.50 ml of 1.0×10^{-3} M KH_2PO_4 solution).

(g) Formation of TPA in solution from tungstic oxide, phosphate and acid

(i) From yellow tungstic oxide ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$). The yellow tungstic oxide was dried at 100°C for 10 hours and then 11.6 mg was added to each of five 100-ml beakers followed, in turn, by 3, 5, 10, 15 and 20 ml of a 1.0×10^{-3} M solution of phosphate and then 2 ml of 1.0 M HClO_4 . The final volume was adjusted to 25 ml with deionized water. The pH values of the solutions ranged from 1.3 to 1.5. The solutions were extracted into n-amyl alcohol, as previously described, under the following conditions: immediately after preparation at room temperature; after the solutions had aged for one day at room temperature; and after freshly prepared corresponding solutions had been boiled for thirty minutes. Spectra were recorded as before.

In another experiment, 11.6 mg of the yellow tungstic oxide

was treated with an excess (5.0 ml) of syrupy phosphoric acid (85% by weight; specific gravity, 1.69). Solutions of phosphate and perchloric acid were not added in this case. The conditions of measurement were otherwise the same as before.

The formation of TPA was also attempted by repeating the above experiments with freshly prepared, undried, yellow tungstic oxide.

(ii) From white tungstic oxide ($\text{WO}_3 \cdot \text{H}_2\text{O}$). Sodium tungstate (14 mg, 16 mg and 20 mg) was treated with 5 ml of 0.3 M HClO_4 in three test-tubes. The precipitated white tungstic oxide was centrifuged and washed five times with distilled water. The precipitates were transferred to three 100-ml beakers and then 5, 10 and 15 ml of a 1.0×10^{-3} M solution of H_2PO_4^- were added in turn. The solutions were adjusted to pH 1.5-1.8 with HClO_4 and then boiled and cooled to room temperature. A 2-ml aliquot from each solution was made up to 25 ml, with addition of HClO_4 solution to maintain the pH between 1.5-1.8. The spectra of the solutions were then recorded over the range 200-350 nm using water as the reference.

In another experiment, solutions prepared under the above conditions were extracted with 25 ml of n-amyl alcohol. The spectra of the organic phases were recorded against corresponding blanks.

(h) Conformity to Beer's law of TPA formed in solution from tungstate, phosphate and acid and extracted into n-amyl alcohol

(i) 0 to 0.25 ppm P^* . To exactly 0.5, 1, 2, 3, 4, 5, 6, and 8 ml of a 1.00×10^{-5} M H_2PO_4^- solution in 50-ml beakers was added

* This concentration corresponds to 0-0.1 ppm P in the 25-ml volume organic phase.

0.60 ml of a 1.0×10^{-2} M tungstate solution. The pH values of the solutions were set in the range 1.3-1.9 with HClO_4 in a final volume of 10 ml adjusted with deionized water. The solutions were brought to just a boil (first appearance of bubbles), cooled to 25°C in a water bath, and extracted for two minutes with exactly 25 ml of n-amyl alcohol. Absorbance values were measured at 267 nm in a 5-cm cylindrical cell. Measurements were made against both n-amyl alcohol and the n-amyl extract of the corresponding blank solutions as reference solutions. Measurements were repeated under the above conditions with 1.2, 2.4, 4.8 and 7.2 ml of 1.0×10^{-2} M WO_4^{-2} solution and 1.2 ml of 1.0×10^{-1} M solution.

The calculated concentration range of phosphate in the 25 ml n-amyl alcohol phase was 0.00620-0.0992 ppm P. In the aqueous phase, the corresponding range was 0.0155-0.249 ppm P.

(ii) 0.3-2.5 ppm P. To exactly 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.8 ml of a 1.00×10^{-3} M KH_2PO_4 solution was added 2.4 ml of a 1.0×10^{-2} M WO_4^{-2} solution. The solutions were treated and absorbance measurements made as above, except that 5-mm cells were used. Measurements were also made using 4.8 and 7.2 ml of 1.0×10^{-2} M WO_4^{-2} solution and 1.2 ml of 1.0×10^{-1} M solution.

The values of phosphate concentration in the n-amyl alcohol phase (25 ml) corresponded to 0.124-0.992 ppm P. The corresponding range for the aqueous phase (10 ml) was 0.310-2.48 ppm P.

(iii) 3-25 ppm P. To exactly 0.2, 0.4, 0.6, 0.8, 1, 1.2 and 1.6 ml of 5.00×10^{-3} M H_2PO_4^- solution were added 1.2 ml of a 0.10 M tungstate solution. The solutions were treated as before. After extraction, however, a 1.00 ml aliquot of the alcohol phase was pipetted into a 10-ml volumetric flask and diluted to the mark with n-amyl alcohol. Values of absorbance were then measured at 267 nm as before, using 5-mm cells. Measurements were repeated using 2.4, 4.8 and 7.2 ml of a 0.10 M tungstate solution under the above conditions.

The concentrations of phosphate in the 25-ml n-amyl alcohol phase corresponded to 1.24-9.92 ppm P. The corresponding range for the 10-ml aqueous phase was 3.10-24.8 ppm P.

Similar studies were made with synthetic sea water prepared by dissolution of 25 g of NaCl, 7 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 3 g KCl⁽⁴⁾ in distilled water and dilution to one litre. This composition corresponds to about 35 parts per thousand salinity.⁽²⁴³⁾ Plots of absorbance versus concentration were obtained for phosphorus in the range 0-0.25 (0-0.1)*, 0-2.5, (0-1.0) and 0-25 (0-10) ppm P in exactly the same way as above.

(1) Test of precision

The test of precision was made at concentrations corresponding

* Bracketed values are P concentrations after extraction into the 25-ml n-amyl alcohol phase.

to 0.00620, 0.0124, 0.0620, 0.620, 2.48 and 6.20 ppm P in the alcohol phase.

Studies at the 0.00620 and 0.0124 ppm levels were made using 0.50 and 1.00 ml of 1.00×10^{-5} M H_2PO_4^- and 2.4, 4.8 and 7.2 ml of 1.0×10^{-2} M WO_4^{-2} solutions and 1.2 ml of 1.0×10^{-1} M solution. Twenty separate measurements were made for each W:P ratio. Similar experiments were done for the other concentrations of phosphorus. For 6.20 ppm P, 1.2, 2.4, 4.8 and 7.2 ml of 0.10 M tungstate solutions were used.

Tests of precision were also made for the synthetic sea water samples.

(j) Effect of foreign ions

The effect of foreign ions on the formation and extraction of DPA was examined. These ions and their effects are listed under RESULTS AND DISCUSSION. The tests were carried out as follows: volumes of the solution containing the foreign ion were added to 0.50 ml of 1.00×10^{-3} M H_2PO_4^- (equivalent to 1.55 ppm P and 0.620 ppm P in the aqueous and organic phases, respectively) and 4.8 ml of a 1.0×10^{-2} M WO_4^{-2} solution. The pH of each solution was set between 0-2 by the addition of perchloric acid. The final volume was 10 ml. The solutions were brought to a boil, cooled, extracted with 25 ml of n-amyl alcohol, and the absorbance of the organic phase was measured against the blank extract as before.

Initially, a significantly higher concentration (of the order of $(1.0-5.0) \times 10^3$ ppm in the aqueous phase) of the foreign ion was taken

and its effect was noted in terms of phosphate recovery by measurement of the absorbance at 267 nm. The concentration of the foreign ion was then progressively decreased until the response corresponded to 100% phosphate recovery. The spectrum of the foreign ion in the absence of tungstate was also recorded to note any spectral interference.

Since arsenic, silicon and germanium are known to form the corresponding heteropolytungstates, the effect of these elements on the formation of TPA from tungstate, phosphate and acid was further studied in some detail, as described below.

(i) Effect of arsenic. The formation and extraction of 12-tungstoarsenic acid (TAA), $H_3AsW_{12}O_{40}$, was studied at 0.75 (0.3)*, 1.5 (0.6), 2.3 (0.9), 3.8 (1.5) and 15.0 (6.0) ppm As in the 10-ml aqueous phase, corresponding to the addition of 0.1, 0.2, 0.3, 0.5 and 2.0 ml, respectively, of 10^{-3} M Na_2HAsO_4 solution. For 0.75 and 1.5 ppm As, 4.8 ml of a 10^{-2} M tungstate solution was used. For the range 2.3-15.0 ppm As, 1.2 ml of a 0.1 M tungstate solution was added. The conditions for the formation of TAA, its extraction and measurement of absorbance were essentially as those for TPA.

The following procedure was used to study the recovery of phosphorus (as phosphate) in the presence of arsenic (as arsenate). A measured volume of phosphate solution (e.g., 0.50 ml of a 1.0×10^{-3} M solution) was added to a known amount of arsenate (e.g., 0.50 ml of a 10^{-3} M solution, equivalent to 3.8 and 1.5 ppm As in the aqueous and

* The values in brackets correspond to the concentrations of As after extraction into the 25-ml alcohol phase.

organic phases, respectively). Then, 1.2 ml of 0.1 M tungstate solution was added. The pH of the solution (final volume, 10 ml) was adjusted to 1.5-1.9. The solution was brought to a boil, cooled to 25°C and extracted with 25 ml n-amyl alcohol and the absorbance measured over the range 200-350 nm in 5-mm cells.

The recovery of phosphorus was also tested by repeating the measurements under identical conditions with 0.1, 0.2, 0.3 and 2 ml of a 10^{-3} M solution of HAsO_4^{-2} . The phosphate concentration was kept constant in each case.

Similar studies were made at phosphate concentrations corresponding to 0.0155 (0.0062)*, 0.155 (0.062) and 15.5 (6.2) ppm P. For each P concentration, the range of arsenate concentrations taken was exactly the same as above.

As will be shown in RESULTS AND DISCUSSION, interference from arsenic can be kept minimal if the pH range for formation of the TPA is set between 1.5-1.9. Even so, some interference results probably because of formation and extraction of some TAA. Therefore, several attempts were made to overcome the interference of arsenate by reduction to arsenite. These attempts involved the addition of excess amounts of oxalic acid, thiosulphate, urea, ascorbic acid or a mixture of sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium thiosulphate. The solution contained 0.5 ml of a 1.0×10^{-3} M HAsO_4^{-2} solution and 4.8 ml of 10^{-2} M tungstate. In a separate series, 0.5 ml of 1.0×10^{-3} M phosphate was

* The bracketed values correspond to P concentrations after extraction into the 25-ml alcohol phase.

also added. The pH of the final solution (volume, 10 ml) was adjusted to 0-2. The solutions were processed and extracted and the absorbance was measured in the usual way.

(ii) Effect of silicon and germanium. To 5 ml of a 1.0×10^{-4} M solution of tungstosilicic acid (TSA), $H_4SiW_{12}O_{40}$, sufficient amounts of perchloric acid and sodium hydroxide were added to give acidities ranging from 4 M $HClO_4$ to pH 12. The final volume of the aqueous solution was 25 ml, after adjustment. The spectra of the various solutions were then recorded over the range 200-350 nm, using 5-mm cells and corresponding blanks as references.

In another experiment, solutions prepared under the above conditions were extracted for two minutes with 25 ml of n-amyl alcohol. The spectrum of the organic phase was then taken, using 5-mm cells and the corresponding blank extract as a reference.

Experiments with the 12-tungstogermanic acid, (TGA), $H_4GeW_{12}O_{40}$, were carried out in the same manner.

(iii) Effect of isopolytungstates. The interferences of metatungstate, paratungstate Z and other isopoly species on the formation and extraction of TPA were also examined. For experimental details regarding these species, see the foregoing sub-section 1 (c) in Section II.C.

II. D. PROCEDURES FOR ANALYTICAL APPLICATION TO PHOSPHORUS-CONTAINING MATERIALS

1. Application to total soluble phosphate in water samples

The following procedure was applied to water samples whose sources are specified under RESULTS AND DISCUSSION. Filtration was

required prior to analysis for the raw sewage sample and the corresponding effluent after primary and secondary treatment. These samples were filtered through 0.45 μ Millipore filters prior to determination of their phosphate content.

An aliquote (Note i) was pipetted into a 125-ml conical flask and 1 ml of 5 M H_2SO_4 and 0.4 g of $(NH_4)_2S_2O_8$ were added (Note ii). The solution was diluted to 50 ml with deionized water, the flask covered with a speedy-vap watch-glass and the solution digested by gentle boiling on a pre-heated hot plate until the volume was reduced to 10-15 ml (about 1 hr). The solution was transferred to a 100-ml beaker with 3-4 washings (2-3 ml each) of deionized water, cooled to room temperature and the pH adjusted potentiometrically to greater than 7 by the drop-wise addition of 5 M NaOH. To this solution was added 1-2 ml of a 0.1 M tungstate solution (Note iii). The pH was readjusted potentiometrically to 1.3-1.9 (if As is absent) or 1.5-1.9 (if As is present) with 1 M $HClO_4$. The solution was then brought to a boil (Note iv), cooled to room temperature in a water bath, and carefully transferred to 125-ml separatory funnel, using a few ml of 0.03 M $HClO_4$ to rinse the beaker, and then exactly 10 ml of n-amyl alcohol was added (Note v). After extraction for two minutes, the absorbance of the alcohol phase was measured at 267 nm against the corresponding n-amyl alcohol extract of the reagent blank, using cells of suitable path length (Note vi). A small correction in absorbance was made due to non-matching of cells (0.005 A units). The concentration of phosphorus was obtained by reference to a calibration curve (covering the range 0-10 ppm P, Note v) prepared from standard phosphate solutions. All samples were done in triplicate.

Notes

- (i) For concentrations of less than 0.1 ppm P, a 25-ml aliquot is recommended. When the phosphorus concentration is >0.1 ppm P, a 10-ml or smaller aliquot is adequate.
- (ii) The $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{S}_2\text{O}_8$ digestion procedure ensures that organically-bound phosphorus (P-O-C and P-C bonds) is fully converted to orthophosphate. (244).
- (iii) The final tungstate concentration in the aqueous phase should be $\sim 10^{-3}$ M for quantitative formation of TPA. For samples which contain up to 10 ppm P, 1-3 ml of 0.1 M tungstate solution is adequate.
- (iv) After the addition of tungstate and the adjustment of pH to the required ranges (i.e., pH 1.3-1.9 or 1.5-1.9), the sample was removed from the hot plate at the first appearance of bubbles. In fact, the solution need be heated to only 60°C for 2-3 minutes, and not boiled. The results for phosphate are not affected by the use of the lower temperature (see RESULTS AND DISCUSSION).
- (v) Extraction with a 10-ml rather than a 25-ml aliquot of n-amyl alcohol was found suitable for all concentrations of P encountered in the samples. The smaller volume enhances the sensitivity. In either case, the volume must be delivered by pipette.
- (vi) The absorbance of the n-amyl alcohol extract of the reagent blank (all ingredients present except the sample) was always less than 0.01 absorbance units and was used to correct the absorbance of samples. For samples in the range 0-0.1 ppm P, 2- or 5- cm cells were used. For higher concentrations, either smaller cells were used or a suitable aliquot of the organic phase was diluted with

n-amyl alcohol to a known volume before measurement, to keep the absorbance within a suitable analytical range. Between measurements, the cell should be rinsed with the next sample, and not with solvents (e.g., acetone) that absorb in 200-300 nm range. The alcohol phase must be clear before measurement. Excessive water in the alcohol phase causes cloudiness; in such cases, a period of about 40 minutes is required for the water to settle.

2. Application to the determination of phosphorus in steels

The following procedure was applied to the determination of phosphorus in NBS steels specified under RESULTS AND DISCUSSION.

Because high concentrations of iron interfere with the determination of phosphorus as the TPA, a preliminary separation of iron in the samples was required. The separation was effected by ion-exchange. A plug of glass wool, previously cleaned with CCl_4 was inserted at the base of a 50-ml burette. The resin (Amberlite, CG-120, type $\text{RSO}_3^- \text{Na}^+$) was added as an aqueous slurry at a slow rate until the 25-ml graduation mark was reached. The resin was converted to the hydrogen-form with 100 ml of 4 M HCl and washed with deionized water until the final 100 ml of the effluent required less than 1 ml of a 0.02 M NaOH to neutralize the acidity to methyl orange.

To accurately-weighed steel samples (0.05 to 0.1 g) in 100-ml beakers was added 5 ml of a 1:1 solution of HNO_3 . The solution was gently boiled on a hot plate until all the oxides of nitrogen had been expelled and then 10 ml of freshly-prepared 2% ammonium persulphate solution was added. After the solution was boiled for five minutes, 4 ml of conc. HCl was added and the solution evaporated to dryness. The residue was dissolved in 40 ml of a 0.01 M solution of HCl, by boiling if necessary, The solution was cooled to room temperature

and passed through the ion-exchange column. The phosphate was eluted through the column with 60-80 ml of a 0.2 M HCl (3 ml/minute flow rate) and collected in a 250-ml beaker. The solution was evaporated to 10-15 ml, cooled and transferred to a 100-ml volumetric flask and diluted to the mark with deionized water.

A suitable aliquot (e.g., 10 ml for samples containing 0.02% P) was now withdrawn and placed in a 100-ml beaker. The pH of the solution was set to 1.5 to 1.9 by the drop-wise addition of 1 M NaOH, and 1 to 2 ml of a 0.1 M solution of tungstate was added. The pH was readjusted between 1.5-1.9, if necessary, by the drop-wise addition of 1 M HClO₄. The solution was boiled (alternately, the solution could be heated to 60°C for 2 or 3 minutes), cooled to 25°C and extracted for two minutes with 10 ml of n-amyl alcohol. The absorbance of the organic phase was measured at 267 nm. A 1-cm cell was used for amounts of phosphorus < 0.02% and for amounts > 0.1%, a suitable aliquot of the organic phase was further diluted (e.g., a 1-ml aliquot diluted to 10 ml) with n-amyl alcohol before measurement. A blank extract was used as the reference. A calibration curve was prepared from suitable aliquots of the standard phosphate solution to cover the range 0-1% P. The determination of phosphorus content in steel samples was carried out in duplicate.

3. Application to phosphor bronzes

The phosphor bronze standards, to be specified later, were in the form of discs (6.0 cm diameter, 0.7 cm thickness, 160 g). The surface of each disc was polished on a grindstone and about 2 mm was removed by lathe from the face opposite the chill-cast surface. The

discs were then milled to obtain enough turnings from the lathed face for chemical analysis. No lubricant or 'cutting' fluid was used and all tools were cleaned carefully between samples. The turnings from each sample were washed with 5 ml of anhydrous ether and dried in the atmosphere for 10 minutes.

An accurately-weighed sample (0.05-0.08 g) was placed in a 100-ml beaker and 0.5 ml of conc. HNO_3 and 1 ml of conc. HCl were added. When the initially vigorous reaction had subsided, 10 ml of deionized water was added and the mixture heated on a hot plate until dissolution was complete. After the solution had cooled, it was transferred into a 50-ml volumetric flask and diluted to the mark with deionized water. A suitable aliquot (5 or 10 ml) was pipetted into a 100-ml beaker, diluted to about 15 ml with deionized water, the pH set to 1.5-1.9 by the drop-wise addition of 1 M NaOH , and 1-2 ml of a 0.1 M tungstate solution added. If necessary, the pH was re-adjusted to 1.5-1.9 with 1 M HClO_4 . The solution was brought to a boil, cooled to 25°C and extracted with 10 ml of n-amyl alcohol. The absorbance of the organic phase* was measured at 267 nm using a 1-cm cell and corresponding blank as reference. Three different phosphor bronzes were analysed, each in triplicate.

4. Application to ores and a mineral

(a) Nickel-Copper-Cobalt ore, SU-1 (Standard Reference Material, Canada Centre for Mineral and Energy Technology)

The ore was dried at 110°C for 2 hours and samples (0.05-0.06 g) were accurately weighed into 100-ml beakers. Concentrated HNO_3 (5 ml)

* If the phosphorus content is $> 0.2\%$, a known aliquot of the n-amyl alcohol phase should be diluted for the absorbance measurement.

was added and the mixture heated on a hot plate until only silica remained undissolved. After evaporation of the nitric acid, 2 ml of conc. HCl was added and evaporated, followed by the addition of 10 ml of deionized water and filtration of the silica. The filtrate was passed through the cation-exchange column (described previously) to remove iron. The eluate (about 100 ml) was evaporated to about 25-30 ml and diluted to 50 ml with deionized water in a volumetric flask. A 10-ml aliquot was taken, the pH was set to 1.5-1.9, 5 ml of a 10^{-2} M tungstate solution was added and the solution was boiled, cooled to 25°C, and extracted (10 ml of n-amyl alcohol). The absorbance was measured in 1-cm cells as previously described. The determination was carried out in triplicate.

(b) Manganese ore (NBS Reference Material, 25c)

The ore was dried at 120°C for 2 hours and samples (0.07-0.08 g) were accurately weighed into 100-ml beakers. About 10 ml of a 0.05 M solution of nitric acid was added, followed by the drop-wise addition of H_2O_2 (30-32% w/w) until all vigorous action had ceased. The mixture was heated until only the silica remained undissolved, diluted to 20-25 ml with deionized water, the silica filtered and the filtrate made up to 50 ml with deionized water in a volumetric flask. A 5-ml aliquot was diluted with 5 ml of deionized water, the pH set to 1.5-1.9 with 1 M NaOH, and 1.5 ml of a 0.1 M solution of sodium tungstate was added. The solution was processed, extracted and the absorbance measured in 1-cm cells as before. The determination was carried out in triplicate.

(c) Feldspar (NBS Reference Material, 99a)

The mineral was dried at 105°C for 2 hours and samples (0.1-0.2 g) were accurately weighed into porcelain crucibles. Each sample was fused with 8 times its weight of potassium pyrosulphate for 90 minutes. (The crucible was kept covered during the fusion). After cooling, the crucible was transferred to a 150-ml beaker containing 40-50 ml deionized water and boiled until only the silica remained undissolved. The silica was filtered and the filtrate collected directly in a 100-ml volumetric flask and diluted to the mark with deionized water. A 10-ml aliquot was taken, the pH was set between 1.5-1.9 with 1 M HClO_4 and the phosphate determined as in the case of the manganese ore.

5. Application to an organophosphorus compound (triphenyl phosphate, NBS Standard Sample, 1071a)

The compound was dried as directed over fresh P_2O_5 in a desiccator for 2 hours. Samples (2-3 mg) were weighed out on a microbalance and quickly transferred into 150-ml beakers. Deionized water (50 ml), 6 M H_2SO_4 (1.5 ml) and ammonium persulphate (1 g) were added. The solution was evaporated to 15-20 ml on a hot plate, cooled and then diluted to 100 ml in a volumetric flask with deionized water. A 5-ml aliquot was pipetted into a 100-ml beaker, diluted to 10-15 ml with deionized water, the pH set to 1.3-1.9 by the drop-wise addition of 5 M sodium hydroxide, 1.2 ml of a 1.0×10^{-1} M tungstate solution added, and the pH readjusted to 1.3-1.9, if necessary, by the addition of 1 M HClO_4 . The remaining steps were as previously described. The determination was carried out in triplicate.

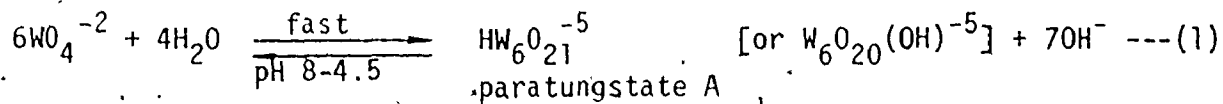
III. RESULTS AND DISCUSSION

III. A. SOLUTION STUDIES

1. Isopolytungstate systems

(a) Potentiometric titration of tungstate (WO_4^{-2}) solutions

The curves for the titration of standard WO_4^{-2} solutions (1.0, 0.1, 0.01 and 0.001 M) with standard $HClO_4$ solutions (10.0, 1.0, 0.1 and 0.01 M, respectively) are shown in Figure 3. The parameter ρ is the ratio of moles of standard acid added to moles of WO_4^{-2} taken (analytical concentration). These curves are similar in form: an initial strong buffer region followed, in turn, by a sharp drop in pH, a weak buffer region and another pH-drop. The pH corresponding to the end of the titration is determined by the concentration of standard $HClO_4$. The first inflection point occurs in the pH region 6-4.5 and corresponds to $\rho = 7/6 = 1.17$. The second inflection occurs in the pH region 4.5-2.5 and at $\rho = 9/6 = 1.50$. These inflections are in substantial agreement with those reported by earlier workers (111,131,140,143,144,149,160,173,245-247) and are explained as follows. For $\rho = 1.17$, the reaction involves the formation of the hexameric paratungstate A and the liberation of 7 hydroxyl ions, which are consumed in the titration:



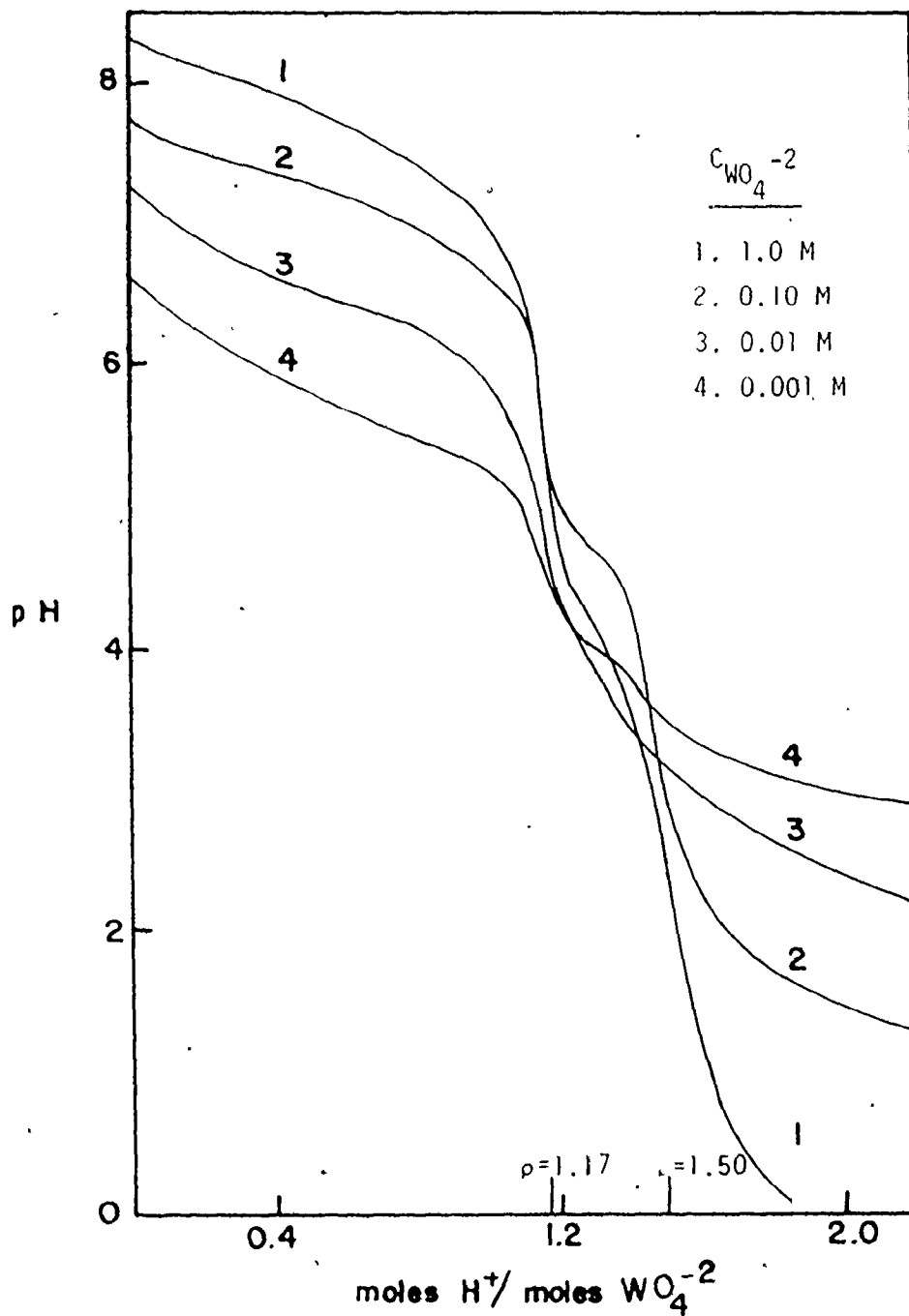
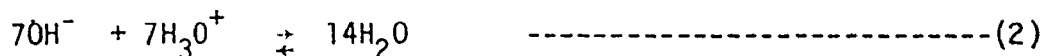
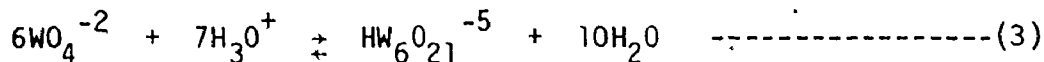


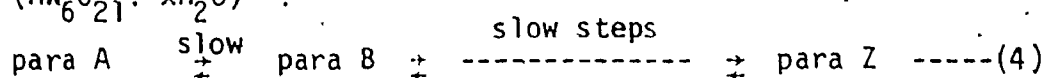
Figure 3. Potentiometric titration of sodium tungstate (50 ml) with perchloric acid. [25°C, no NaClO_4 added. With NaClO_4 , ($\mu = 1.0$), the pH drops are sharper.]



The overall reaction is:

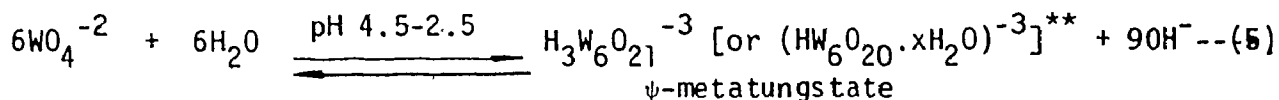


In a pH-independent process, the para A ion is thought to slowly come into equilibrium with a dodecameric species called para Z*, $\text{H}_2\text{W}_{12}\text{O}_{42}^{-10}$ [or $\text{W}_{12}\text{O}_{40}(\text{OH})_2^{-10}$], through at least one intermediate, termed para B, $(\text{HW}_6\text{O}_{21} \cdot x\text{H}_2\text{O})^{-5}$:

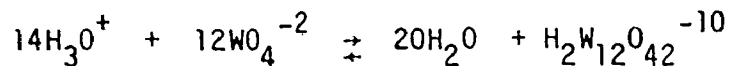


Since the equilibrium between para A and para Z is pH-independent, the pH values up to $\rho = 1.17$ show no drift with time.

For $\rho = 1.50$, the reaction involves the formation of the hexameric ψ -metatungstate species, with the liberation of a total of 9 hydroxyl ions which are subsequently consumed in the titration:

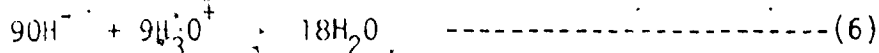


* Aveston⁽¹⁴⁸⁾ believes that at concentrations of tungstate ≥ 0.1 M, the para Z may be favoured over para A. Thus,

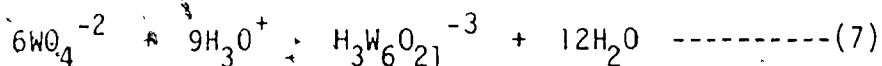


Potentiometry shows only ratios, not the absolute stoichiometry.

** The degree of condensation of the ψ -meta species has not been unequivocally established.⁽¹⁴⁸⁾ Claims exist that it is an aggregate of 6,⁽¹⁴⁰⁾ 12⁽¹⁶⁸⁾ or 24⁽¹¹¹⁾ tungsten atoms. The dodecameric nature of metatungstate has been determined by X-ray diffraction.⁽¹¹⁶⁾



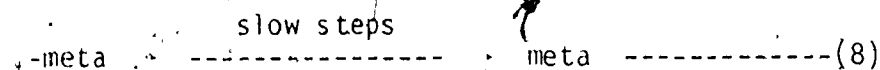
The overall reaction is:



The ψ -meta ion, is thought to come slowly into equilibrium through

other intermediates with the metatungstate, $\text{H}_2\text{W}_{12}\text{O}_{40}^{-6}$

or $[\text{W}_{12}\text{O}_{38}(\text{OH})_2]^{-6}$: (112)



(b) Point titration of WO_4^{-2} solutions

Although no drift in pH is observed up to $p = 1.17$, a slow upward drift is obtained in the region between $p = 1.17$ and 1.50. This drift has been observed by others (140,143,144,248) and confirmed in the present work. In the "instant" or conventional titration (as represented by Figure 3), the points in this region do not correspond to equilibrium values. That is to say, for slow acid-base reactions such as hydrolysis or condensation, the instant titration method is not an equilibrium probe. For equilibrium values, one needs to use either the point-titration technique (i.e., each point followed with respect to pH and time, where each point represents a separate solution in a beaker), or conventional titration at higher temperatures. Figure 4 shows the change in the point-titration curve with time for a 0.1 M tungstate solution. The increase in pH with time, together with the

* Similar changes were observed with 0.01 M WO_4^{-2} solution.

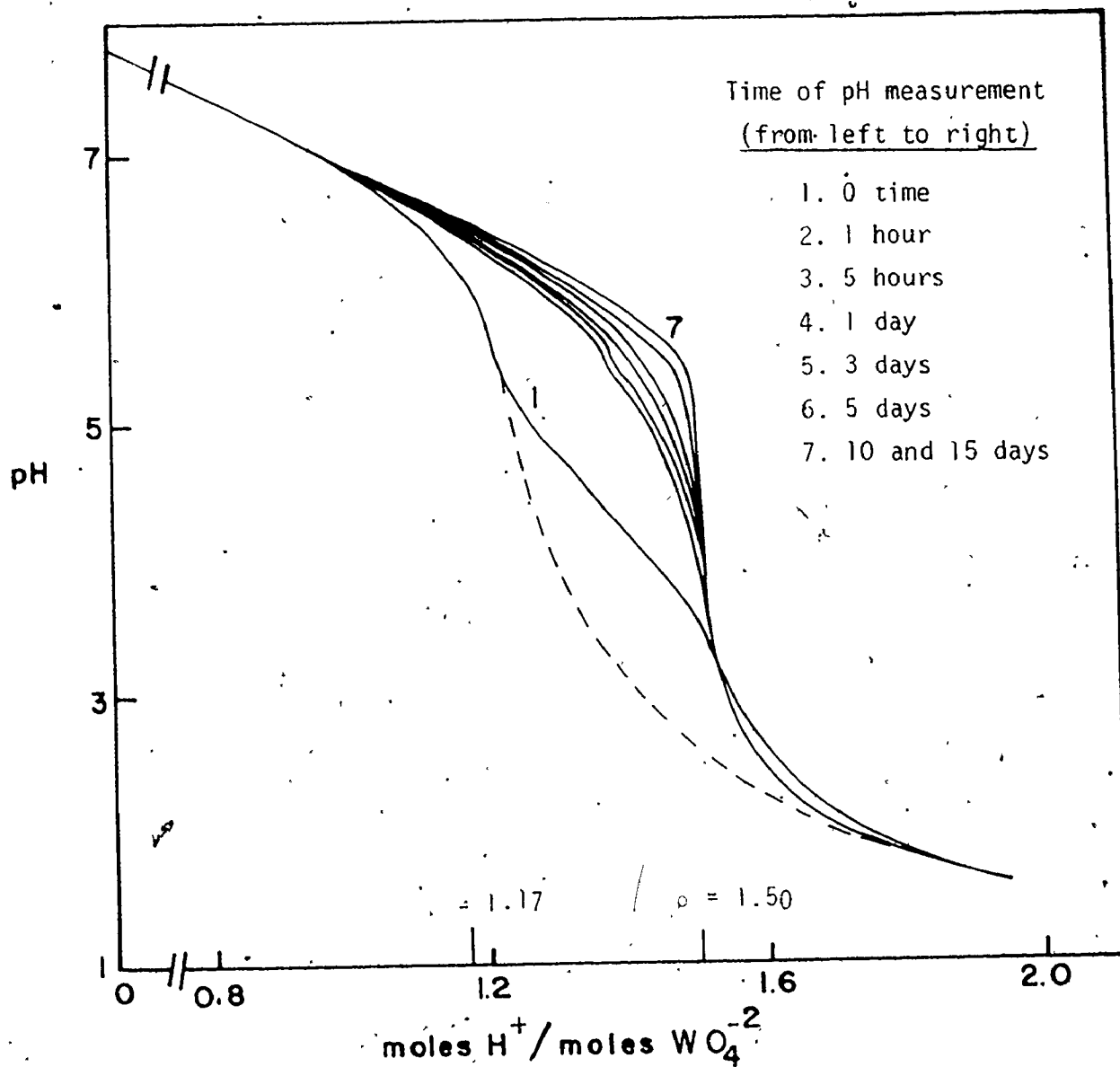


Figure 4: Point titration of sodium tungstate (50 ml) with perchloric acid
($C_{WO_4^{2-}} = 0.10$ M, 25°C, no $HClO_4$ added)

disappearance of the first inflection point, is clearly seen. For curve 1, the first inflection point corresponds to $\rho = 1.17$ [i.e., the formation of the para A species as per reaction (3)]. An indication of a second inflection point is just apparent at $\rho = 1.50$. The term '0 time' is not precise but is used for convenience. In reality, curve 1 represents a point titration in which the addition of the desired volume of HClO_4 solution to each WO_4^{-2} solution and the subsequent pH measurement required approximately 5 minutes. If the acid were added at once in bulk volume and the pH were recorded instantly, an extension of curve 1 along the broken line would be observed. The actual experimental curve (i.e., curve 1) shows that chemical change has already begun by the time of measurement. In curve 7, taken after 10 and 15 days, the chemical transformation has been completed and only the inflection at $\rho = 1.50$ is observed. The obvious interpretation of these results is that while the reaction of the WO_4^{-2} with the acid to yield the para A species, $\text{HW}_6\text{O}_{21}^{-5}$ [reaction (3)], is fast, the reaction of one mole of para A ion with 2 moles of acid to yield the ψ -meta species is considerably slower ($\rho = 1.50$ overall). This second reaction is complete only after 10 or more days (under the experimental conditions). Since protonic acid-base reactions in aqueous solution are very fast, the conversion of para A to ψ -meta must involve structural rearrangement and not merely the addition of two protons as suggested by the stoichiometry of the reaction. To date, literature interpretations^(109,111) of the pH drift have stated merely that it is the result of hydrolysis of the para A species to an anion of a weaker acid.

The irreversible nature of curve 1 has been further confirmed by conventional forward and reverse titration. Curve 1 is an approximation of the conventional forward titration. When a reverse conventional titration is performed immediately after the forward titration, a curve intermediate to curves 1 and 7 is generated.

In figure 5, the effect of adjusting the ionic strength to unity (by the addition of NaClO_4) is shown. The most apparent feature in Figure 5 with respect to Figure 4 is the sharper and more persistent inflection point for the para A species. The enhancement of this endpoint contradicts the findings of Jander et al.,⁽¹⁴⁴⁾ who claimed that NaClO_4 caused the disappearance of the para A inflection. Clearly, this claim is incorrect and the present results are in agreement with the reports of Souchay⁽¹⁴⁰⁾ and Biehler⁽²⁴⁹⁾ who found the para A endpoint to be sharper in the presence of Na_2SO_4 and NaCl . The stabilization of anions and cations and the promotion of dissociation equilibria by inert electrolytes is well-known.⁽²⁵⁰⁾ In the present work, the enhancement of the para A endpoint by NaClO_4 , relative to the metatungstate endpoint, is probably the result of greater stabilization of the para A anion (-5 charge compared to -3 for the ν -meta species).

(c) Spectrophotometric-pH studies on tungstate solutions

(i) In aqueous solution. Several workers^(111,132-135,144,164,248,251) have studied the optical properties of unacidified and acidified tungstate solutions. The tungstate ion, WO_4^{-2} , absorbs strongly below 250 nm (molar absorptivity unknown) at $\text{pH} \geq 8$. The absorbance is independent of time, which suggests that tungstate ion exists as a

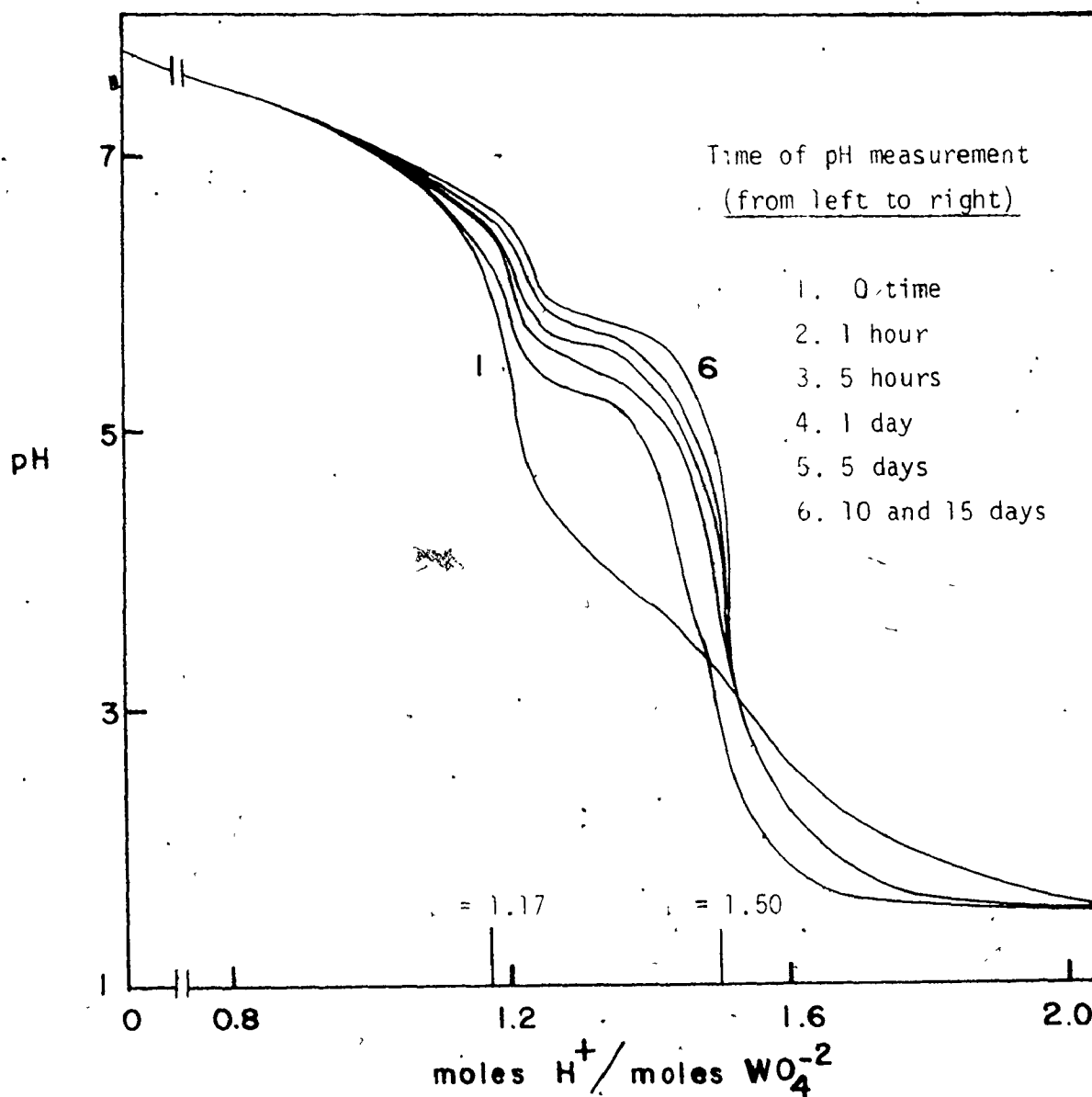


Figure 5. Point titration of sodium tungstate (50 ml) with perchloric acid ($C_{WO_4^{-2}} = 0.10$ M, $25^\circ C$, $NaClO_4$ added to give $\mu = 1$)

monomer at pH values ≥ 8 .

On acidification, the absorption edge moves to longer wavelengths. In Figure 6, the absorption spectra of tungstate solutions ($C_{\text{WO}_4^{-2}} = 4.8 \times 10^{-4}$ M, 25°C, ionic strength, $\mu = 1$) in the pH range 0-8 are presented. The spectra were recorded immediately after the solutions were prepared ('0 time'). There is a progressive increase in structure with decreasing pH. In conjunction with the observations made in the potentiometric studies above, and with existing observations in the literature, the absorption bands are explained as follows. The curve at pH 7.9 is due to absorption by the simple tungstate ion, WO_4^{-2} . The absorption edge does not change with time. The absorption in the pH region 6-4.6 (curves 2 and 3) likely results from a mixture of para A hexamer and monomeric WO_4^{-2} . Not apparent in curves 2 and 3 is a "weak" shoulder at about 270 nm which Glemser et al.⁽¹¹¹⁾ observed on dissolution of the potassium salt of para A in water in the pH region 6-5. The shift of curves 2 and 3 to the right of curve 1, however, is in accordance with the observation of Glemser et al.⁽¹¹¹⁾ The curves in the pH region 4.4-3 (curves 4 and 5) likely represent absorption by a mixture of para A and ψ -meta species. Glemser et al.⁽¹¹¹⁾ have prepared the potassium salt of ψ -metatungstate. Its spectrum in aqueous solution exhibits a shoulder at 262-265 nm, as in curve 5. In curve 6 (pH region 2.8-1.2), the shoulder is more fully developed. In addition, a new absorption maximum at 320-325 nm is observed, which might be due to a species termed polytungstate Y. Chauveau et al.⁽¹⁶⁸⁾ have recently prepared the potassium salt of the so-called poly Y species (composition, $\text{K}_5\text{HW}_{12}\text{O}_{39}$) and have shown that in aqueous solution at

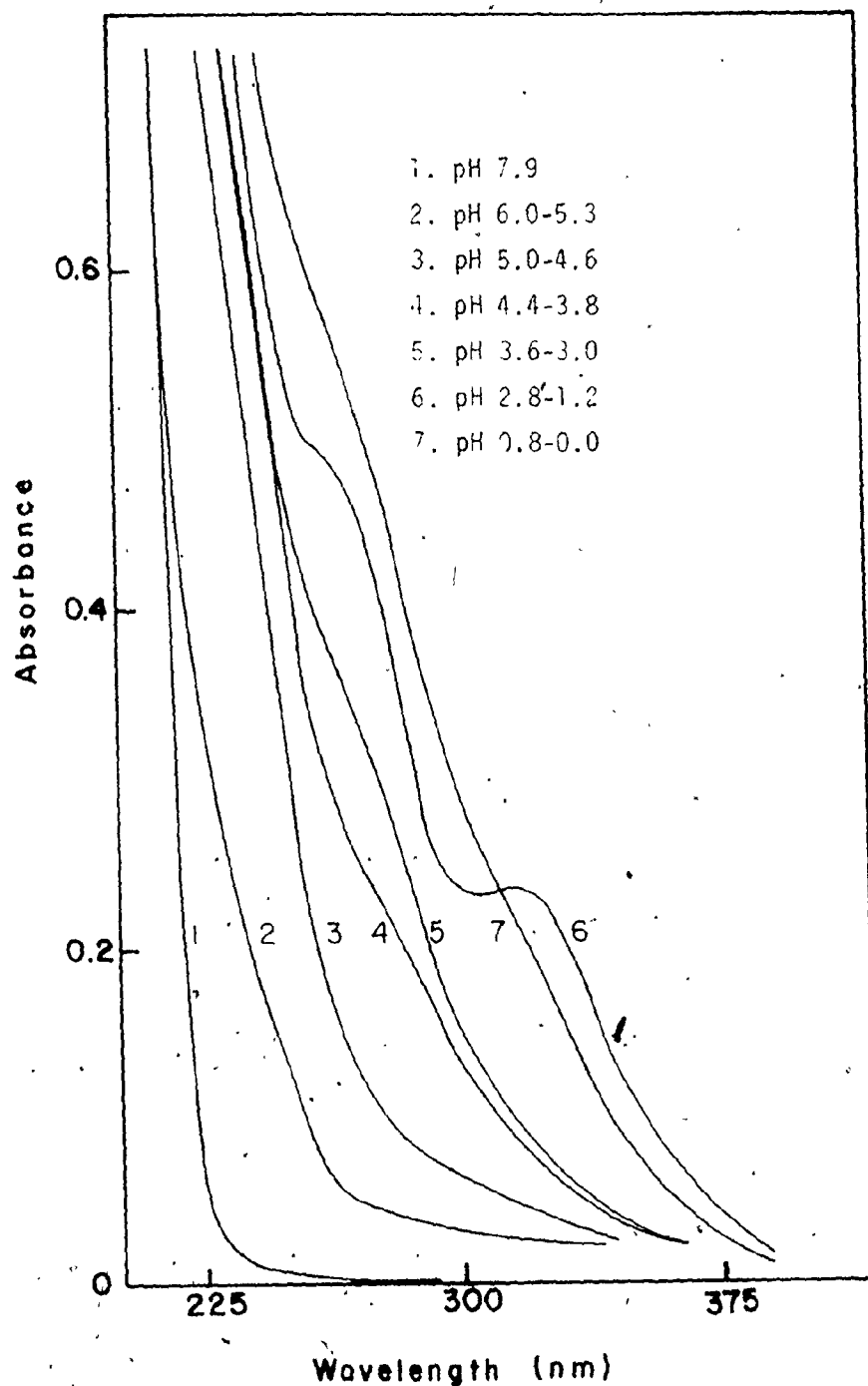


Figure 6. Absorption spectra of tungstate solutions at 0 time as a function of pH ($C_{\text{WO}_4^{2-}} = 4.8 \times 10^{-4}$ M, 25°C, $\mu = 1$, 5-mm cells, corresponding aqueous solution without tungstate as reference)

a pH < 2.5, it has an absorption shoulder at about 320 nm. At pH values < 1 (curve 7), the poly Y shoulder disappears. When the spectra of the above solutions were recorded one day later, all features were the same except that the poly Y shoulder in curve 6 had disappeared and the shoulder at about 260-265 nm had been enhanced. The enhancement of the ψ -meta shoulder with time is consistent with the point-titration data. With further aging, the spectra of the tungstate solutions ($C_{\text{WO}_4^{-2}} = 4.8 \times 10^{-4} \text{ M}$) change significantly. For example, Figure 7 depicts the spectra recorded after the solutions had been allowed to stand for 60 days. Curve 1 (for WO_4^{-2}) is unchanged. Curve 2 (pH 6-5.3) shows a well-defined peak at 240-245 nm which is identified as resulting from the paratungstate Z species, thought to have been formed in a slow reaction from para A. Solid para Z, dissolved in water at the stated pH range, yields the 240-245 absorption band (discussed later). At a lower pH (pH 5-4.6, curve 3), the para-Z peak has become a shoulder, and in the pH range 4.4-3.0 (curves 4 and 5) a new band has developed at 255-260 nm, which in curve 6 (pH 2.8-1.2) is a well-defined maximum (at 260 nm). This maximum represents the metatungstate species, $\text{H}_2\text{W}_{12}\text{O}_{40}^{-6}$, which is believed to form slowly from the ψ -meta species (shoulder at 260-265 nm, curve 6 in Figure 6). Curve 6 in Figure 7, is identical to curve 1 in Figure 8 which is the spectrum of solid metatungstate dissolved in acid solution (acidity range, 5 M HClO_4 to pH 8.3). Curves 2-5, Figure 8 show, incidentally, the decomposition of the metatungstate ultimately to WO_4^{-2} in alkaline solution. The spectra (Figure 8) were recorded immediately after preparation of the solutions. For each spectrum (except 1), the maximum decreased with time or with heating of the solutions.

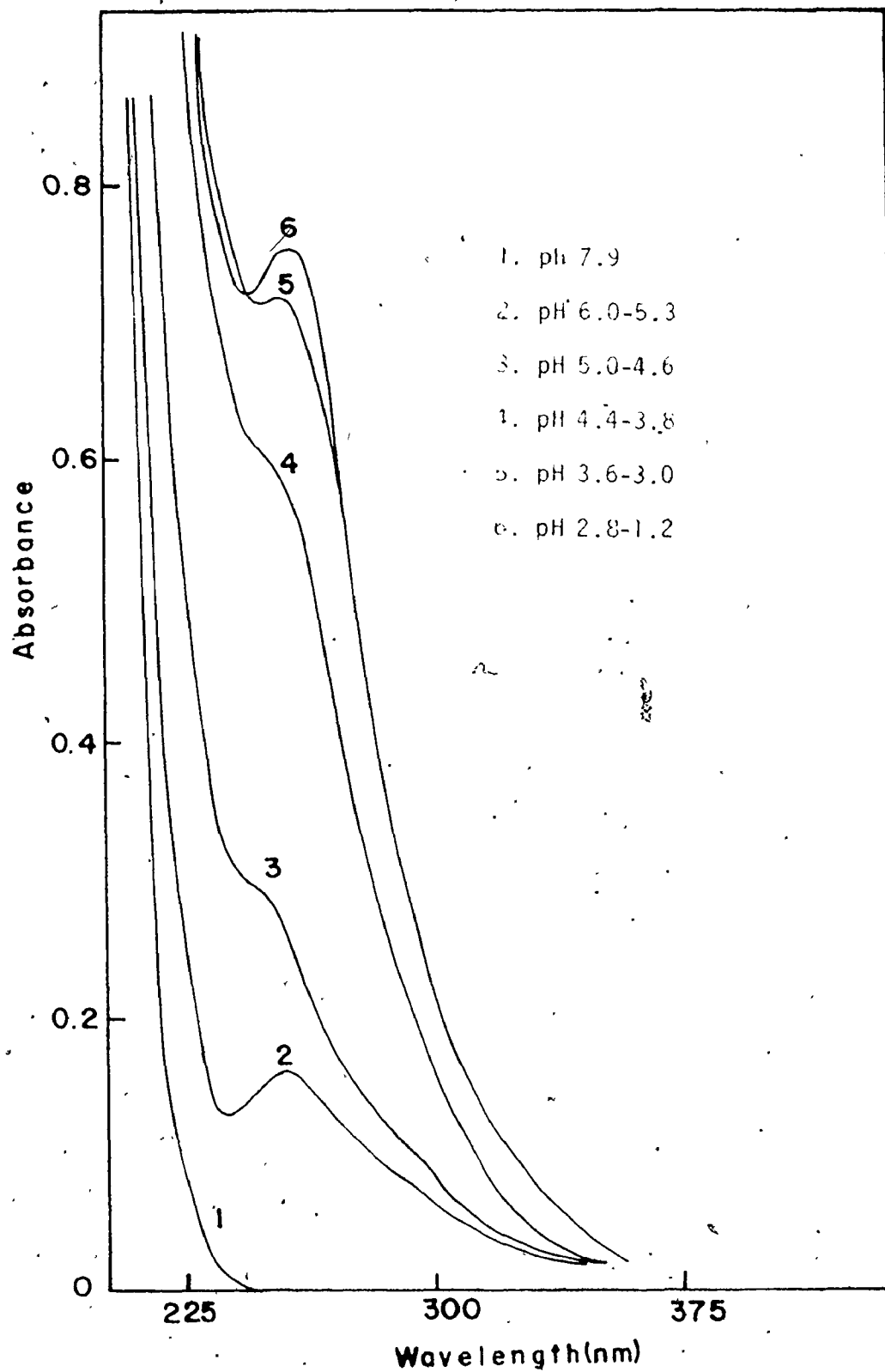


Figure 7. Absorption spectra of tungstate solutions, $\tau = 60$ days
(conditions same as for Figure 6)

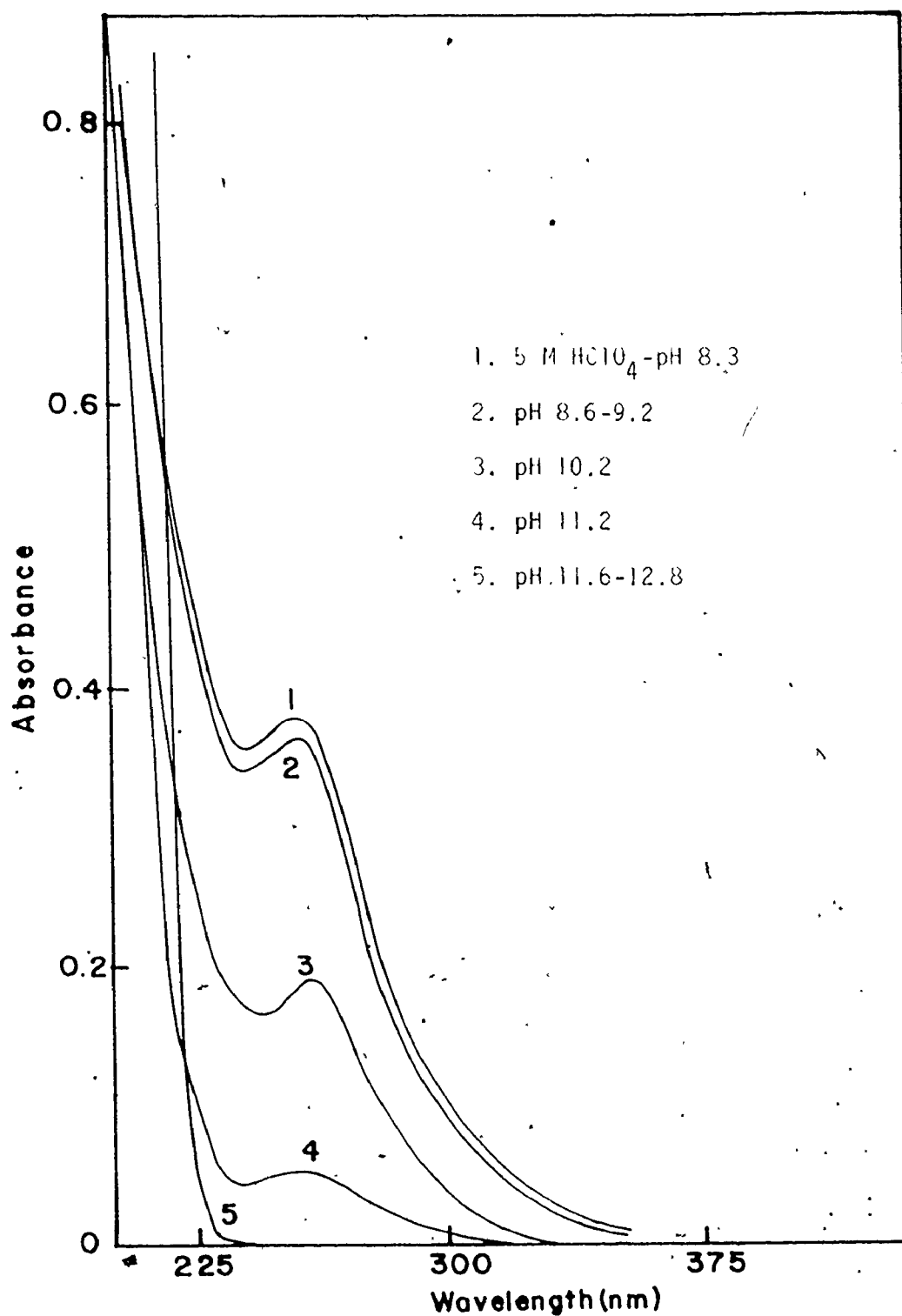


Figure 8. Absorption spectra of metatungstate solutions as a function of acidity. ($C_{\text{meta}} = 2.0 \times 10^{-5}$ M, $\mu = 1$, 25°C, 5-mm cell, corresponding blank reference).

The spectra for solutions which had been aged between '0 time' and 60 days are, in essence, intermediate to those shown in Figures 6 and 7. Also, at analytical concentrations of WO_4^{-2} of the order of 0.01 M and higher, the absorption is very intense (absorption edges are shifted to the right) and at about pH 2, yellow tungstic oxide is precipitated.

Because preliminary studies had indicated that possible analytical applications of the 12-tungstophosphate system were more likely to be successful in strongly acid rather than weakly acid or alkaline solution, the behaviour of the tungstate ion in the pH range 0-2 was studied in more detail. Figure 9 shows the absorption spectra for tungstate solutions ($C_{\text{WO}_4^{-2}} = 4.8 \times 10^{-4}$ M) in the pH range 0.7-2.0. No significant differences are observed (c.f., curves 6, Figures 6,7). The maximum (320-325 nm) due to poly Y (curve 1) is significantly decreased after one day and the shoulder at about 260 nm develops with time into a well-defined maximum. Also, when freshly-prepared solutions in this pH range are boiled and their spectra recorded immediately after the solutions had been cooled, the peak at 260 nm is enhanced, indicating an increased rate of formation of the metatungstate species.

In the pH range 0-0.5, significant differences are noted (Figure 10). The maximum at 320-325 nm due to poly Y is not observed, the shoulder at about 260 nm is less obvious, and after one day, the solution becomes cloudy due to the precipitation of white tungstic oxide.

In summary, the above spectrophotometric studies of acidified tungstate solutions show that in the pH region 6-5, para A is a significant species; with time, it comes into equilibrium with the

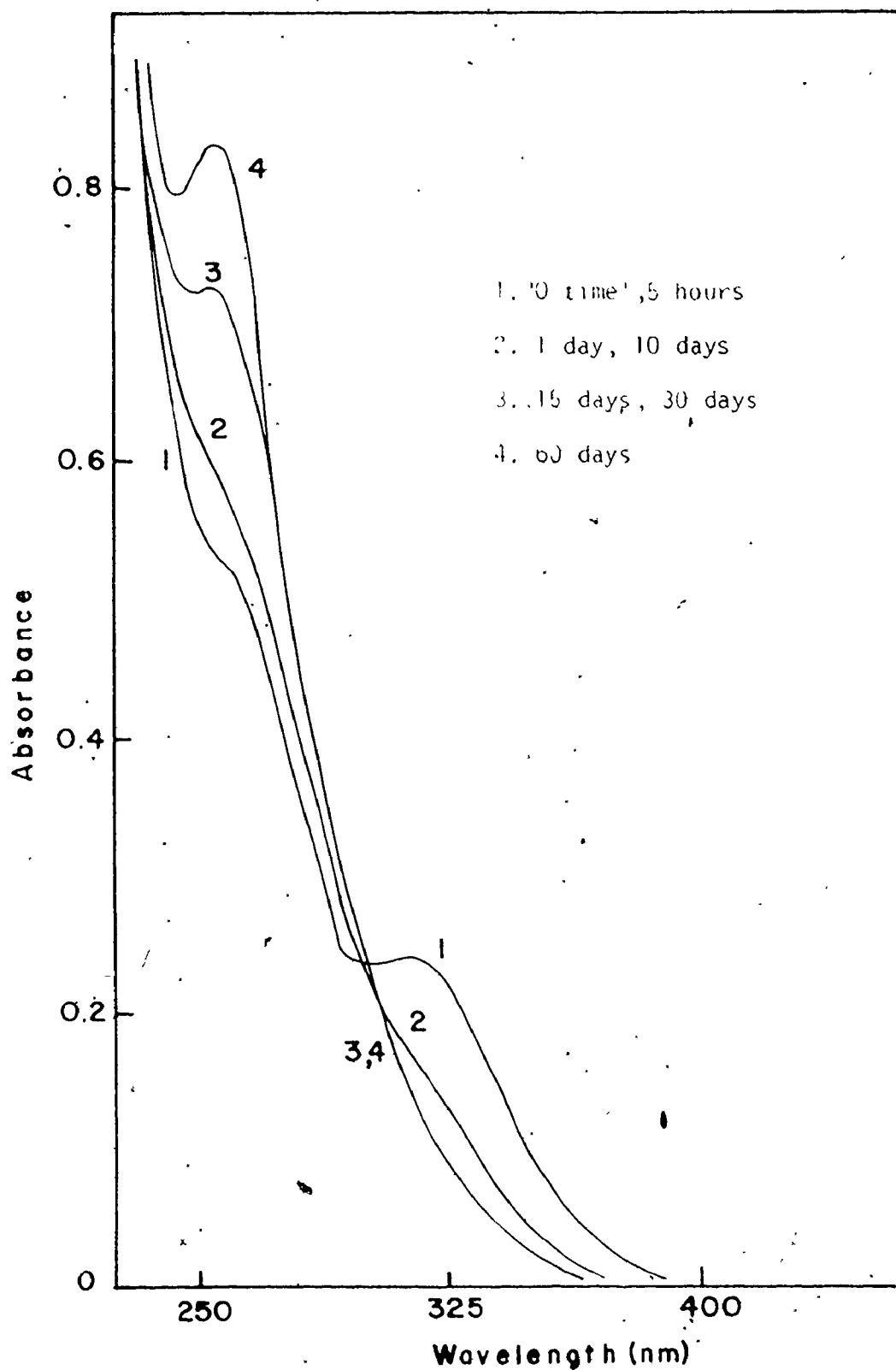


Figure 9. Absorption spectra of tungstate solutions, pH 0.7-2, as a function of time. (Conditions same as for Figure 6)

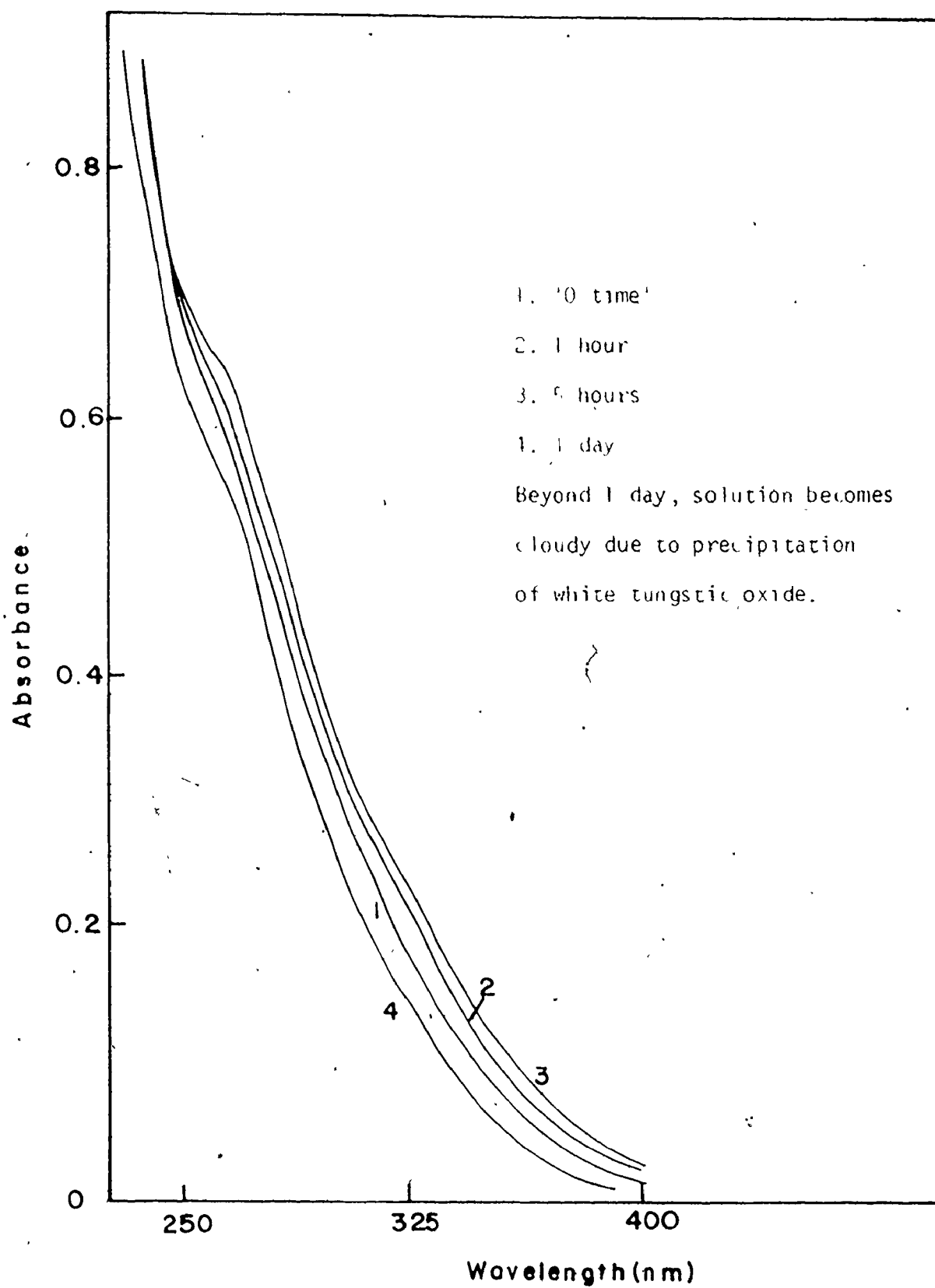


Figure 10. Absorption spectra of tungstate solutions, pH 0-0.5, as a function of time. (Conditions same as in Figure 6)

para Z species which, in turn, leads ultimately to the formation of some metatungstate ion. At pH values about 4 or lower, the absorption is due to three dominant species: ψ -metatungstate, metatungstate and polytungstate Y (a transient species). All solutions in the pH range about 0.5-6 yield the metatungstate ion on aging. In strongly acidic solutions (e.g., pH 0) white tungstic oxide is precipitated.

Because of the commercial availability of sodium paratungstate Z, spectral studies of the aqueous solutions ($C_{\text{para Z}} = 8.02 \times 10^{-6}$ M) of this species were made at pH 6.4, 4.4, 2.5 and 0.5 as a function of time (0 time-40 days). The spectra for the solutions at pH 2.5 are given in Figure 11. Curve 1 ('0 time') features only the para Z absorption edge but after 5 hours, a shoulder at 255-260 nm (ψ -metatungstate) is observed (curve 2), which, after 40 days (curve 4), has developed into a maximum at 260 nm (metatungstate). Also, curve 2 exhibits a maximum at 320 nm, which suggests the formation of some poly Y species in solution after 5 hours. This species is unstable under the conditions, however, and no evidence of the band is observed in curve 4. The spectra for the solution at pH 0.5 were essentially the same (not shown) except that the metatungstate peak was more intense (0.45 absorbance units after 40 days). At pH 6.4 and 4.4, the absorbance of the metatungstate peak was about 0.2 and 0.25 (after 40 days) and no spectral evidence of poly Y formation was observed.

Spectra of para Z solutions ($C_{\text{para Z}} = 8.02 \times 10^{-6}$ M) taken at 0 time over a broader pH range are shown in Figure 12. Curve 1 (pH 9-11) is consistent with the spectrum of WO_4^{-2} , showing that in

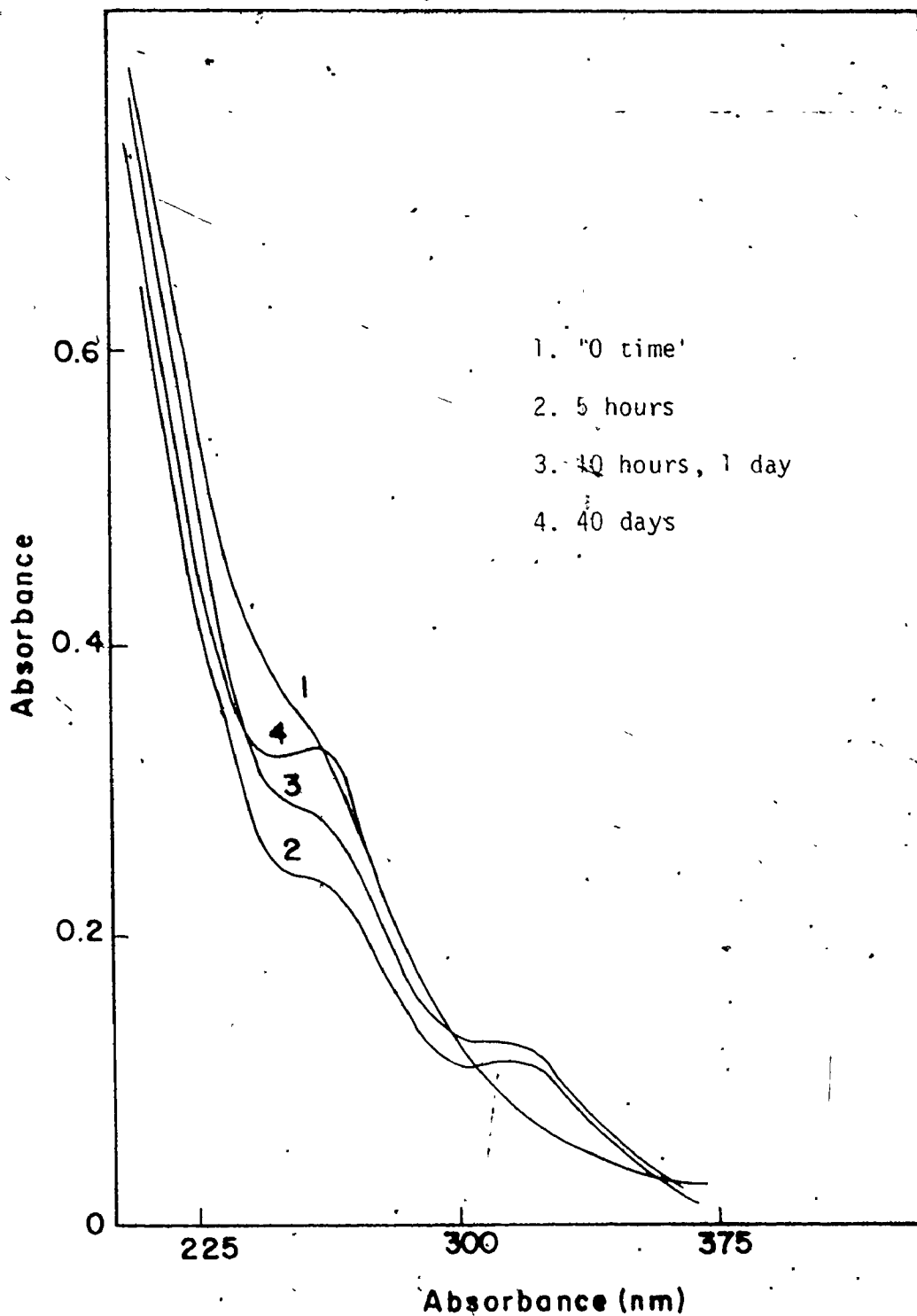


Figure 11. Absorption spectra of paratungstate solutions at pH 2.5 as a function of time. ($C_{\text{para Z}} = 8.02 \times 10^{-6} \text{ M}$, $\mu = 1$, 25°C , 5-mm cells, corresponding aqueous solution without para Z as reference)

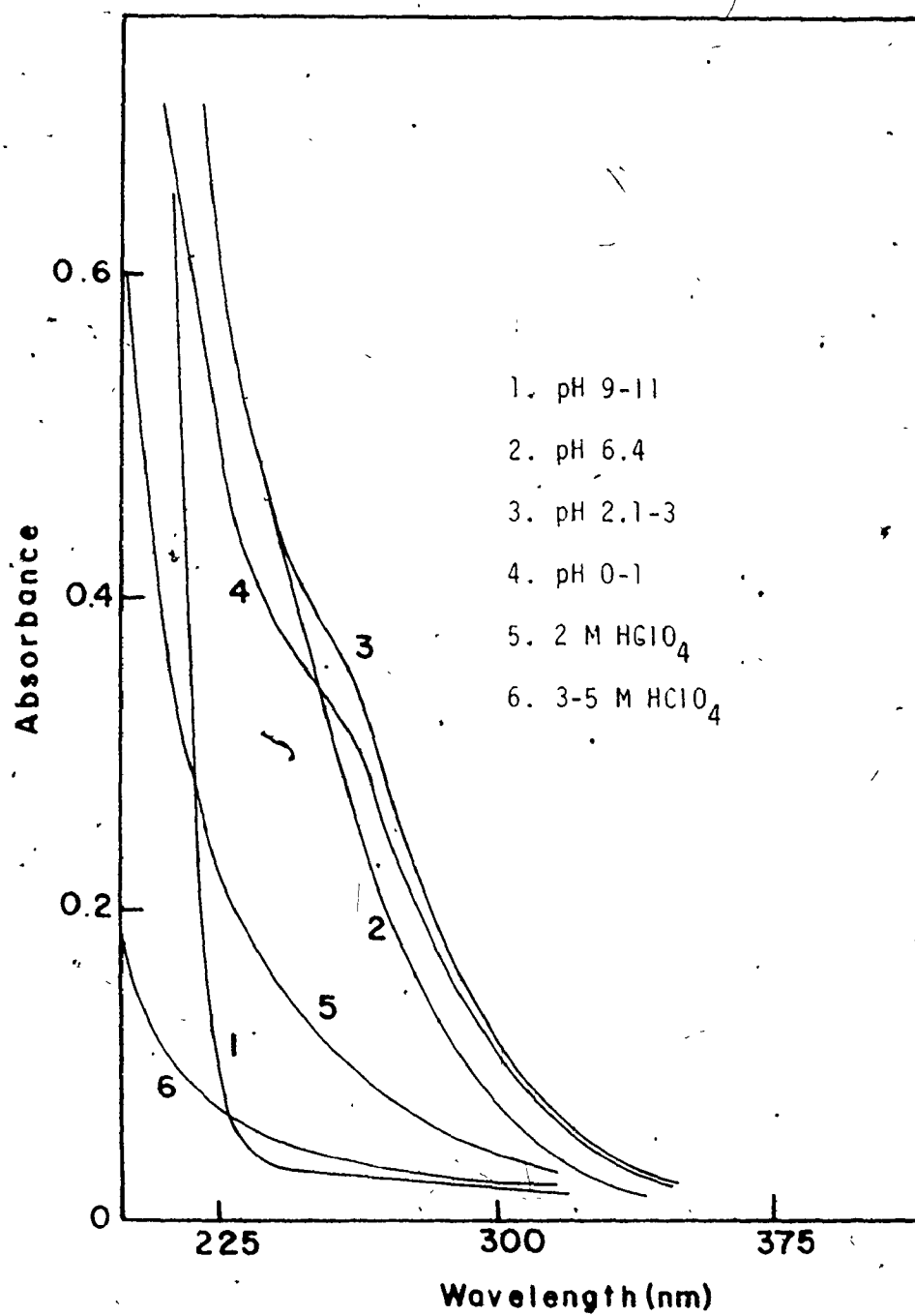
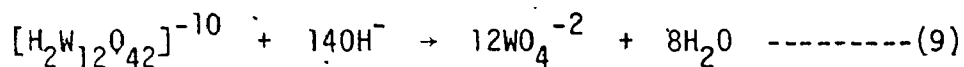


Figure 12. Absorption spectra of paratungstate solutions at '0 time' as a function of acidity. (Conditions same as for Figure 11)

alkaline solution, decomposition of para Z to monomeric tungstate occurs:



Curve 2 shows the absorption edge of the para Z species and curves 3 and 4 (pH 2.1-0) exhibit shoulders in the 260 nm region that are likely due to ψ -metatungstate. The low absorption of curves 5 and 6 (2-5 M HClO_4) are due to the decomposition of para Z to tungstic oxide which occurred in these strongly acidic solutions. For identical solutions that were aged, the main changes occurred in curves 3, 4 and 5 which showed some development of bands in the 265 nm (metatungstate) and 320 nm (poly Y) regions. The spectra of the freshly-prepared solutions, which were recorded immediately after they were boiled and cooled to 25°C, were essentially the same as those obtained after aging them for one day at 25°C except for the solution at pH 6.4. It (curve 2, pH 6.4) now showed some development (0.15 absorbance units) in the 265 nm region. Aging the solutions for 40 days at 25°C, yielded spectra (Figure 13) in which only the 265 nm maximum (metatungstate ion) was evident.

These observations show that from paratungstate Z solutions, one obtains (in addition to the para A species with which it comes into equilibrium) the ψ -metatungstate, the metatungstate and the polytungstate Y species, at appropriate pH values. Ultimately, however, all solutions at all pH values except those at pH > 9 yield the metatungstate ion. Interestingly, Figure 13 shows that the rate of formation of the metatungstate is pH-dependent.

As shown by the above studies on tungstate and paratungstate Z solutions, the metatungstate ion is apparently the most thermodynamically stable of all the isopoly species.

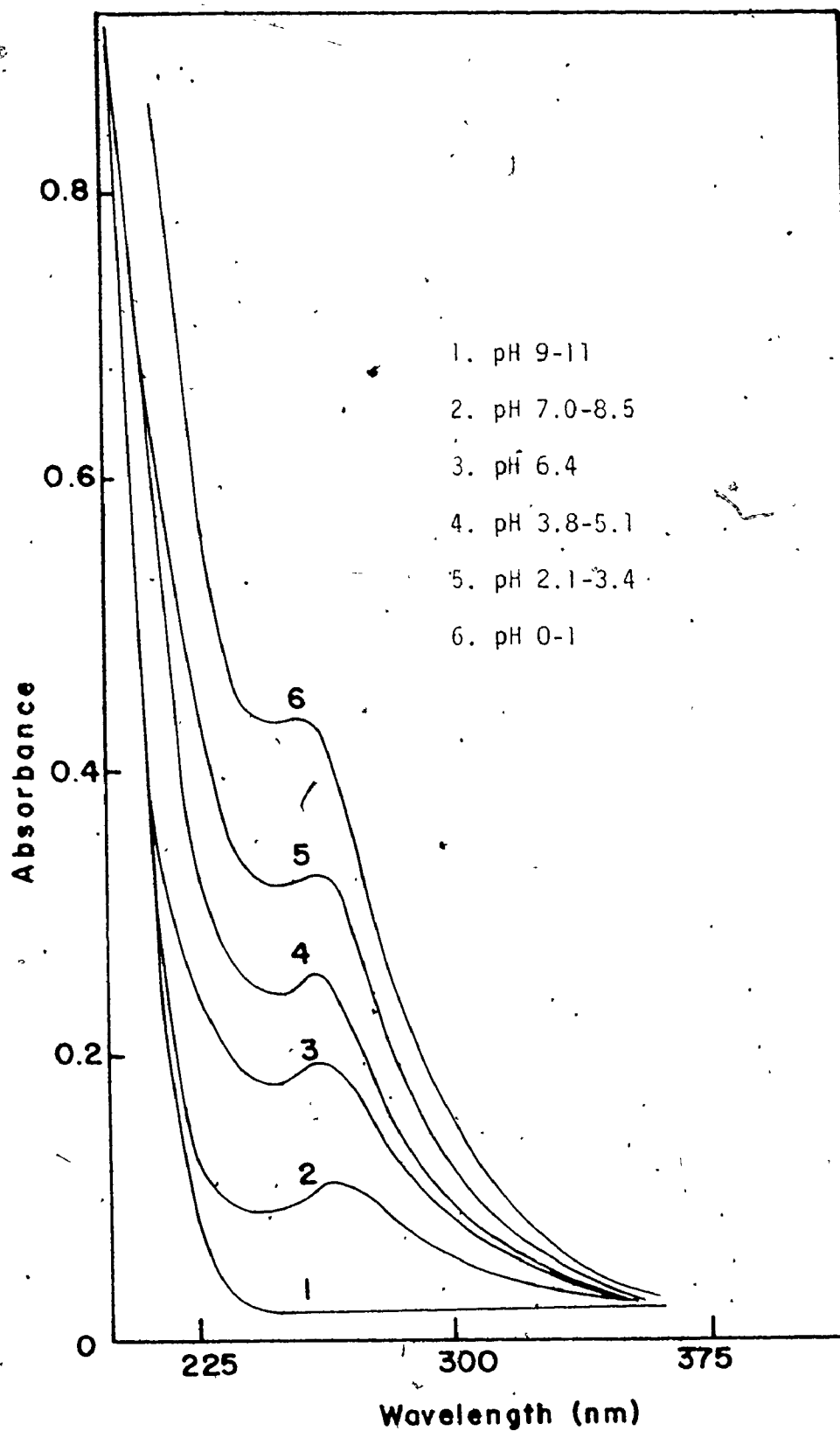


Figure 13. Absorption spectra of paratungstate solutions at 40 days as a function of acidity. (Conditions same as for Figure 11).

(ii) In *n*-amyl alcohol. Preliminary experiments showed that maximum formation of 12-tungstophosphoric acid (TPA) occurs at $\text{pH} \leq 2$ and that its absorption maximum is at 267 nm (see Section 2 below). Quantitative spectrophotometric advantage of the formation of TPA would therefore be possible only if the absorption due to the isopolytungstates could be eliminated or made relatively insignificant at $\text{pH} \leq 2$. In particular, the metatungstate, which is stable in aqueous acid solution, might interfere since its absorption maximum (265 nm) coincides with that of TPA.

Since the extraction of 12-heteropoly acids, including TPA, into oxygenated organic solvents is well-known, it was felt that perhaps TPA could be isolated from the isopolytungstates by solvent extraction prior to its absorbance measurement. As little information is available on the extraction properties of isopolytungstates, experiments were carried out for this purpose and the results obtained are discussed below.

The solvent selected was *n*-amyl alcohol. The solubility of TPA in this solvent is about 220 g/litre at 25°C. *n*-Amyl alcohol, as obtained commercially, absorbs appreciably above 250 nm (Figure 14 A, curve 2) due to the presence of impurities, particularly iso-amyl alcohol (curve 3). The absorbance of distilled *n*-amyl alcohol is, however, insignificant above 250 nm (curve 1). A substantial drop below zero absorbance is obtained if distilled *n*-amyl alcohol is used as the reference and water as the sample (curve 4). In practice, the absorbance of, say, TPA would be measured in an *n*-amyl alcohol phase which had been equilibrated with an acid-aqueous phase against *n*-amyl alcohol as a reference. The baseline

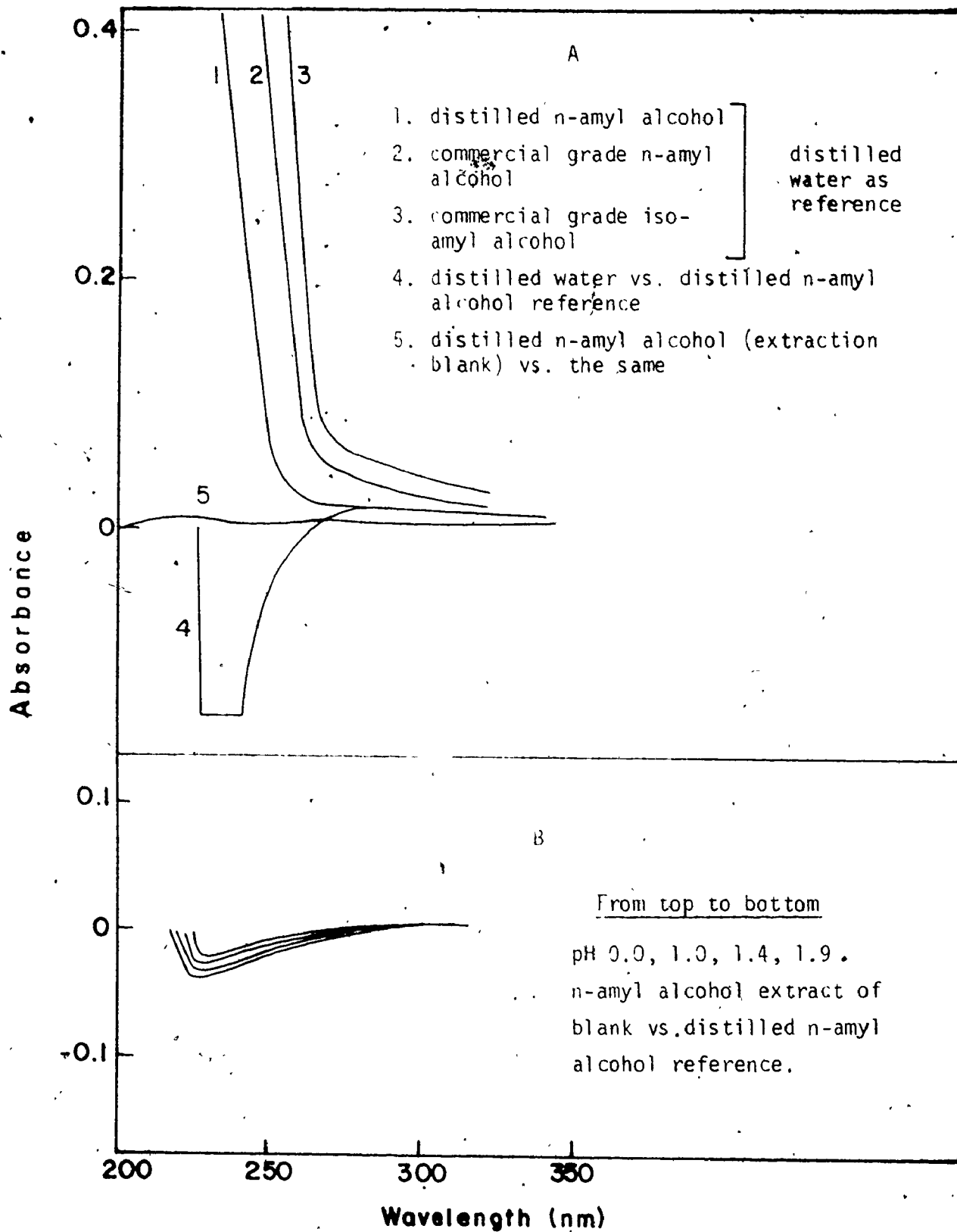


Figure 14. Absorption spectra of n-amy] alcohol (5-mm cells, 25°C)

for such a procedure in the pH range 0-2 is shown in Figure 14 B. The negative absorbance in the 240 nm region shows the unsatisfactory nature of this procedure. This negative absorption is due to the solubility of water in n-amyl alcohol (2.19% by weight at 25°C⁽³⁹⁾) which, in effect, reduces the concentration of the alcohol in the test solution relative to that in the reference liquid, n-amyl alcohol. (Note that Figure 14 B shows that the solubility is dependent upon the pH of the aqueous phase.) This negative absorbance is, however, easily overcome by the use of an equilibrated alcohol solution (rather than the n-amyl alcohol solvent itself) as the reference. Curve 5, Figure 14 A, shows that the baseline is practically zero when equilibrated n-amyl alcohol solution is used in both the cells. Therefore, in all subsequent studies involving extraction with n-amyl alcohol, the corresponding blank extract solution was used as the reference.

The absorption curves of the n-amyl alcohol phase after extraction of the tungstate solutions ($C_{W_4}^{-2} = 1.2 \times 10^{-2}$ M) are given in Figure 15. These curves were obtained at '0 time' in the pH range 0-2.2. In the range 1.0-0.5 M HClO₄ (curves 1 and 2), absorption maxima due to the ψ -meta (262 nm)* and poly Y (325 nm) species are in evidence. In the pH range 1.0-2.2, only the ψ -meta peaks are present but the absorption intensity is considerably reduced. In aqueous solution, the presence of poly Y at pH values 1-2 was observed, as described previously. Therefore, its absence is likely due to its non-extractability into

* In aqueous solution, the ψ -meta gives only an ill-defined shoulder.

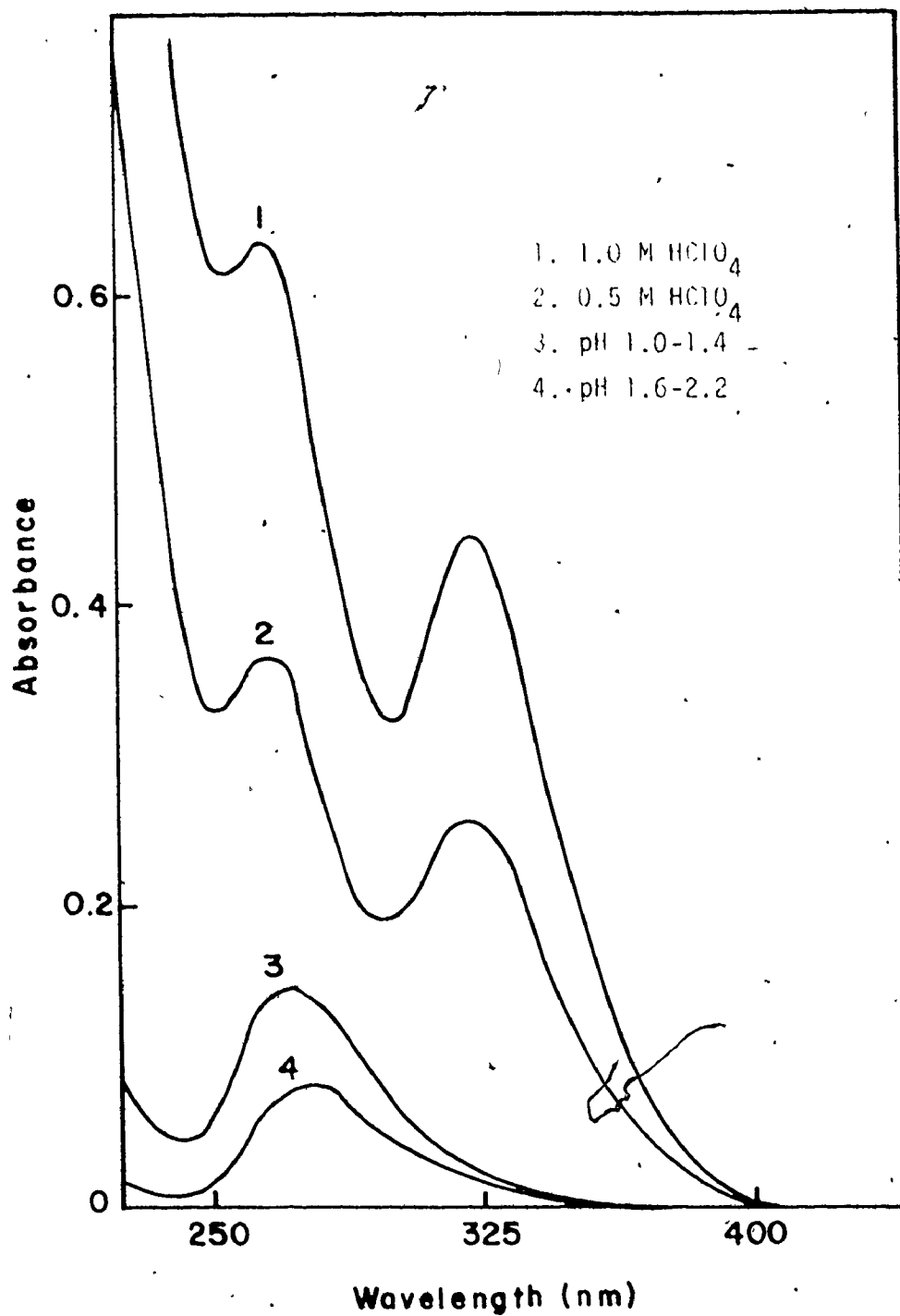


Figure 15. Absorption spectra of tungstate solutions in n-amyl alcohol after extraction from aqueous phase at '0 time' as a function of acidity ($C_{WO_4^{2-}} = 1.2 \times 10^{-2}$ M, 25°C, 5-mm cells, n-amyl alcohol extract of corresponding blank reference)

n-amy1 alcohol over this pH range (perhaps because of an unstable ion-association species involving H_3O^+ or ROH_2^+ as the counter-ion).

The changes that occur on aging or boiling the acidified tungstate solutions prior to extraction are also of interest. Figure 16 A, represents the absorption spectra of the n-amy1 alcohol phase after extraction of aqueous tungstate solutions aged for one day at 25°C. The absorption at 260-265 nm and 320 nm is now significantly reduced in the acid range 1 M-0.5 M $HClO_4$ (curves 1 and 2). This reduction in absorption is more drastic on boiling the solution (and then cooling to 25°C) prior to extraction (Figure 16 B, curves 1 and 2). In the pH range, 1.0-2.2, essentially a baseline of zero absorbance is obtained either on aging or on boiling the tungstate solutions prior to extraction. The reduction in absorbance at 260-265 nm is the result of conversion of the γ -meta species to the metatungstate which itself is not extractable at acidities of 1 M or less. Figure 17 represents the absorption spectra of the metatungstate species after extraction of aqueous solutions ($C_{meta} = 1.97 \times 10^{-5}$ M) into n-amy1 alcohol. As can be seen, the extraction of metatungstate into n-amy1 alcohol is appreciable only above 2 M $HClO_4$, and is insignificant below 1 M $HClO_4$.

The decrease in absorbance at 320 nm (Figure 16 B) on aging or boiling the tungstate solutions (1.0-0.5 M $HClO_4$) is due to the instability of the poly γ species in aqueous solution as previously described.

Similar studies at other tungstate concentrations showed the same absorption pattern as that at $C_{WO_4}^{-2} = 1.2 \times 10^{-2}$ M, except for expected variations in absorption intensity with concentration. But

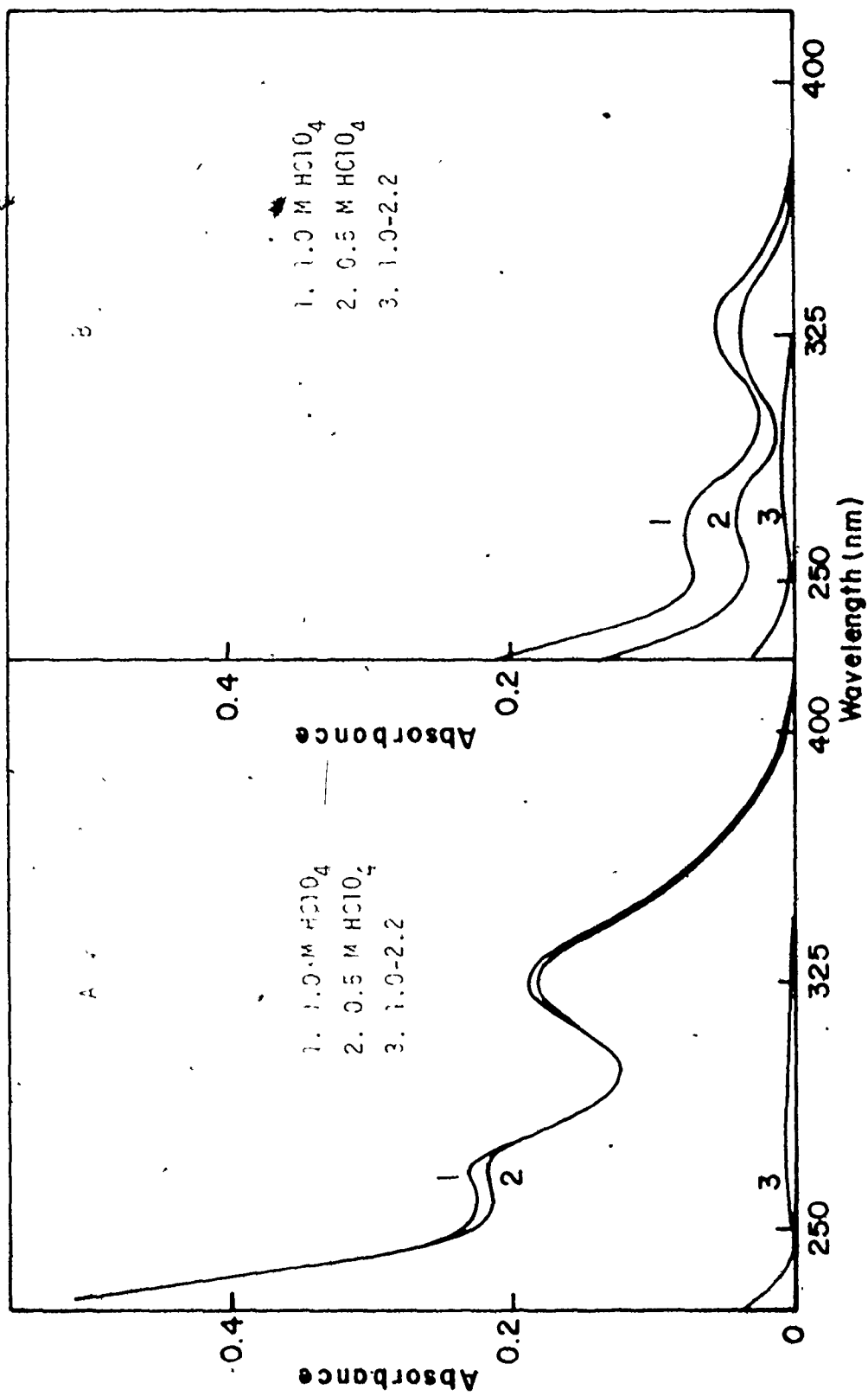


Figure 16. Absorption spectra of tungstate solutions in n-amyl alcohol after extraction from aqueous phase as a function of acidity (H^+ concentration = 1.2×10^{-2} M, 5-mm cells, n-amyl alcohol extract of corresponding blank reference)

A. extracted after aging for 1 day at 25°C

B. extracted after the solutions had been brought to a boil and cooled to 25°C

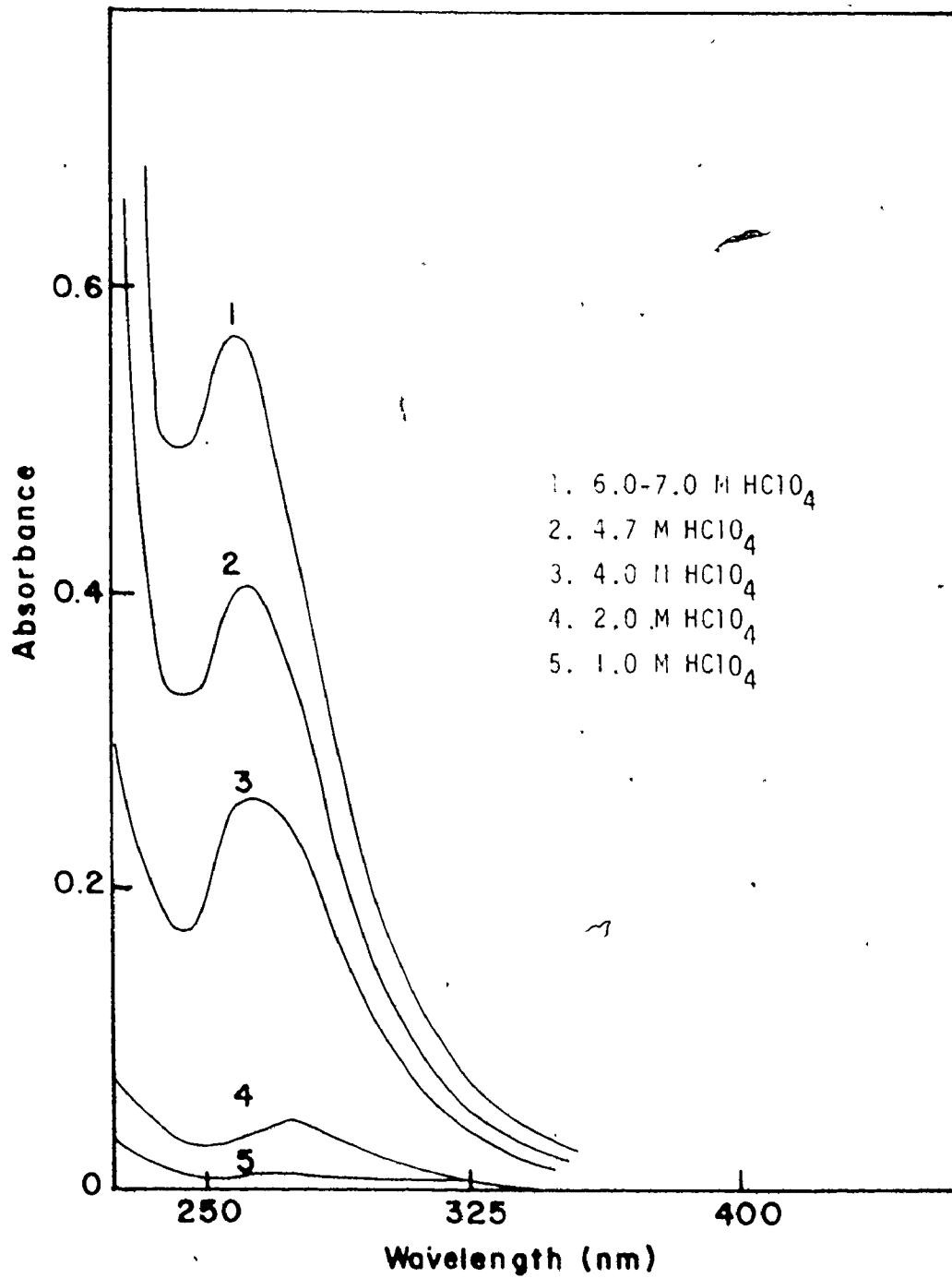


Figure 17. Absorption spectra of metatungstate solutions in n-amyl alcohol after extraction from aqueous solution as a function of acidity ($C_{\text{meta}} = 1.97 \times 10^{-5} \text{ M}$, 25°C , 5-mm cells, n-amyl alcohol extract of corresponding blank reference)

at all concentrations, even ${}^{\infty}C_{\text{WO}_4}{}^{-2} = 1.2 \times 10^{-1} \text{ M}$, the baseline was essentially zero in the pH range 1-2 after aging or boiling the tungstate solutions.

In this study, it was also of interest to extract the acidified paratungstate solutions ($C_{\text{para Z}} = 8.0 \times 10^{-5} - 3.2 \times 10^{-4} \text{ M}$) with *n*-amyl alcohol and to compare the spectra obtained with those in aqueous solution. Figure 18 represents the absorption spectra of paratungstate Z solutions ($C_{\text{para Z}} = 1.6 \times 10^{-4} \text{ M}$) after extraction into the *n*-amyl alcohol phase at '0 time' (Figure 18 A), 1 day (Figure 18 B) and after the aqueous solutions had been brought to a boil and cooled to 25°C (Figure 18 C). As can be seen, the spectra parallel closely those in aqueous solution. Of importance is the zero-baseline in the pH range 0-2.

The important conclusion that emerges from these studies is that interference of isopolytungstates will be of no significance in absorbance measurements of TPA after its formation in aqueous solution and subsequent extraction into *n*-amyl alcohol, provided the pH range is restricted to 1-2. The stable metatungstate species and the less stable paratungstate and poly Y species are not extractable above pH 1 and the α -meta converts to the meta species on aging or heating. The upper limit of pH 2 is imposed by the non-quantitative formation and extraction of TPA above this value (see Section 2 below).

In summary, the following contributions have been made to the chemistry of the isopolytungstates:

(i) The rise in pH that occurs between the two points of inflection (i.e., $p = 1.17$ and $p = 1.50$) in the point-titration of

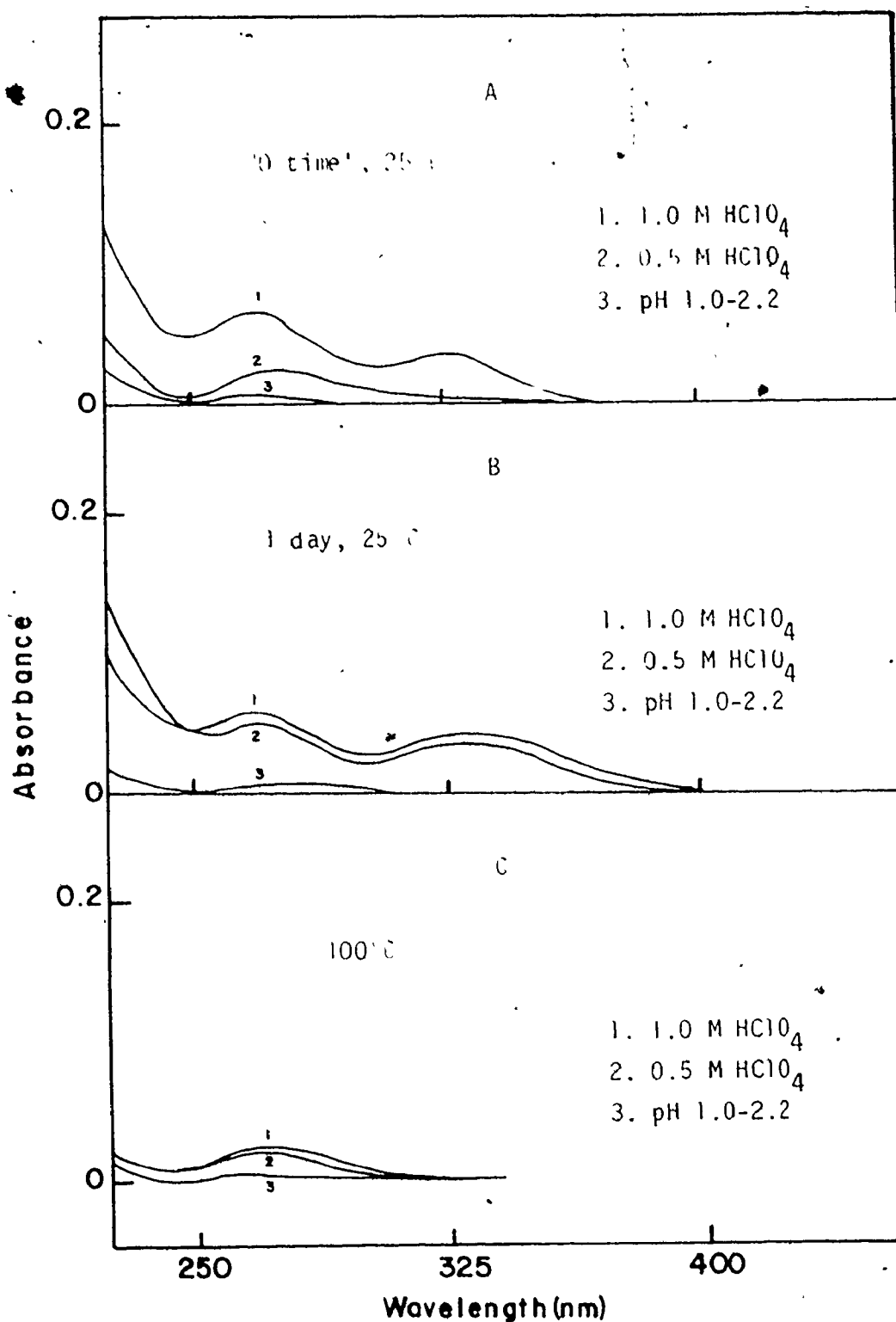


Figure 18. Absorption spectra of paratungstate solutions in *n*-amyl alcohol after extraction from aqueous solution as a function of acidity ($C_{\text{paratungstate}} = 1.6 \times 10^{-4}$ M, 5-mm cells, *n*-amyl alcohol extract of corresponding blank reference)

tungstate solutions has been re-interpreted in terms of a slow structural rearrangement of the paratungstate A species, with the consumption of 2 protons per molecule of para A. Although the direct titration clearly shows two inflection points, suggestive of two rapid successive protonation steps, the second step is only an apparent one and is observed because the structural rearrangement has already begun during the titration.

(ii) In the presence of the electrolyte, NaClO_4 , the above rearrangement is not complete, at least, after 15 days. This observation is in agreement with the findings of Souchay⁽¹⁴⁰⁾ and Biehler⁽²⁴⁹⁾ and not of Jander et al.⁽¹⁴⁴⁾ who claimed the disappearance of the para A endpoint in the presence of electrolytes.

(iii) The metatungstate and polytungstate Y species are extractable into n-amy1 alcohol but only from strongly acid aqueous solutions ($< \text{pH } 1$). These observations are of particular importance in the application of the heteropoly acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, to the determination of phosphate.

(iv) Unlike in aqueous solution, the poly Y species is very stable in n-amy1 alcohol. The enhanced stability should facilitate the unambiguous characterization of this poorly defined entity.

2. Heteropolytungstate systems

(a) Potentiometric titration of 12-tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$

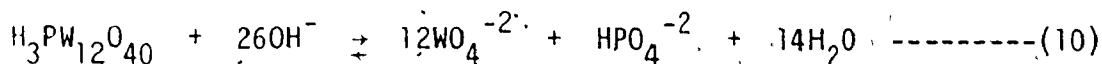
(TPA)

According to Miolati⁽¹²⁹⁾ and Rosenheim,⁽¹³⁰⁾ the composition of TPA in aqueous solution is $\text{H}_7\text{PW}_{12}\text{O}_{42}$, with 7 dissociable protons.

This conclusion was apparently supported, at least in part, by potentiometric titrations. For example, Malaprade found a potential jump in the titration of TPA in aqueous solution that corresponded to 7 equivalents of base per mole of TPA.⁽²²⁰⁾ The titration showed a single step rather than the multiple steps typical of polyprotic acids and indicated that the protons are of about the same acid strength. The isolation of Ag(I) and guanidine hepta salts also seemed to support the heptabasicity of TPA.⁽¹³⁰⁾

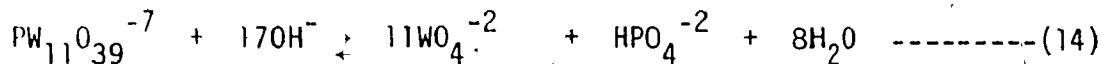
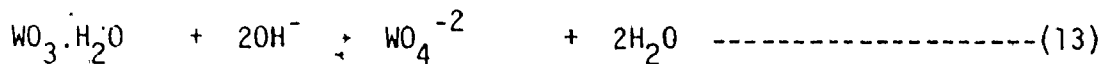
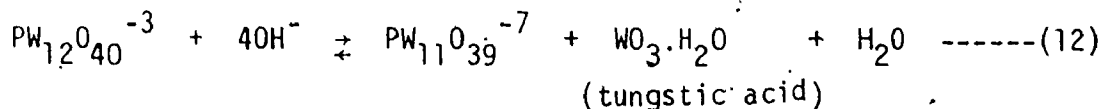
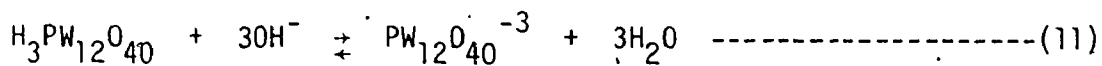
Some element of uncertainty with regard to the proposed heptabasicity was introduced after Keggin determined the X-ray structure of TPA.⁽¹⁸⁸⁾ A basic proposal of Keggin's structure was the formulation of the heteropolyanion as $PW_{12}O_{40}^{-3}$, with the neutrality of charge preserved by three protons situated on three-fold axes of the anion.⁽²¹⁹⁾ The results of several physicochemical experiments, which followed Keggin's formulation of TPA as $H_3PW_{12}O_{40}$, confused the issue once again. For example, a cryometric neutralization suggested TPA to be heptabasic.⁽²⁵²⁾ Coagulation, light-scattering and spectrophotometric techniques seemed to favour the formulation of the anion as $PW_{12}O_{42}^{-7}$ ⁽²²⁶⁻²³⁰⁾. Molecular-weight determinations in aqueous solutions gave a value of only 1700^(227,228) as against the expected value of 2916 for $H_7PW_{12}O_{42}$, indicating some degree of dissociation. In a polarographic study, Souchay⁽²³⁴⁾ concluded that under the conditions used, dissociation of TPA to $PW_{11}O_{39}^{-7}$ did occur. Finally, in a heat of neutralization study, Spitsyn et al.⁽²³²⁾ concluded that in aqueous solution, TPA is intrinsically triprotic and that its apparent high basicity was due to degradation to species of higher charge.

In the present study, no evidence for the intrinsic triprotic character of TPA in aqueous solution was obtained in a potentiometric neutralization titration. In Figure 19, the first step corresponds to the consumption of 7 moles of NaOH per mole of TPA (No intermediate inflections characteristic of step-wise dissociation are apparent in the curve). The second inflection is equivalent to 19 moles of NaOH per mole of TPA. Based on TPA as $H_3PW_{12}O_{40}$, the overall titration reaction is:



i.e., complete dissociation to WO_4^{-2} and HPO_4^{-2} occurs.

A possible empirical step-wise scheme that would reasonably account for the overall reaction stoichiometry is*:



To be consistent with Figure 19, reactions (11) and (12) are postulated to occur over the pH range 2-4 without step-wise differentiation. These two reactions together could have led earlier workers to conclude that TPA is heptabasic. Similarly, reactions (13) and (14) are postulated to occur over the pH range 6-9. The unit $PW_{11}O_{39}^{-7}$ has been previously

* No attempts were made in this work to obtain evidence for this scheme.

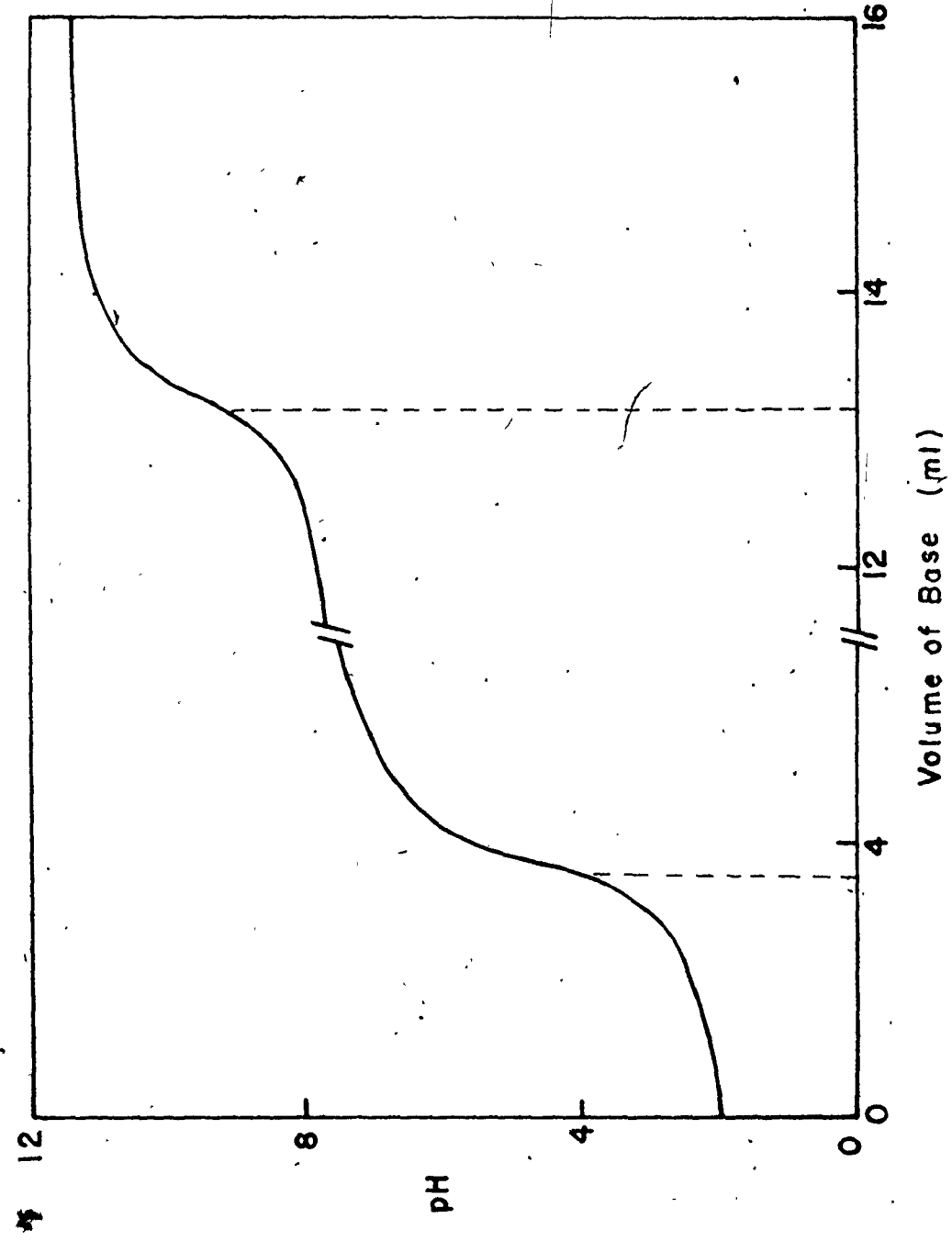


Figure 19. Potentiometric titration of TPA (50 ml, 1.0×10^{-3} M) with 9.9×10^{-2} M NaOH in aqueous solution (25°C , $\mu = 1$)

proposed⁽²³⁴⁾ but not characterized, and the degradation of heteropolytungstate anions to WO_4^{-2} in alkaline solution is well-known.⁽²³²⁾

In the present study, unequivocal evidence for the intrinsic triprotic behaviour of TPA was obtained by its titration in two non-aqueous solvents, n-amyl alcohol and 2-butanone, with tetra-n-butylammonium hydroxide, $(\text{C}_4\text{H}_9)_4\text{N}^+\text{OH}^-$ (Figure 20). The number of moles of TPA taken for titrations 1 and 2 were 0.050 and 0.053, respectively. The number of moles of base consumed were 0.148 and 0.156, respectively, i.e., 3 moles of base per mole of TPA. These results show that the high basicity of TPA in water is due to hydrolysis and that TPA is intrinsically triprotic, with no discernible differentiation in the acid-strength of the protons.

(b) Spectrophotometric-pH studies on TPA

The absorption spectra of aqueous solutions of TPA ($C_{\text{TPA}} = 3.21 \times 10^{-5} \text{ M}$)* in the range 4 M HClO_4 to pH 12 are presented in Figure 21. The constant absorbance at 267 nm over the pH range 0-2.0 (curve 2) is a notable feature and suggests that TPA exists as the undissociated acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, over this range. At pH 2.4 (curve 3), the absorbance is significantly decreased and a slight shift in maximum (to 257 nm) has occurred. In the pH range 3.6-5.0 (curves 4, 5, 6), a shift to 248 nm has resulted. Although curves 2-6 give the impression of the existence of an isosbestic point, in fact there is none. The

* The solutions of TPA were prepared from the commercially available compound, i.e., the TPA was not generated in solution from WO_4^{-2} , H_2PO_4^- and acid.

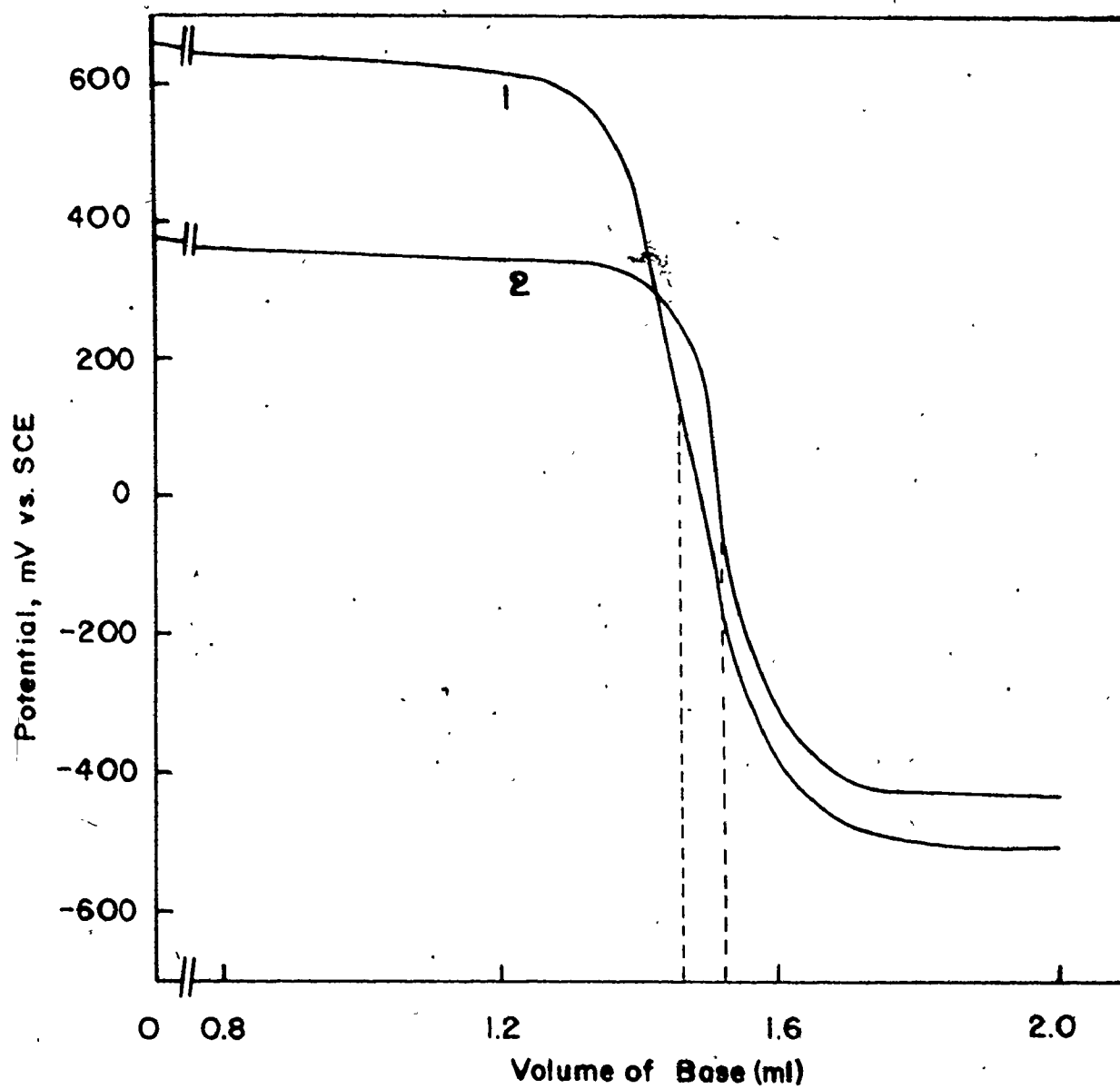


Figure 20. Potentiometric titration of TPA in non-aqueous media with 0.101 M tetra-n-butylammonium hydroxide at 25°C

1. 0.144 g TPA in 2-butanone (50.0 ml)
2. 0.153 g TPA in n-amyl alcohol (50.0 ml)

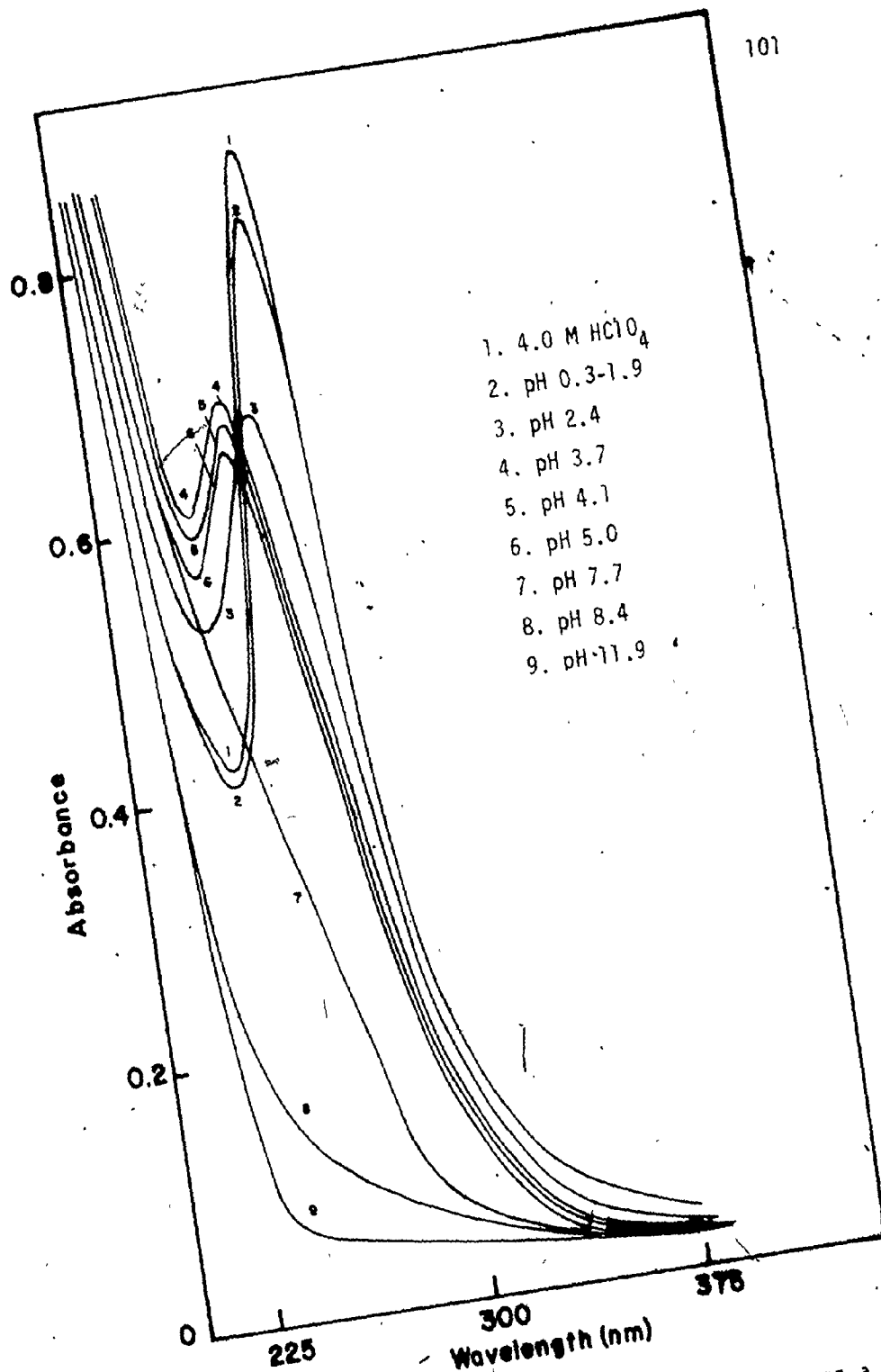


Figure 21. Absorption spectra of TPA in aqueous solution as a function of pH ($C_{\text{TPA}} = 3.21 \times 10^{-5}$ M, 25°C, $\mu = 1$, 5-mm cells, corresponding solution without TPA as reference)

absence of an isosbestic point is indicative of rather complex behaviour in solution; i.e., a simple acid-base protonic dissociation is not the sole process taking place in the pH range 0-5. Indeed, the time dependence of the absorbance at 248 nm (the absorbance decreases with time for curves 4, 5 and 6) is additional evidence of complicated processes. Bearing in mind that each mole of TPA consumed 7 moles of NaOH up to about pH 4 (3 moles for neutralization, 4 moles for a first-stage decomposition to a species postulated to be $\text{PW}_{11}\text{O}_{39}^{-7}$) in the potentiometric titration discussed above, the assignment of the maximum at 248 nm to the $\text{PW}_{11}\text{O}_{39}^{-7}$ species is not unreasonable. The order of absorbance at 248 nm (curve 4 > 5 > 6) is consistent with the increasing amount of decomposition of the $\text{PW}_{11}\text{O}_{39}^{-7}$ species with increasing pH. Ultimately, at pH 11 (curve 9), complete decomposition to WO_4^{-2} has taken place.

For 4 M HClO_4 solutions of TPA, the absorbance at 267 nm (curve 1) is greater than that for solutions of pH 0-2 (curve 2). Similarly, for 6 M HClO_4 solutions of TPA, the absorbance is somewhat greater (by 0.05 A units, curve not shown) than for 4 M HClO_4 solutions. This behaviour is almost certainly attributable to secondary medium effects. In concentrated electrolyte solutions, it is not uncommon to find the activity coefficient of a species (involved in a chemical reaction) to be greater than unity,⁽²⁵⁰⁾ and as a consequence, the activity to be greater than the stoichiometric concentration. This enhanced activity of a species is due, in part, to the decrease in the activity of the solvent water at high concentrations of electrolyte. Such a medium effect may well explain the increased absorbance of TPA in 4 M and

6 M HClO₄.

In subsequent studies on the quantitative formation of TPA in aqueous solution from tungstate, phosphate and acid [see section (d) below], the measurement of absorbance at 267 nm was restricted to pH 0-2.

Whether TPA exists as an undissociated acid or in the form of electrostatically held ion-pairs [e.g., (3H₃O⁺, PW₁₂O₄₀⁻³)] below pH 2 is a moot point. Recent X-ray diffraction studies have shown the hexahydrated TPA to exist in the solid state as [(H₅O₂⁺)₃(PW₁₂O₄₀⁻³)].^(205,253) This structural arrangement is consistent with TPA being a very strong acid in aqueous solution and, consequently, it might well exist in highly acid solutions as an ion-associated species. In any event, whether TPA exists in ion-paired or undissociated form, its molar absorptivity, ϵ , is 5.1×10^4 litre mole⁻¹ cm⁻¹ in the pH range 0-2.

Attempts have been made in recent years to explain the origin of the absorption bands in the uv spectra of 12-heteropoly anions such as PMo₁₂O₄₀⁻³, P₂Mo₁₈O₆₂⁻⁶, PW₁₂O₄₀⁻³, P₂W₁₈O₆₂⁻⁶, etc.⁽²⁵⁴⁾ Pope⁽²⁵⁴⁾ believes that the absorption bands in these anions arise as a result of charge transfer involving an electron localised mainly at the oxygen atoms to orbitals localised at the metal atoms (Mo or W). However, it is still uncertain whether this charge transfer originates on a terminal or on a shared oxygen atom.⁽¹⁸⁶⁾ Unlike the charge transfer bands for the above heteropoly anions, the heteropoly blue species (i.e., the reduced heteropoly anions used in phosphate determinations) show intervalence charge-transfer transitions,⁽²⁵⁴⁾ i.e., Mo(V) → Mo(VI) and W(V) → W(VI).

(c) Conformity of TPA to Beer's law

The conformity to Beer's law of both aqueous and alcoholic solutions of TPA (prepared by dissolution of solid TPA) was tested prior to the development of analytical procedures for phosphate determinations. Measurements in aqueous solution were carried out in the pH range 0-2. This was based on the above spectrophotometric studies which showed the absorbance of TPA to remain constant over the pH range 0-2. The concentration of TPA was varied from 2.00×10^{-7} M to 1.94×10^{-3} M for each of the following pH values: 0, 1.3, 1.5, 1.8 and 2.0. These concentrations correspond to 0.00620-60.0 ppm P. Identical straight-line plot passing through the origin were obtained for each pH value. Figure 22 shows typical absorption spectra of solutions of TPA for the range 4.00×10^{-6} M- 2.40×10^{-5} M (0.124-0.744 ppm P) at pH 1.5, and Figure 23 shows the least-squares plots for the same solutions and two others at 0.870 and 1.00 ppm.

For n-amyl alcohol solutions, absorption spectra were obtained in the concentration range 2.00×10^{-7} M- 1.78×10^{-3} M TPA (0.00620-55.0 ppm P). Figure 24 A, for example, represents typical absorption spectra for TPA in the range 0.124-0.744 ppm P. The least-square plots were identical to that shown in Figure 22. The molar absorptivity of TPA at 267 nm in n-amyl alcohol was found to be the same as in water ($\epsilon_{267} = 5.1 \times 10^4$ litre mol⁻¹ cm⁻¹).

Conformity to Beer's law was also tested after extraction of the TPA from the aqueous phase (pH 0-2) into n-amyl alcohol. The range of phosphorus concentrations was the same as before (0-60.0 ppm P).

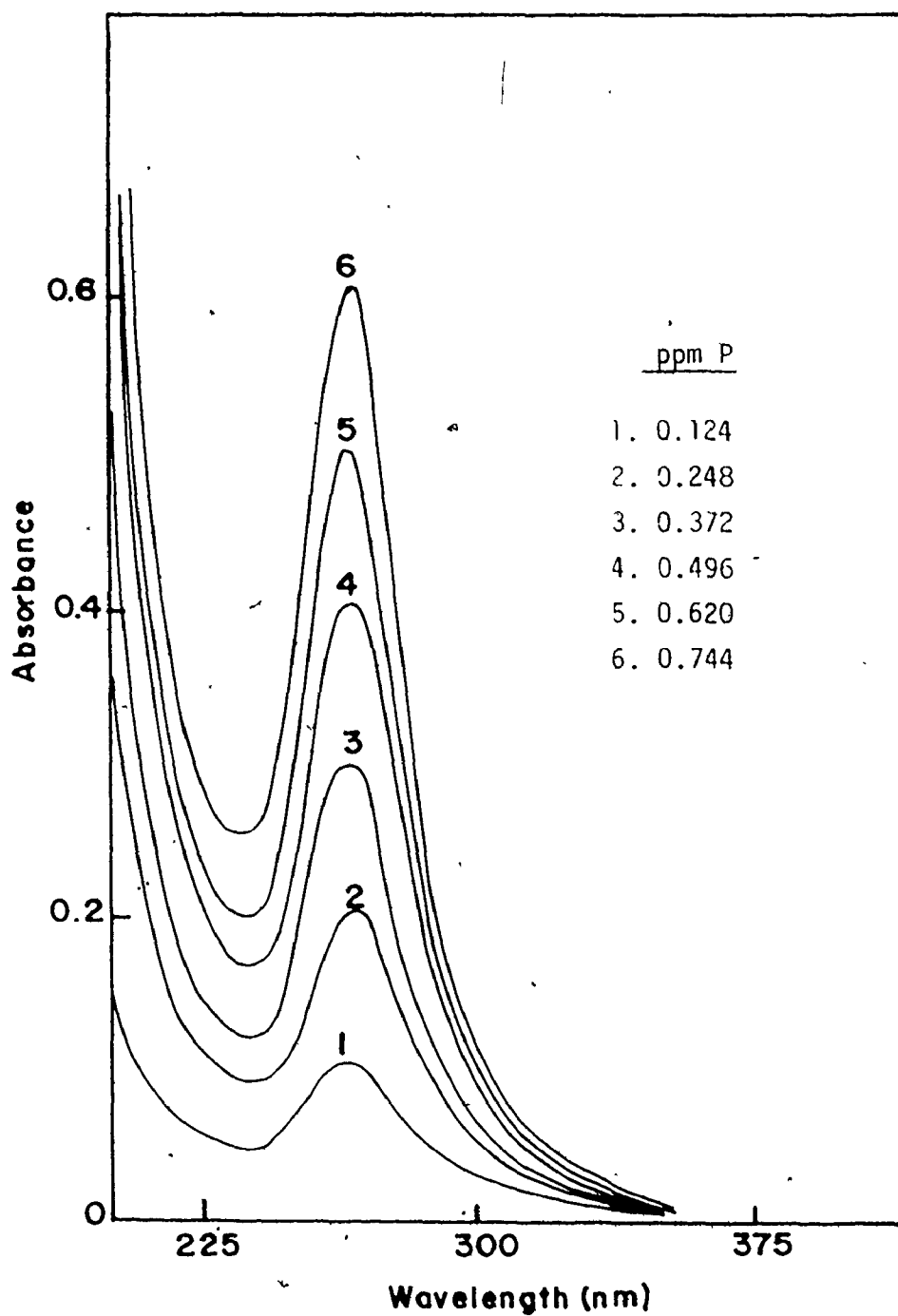


Figure 22. Absorption spectra of TPA in aqueous solution
($C_{\text{TPA}} = 4.00 \times 10^{-6} \text{ M} - 2.40 \times 10^{-5} \text{ M}$, 25°C , $\text{pH } 1.5$,
5-mm cells, corresponding solution without TPA as reference)

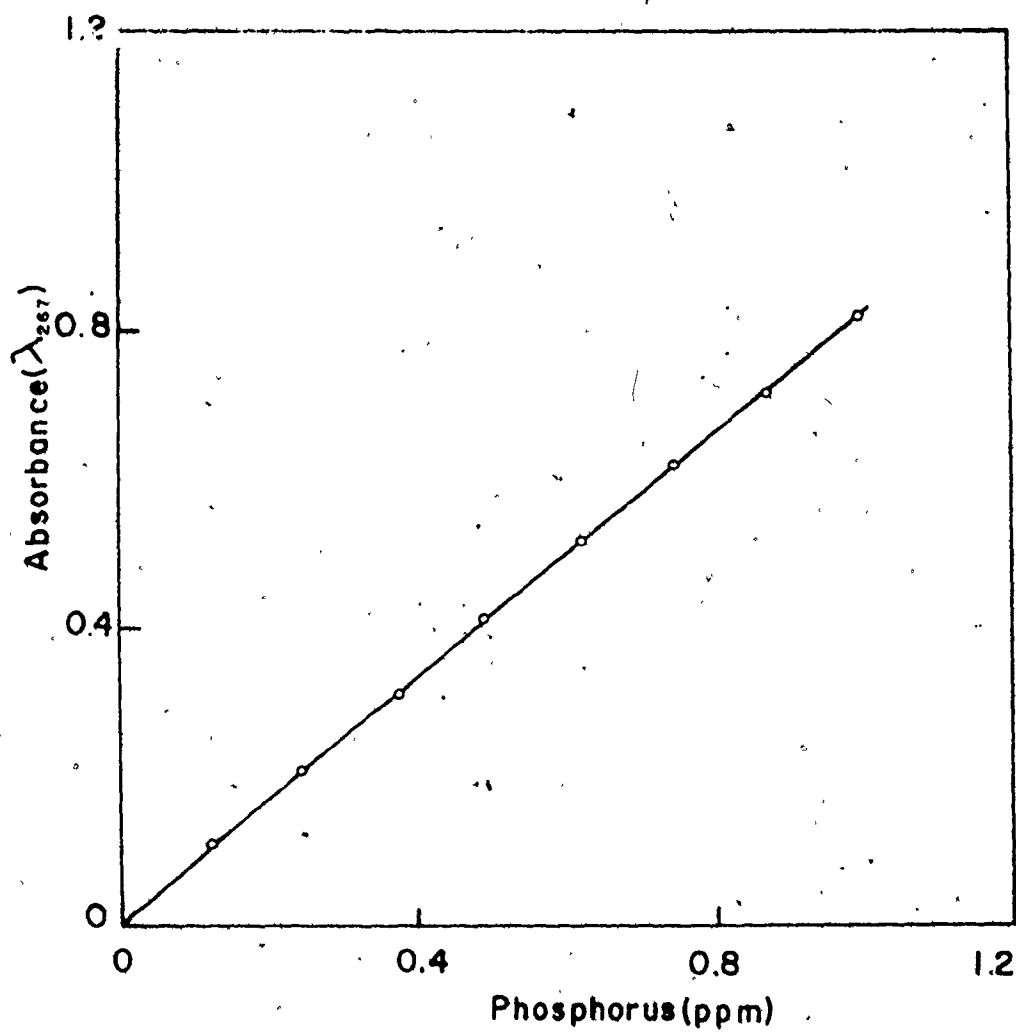


Figure 23. Absorbance (λ_{267}) of TPA in aqueous solution as a function of concentration (conditions same as in Figure 22)

Figure 24 B represents typical absorption curves in the n-amyl alcohol phase for 0.124-0.744 ppm P. The spectra are essentially identical to those obtained in n-amyl alcohol for TPA (Figure 24 A), as are, of course, the least-squares plots. Furthermore, no change in absorbance was observed when the spectra were re-recorded after one day, indicative of the independence of absorbance with time. In recording the spectra, the reference solution was the n-amyl alcohol extract of the corresponding blank aqueous solution.

Figure 25 shows the variation in absorbance with pH, after extraction of an aqueous solution ($C_{\text{TPA}} = 2.00 \times 10^{-5} \text{ M}$) of TPA. Above pH 2, the extraction is no longer quantitative because of ionization of the triprotic acid (or unstable ion-pair formation, see below) and hydrolysis of TPA to $\text{PW}_{11}\text{O}_{39}^{-7}$ and lower degradation products.

The distribution coefficient for the extraction of TPA from aqueous solution (pH 0-2) into n-amyl alcohol was not determined in the present investigation. For practical application to the determination of phosphate in trace amounts, the concentration of TPA required to be extracted from aqueous solution would almost always be less than $1.94 \times 10^{-3} \text{ M}$ (60.0 ppm P). As the above study has shown, this amount is easily extracted quantitatively in a single batch extraction (from 25 to 50 ml aqueous phase, using 10 or 25 ml of n-amyl alcohol). Therefore, there is little need to determine the distribution coefficient.

The mechanism of extraction of heteropoly species is still uncertain. Suggestions such as oxygenated organic solvents extract the heteropoly acids from acid solutions through the formation of oxonium salts [e.g., $(\text{ROH}_2^+)_3$, $(\text{PW}_{12}\text{O}_{40})^{-3}$] (201) have been advanced but not

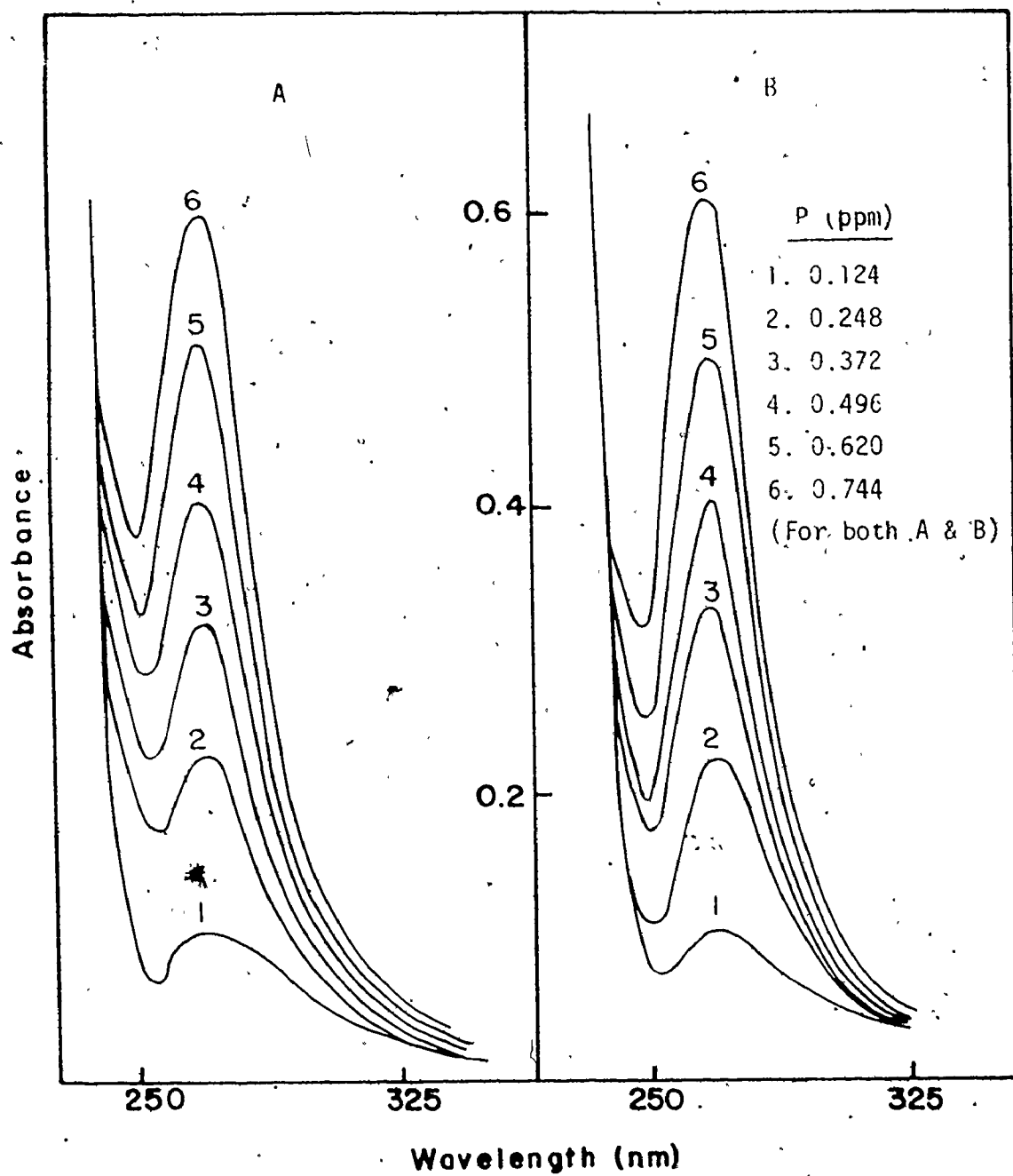


Figure 4. Absorption spectra of TPA

A. In n-amyl alcohol (n-amyl alcohol reference, 5-mm cells, 25°C)

B. In n-amyl alcohol phase after extraction from aqueous phase

(corresponding n-amyl alcohol blank reference, 5-mm cells, 25°C)

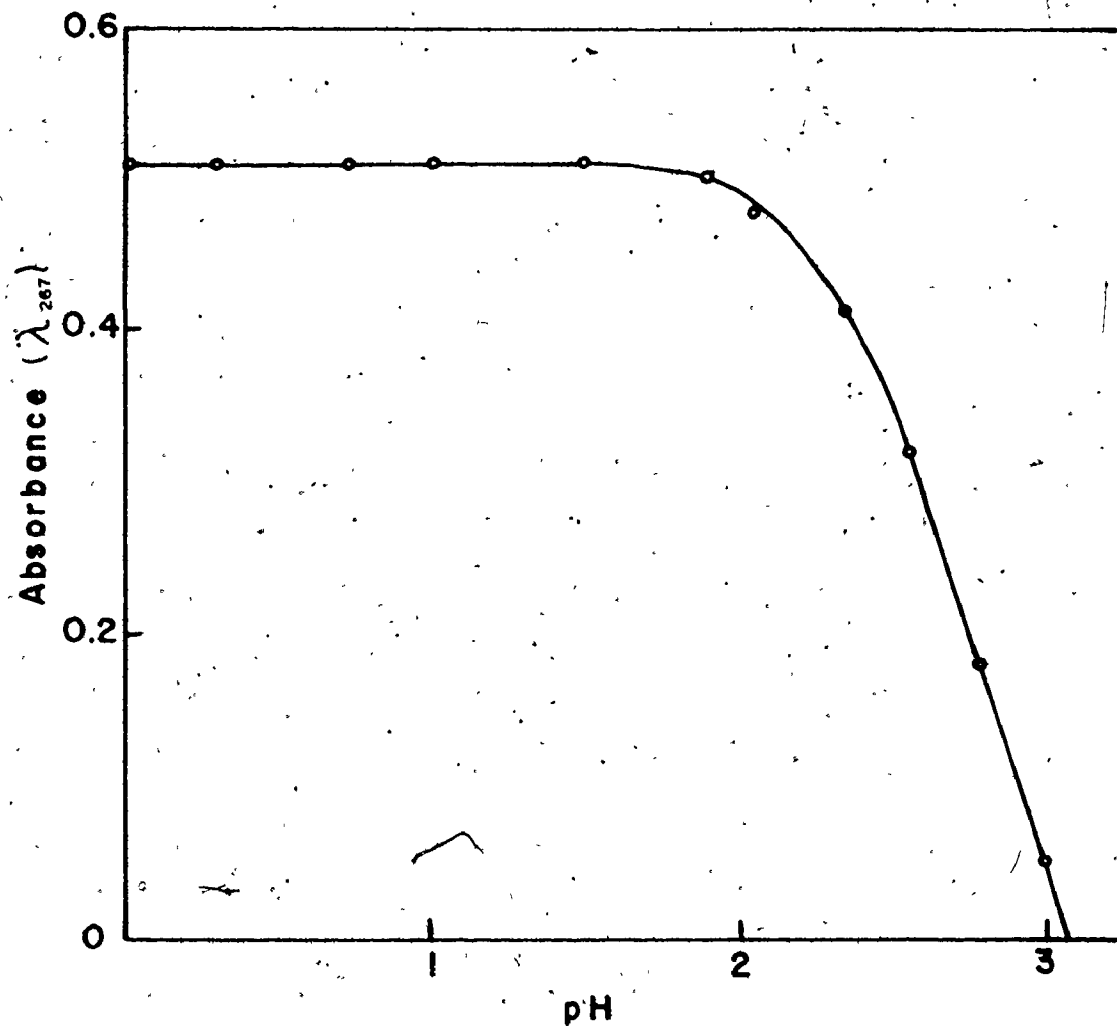
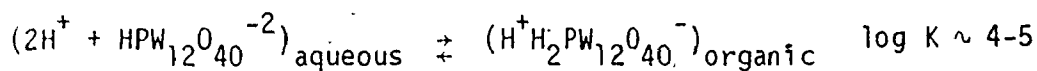


Figure 25. Absorbance of TPA (10/n-amy) alcohol phase after extraction from aqueous solution) as a function of pH (In alcohol phase, $C_{TPA} = 2.00 \times 10^{-5}$ M, 25°C, 5-mm cells, n-amy) alcohol extract of corresponding blank as reference)

experimentally established. Recently, a solvated ion-pair mechanism has been put forward for the extraction of TPA into iso-amyl alcohol in the pH range 2-3, ⁽¹⁰⁴⁾ in accordance with the equation:



Since TPA undergoes hydrolysis in the above pH range, the above equation should not be taken seriously. Studies at pH values < 2 are necessary to verify a mechanistic scheme for the extraction. It could well be that TPA is extracted by an ion-association mechanism involving three H_3O^+ ions (or H_5O_2^+ or H_9O_4^+ ions) and $\text{PW}_{12}\text{O}_{40}^{-3}$ and not as an undissociated acid at pH < 2. With regard to the degree of aggregation of TPA once extracted into n-amyl alcohol, no investigations were made in this work. In ethyl and allyl alcohols, TPA has been found to be monomeric (through molecular weight determinations) ⁽²²⁸⁾ and is likely monomeric in n-amyl alcohol as well. The conformity of TPA to Beer's law is strong evidence that this is so.

(d) Formation of TPA in solution from tungstate, phosphate and acid

(i) Measurement in aqueous solution. Preliminary studies on the formation of TPA in aqueous solution were carried out at 25°C at a tungstate to phosphate molar ratio of 12 to 1 (i.e., the stoichiometric ratio for TPA). These studies showed that the formation of TPA is both time- and pH- dependent (Figure 26 A,B). Thus, maximum formation (not quantitative) of TPA is achieved only at pH < 2 and with increasing time. The formation of TPA is not quantitative even after 15 days. Formation of isopolytungstates is the dominant process at pH values > 2. Indeed, above pH 2, there is little formation of TPA. This is supported by the

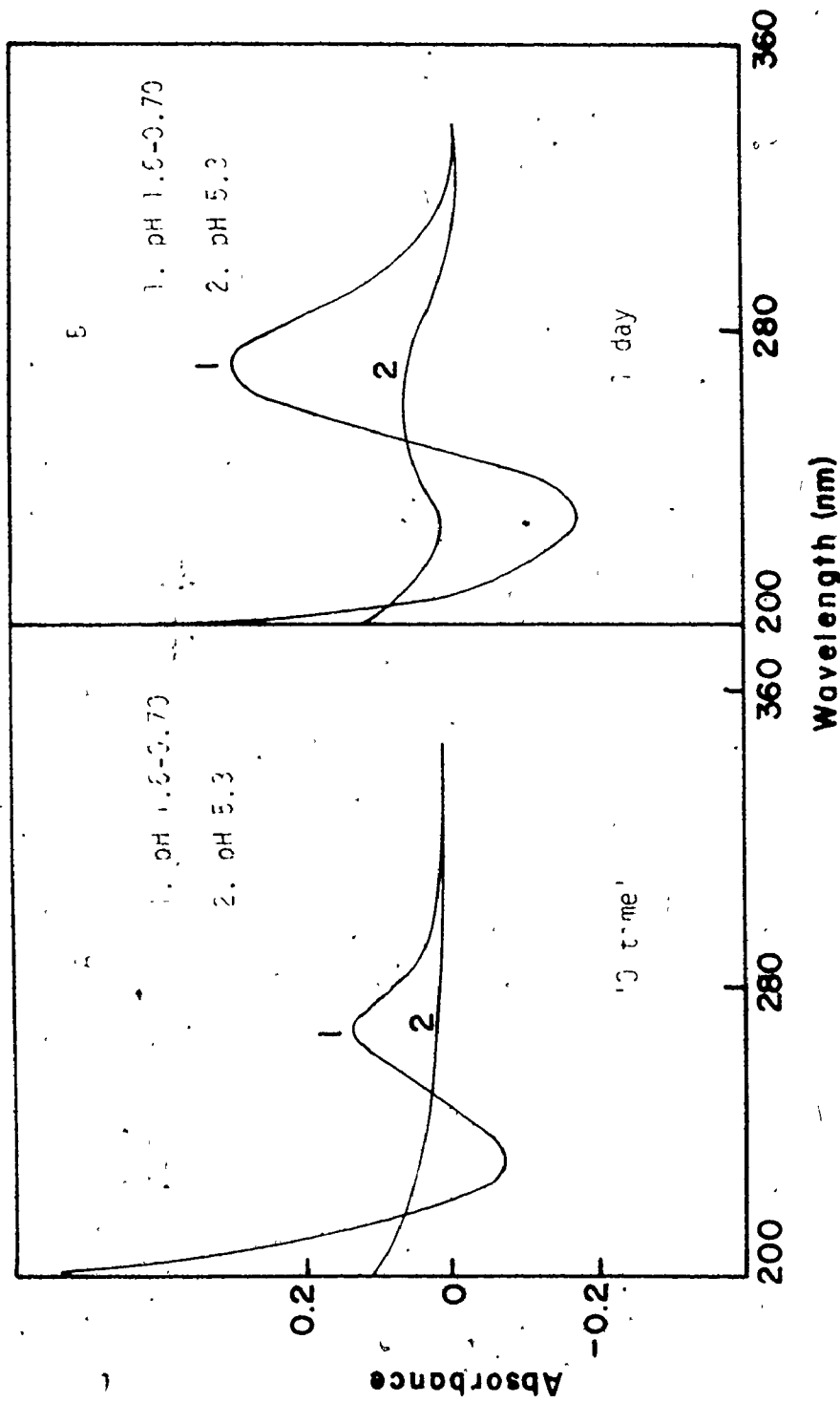


Figure 26. Absorption spectra for the formation of TPA in aqueous solution
 $(C_{WO_4}^{-2} = 4.8 \times 10^{-4} \text{ M}, C_{H_2PO_4}^{-} = 4.0 \times 10^{-5} \text{ M}, W/P = 12, \mu = 1, 25^\circ\text{C}, 5\text{-mm cells},$
 corresponding tungstate solution without phosphate as the reference)

absence of a peak at 267 nm (Figure 26 A,B, curve 2) and is consistent with the results of the spectrophotometric-pH studies [Section 2. (b) above] which showed that TPA dissociates significantly above pH 2. Even at pH < 2, the formation of isopoly species accompanies the formation of TPA. Evidence for this comes mainly from the negative value of the absorbance of the test solution versus the blank solutions (i.e., solutions containing the same concentration of tungstate and acid but no phosphate) in the region of 220-250 nm (Figure 26 A,B, curve 1). This negative absorption is due to one or both of the following reasons: the isopoly species in the test solution are different in nature* from those in the blank; the isopoly species are the same in the test and blank solutions but their concentrations are different.

The above facts showed that in order to achieve quantitative formation of TPA in aqueous solution, one or more of the experimental parameters that affect both the rate and extent of formation of TPA required alteration. These include such factors as the concentration of the tungstate solution, temperature, and stabilization of the tungstophosphate anion ($\text{PW}_{12}\text{O}_{40}^{-3}$) by suitable cations (e.g., the acriflavonium cation). Even the optimization of the above parameters to achieve quantitative formation of TPA would not, however, lead to a useful analytical method for the determination of phosphate unless the

* Pungor et al.,⁽³⁸⁾ in their studies on the formation of the 12-molybdophosphoric acid in aqueous solution, found that an octapoly-molybdate was present in the blank solution whereas a heptapoly-molybdate was present in the test solution.

interference from the isopolytungstates which accompany the formation of TPA could be overcome. In Sections 1. (c) (ii) and 2. (c) above, it was shown that isopolytungstates are not extracted into n-amyl alcohol at pH = 1 and that TPA is quantitatively extracted up to nearly pH 2. Thus, subsequent measurements of the TPA were carried out after its extraction into n-amyl alcohol from the aqueous phase set at pH 0-3, with particular interest in the pH range 1-2.

(ii) Measurement in n-amyl alcohol after its extraction from the aqueous phase. Figure 27 represents the formation and extraction of TPA as a function of pH and time at 25°C when a stoichiometric amount of tungstate solution is added to a known concentration of phosphate solution ($C_{WO_4^{2-}} = 6.0 \times 10^{-4}$ M; $C_{H_2PO_4^-} = 5.0 \times 10^{-5}$ M, equivalent to 1.55 ppm P* ; W/P = 12). Maximum formation of TPA (~ 50% after 30 minutes and 80% after one day) occurs in the pH range of about 0.90-1.6.

The decrease in the formation/extraction of TPA below pH 1 is due to two factors. The first is a competing side reaction involving tungstate ion to give tungstic oxide hydrates ($WO_3 \cdot xH_2O$). The formation of $WO_3 \cdot xH_2O$ reduces the effective analytical concentration of tungstate ion available for the reaction with phosphate, causing a decrease in the amount of TPA formed. In these experiments, precipitation of $WO_3 \cdot xH_2O$ was observed below pH 1. The second factor is the extraction of isopoly species at pH < 1, which occurs to a greater

* This concentration of phosphorus corresponds to 0.62 ppm in the 25-ml n-amyl alcohol phase, (2.00×10^{-5} M TPA, theoretical absorbance = 0.51).

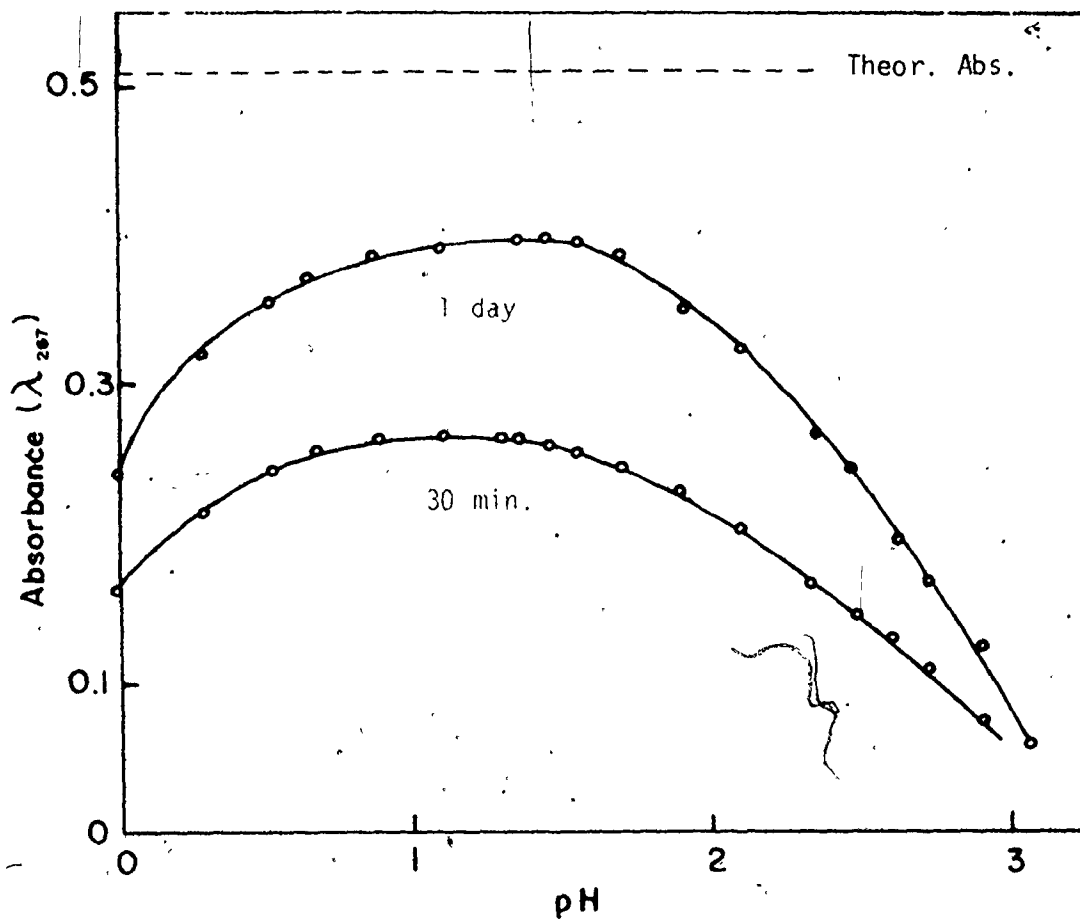
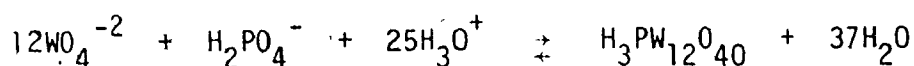


Figure . . . formation/extraction of TPA as a function of pH
 $[WO_4^{2-}] = 6.0 \times 10^{-4}$ M, $[CH_2PO_4^-] = 5.0 \times 10^{-5}$ M; W/P = 12,
 25 °C, 5-mm cells, corresponding n-amyl alcohol extract of
 blank as reference)

extent in the blank than in the test solution, and which results in a decrease in absorbance, giving the appearance of decreased formation/extraction of TPA. The decrease in absorbance beyond about pH 1.6 is due to the increasing dissociation of TPA as an acid or ion-associated complex, and to decomposition of the $PW_{12}O_{40}^{-3}$ anion, as previously discussed.

An increase in the tungstate to phosphate molar ratio* to $W/P \geq 24$ increases both the rate and extent of formation of TPA. The formation is quantitative after one day in the pH range 1.2-1.9. Typical curves are presented in Figures 28 and 29 for the formation of TPA at ratios of $W/P = 48$ and 240 , respectively. Similar curves have been obtained for $W/P = 24, 96$ and 144 . TABLE VI summarizes the percentage of TPA formed both as a function of the W/P molar ratio and time in the pH range 1.2-1.9. The overall reaction for the formation of TPA in acid solutions can be represented as:



The quantitative formation of TPA at room temperature is too slow (i.e., one day) to be suitable for the rapid determination of phosphate. Therefore, attempts were made to accelerate the reaction rate by use of higher temperatures. Figure 30 shows that quantitative formation of TPA is, for all practical purposes, instant in the pH range 1.2-1.9 for molar ratios $W/P \geq 24$. At $W/P = 12$, the yield of TPA was 84% under the same conditions. Figures 31 A and B summarize the data obtained for the formation of TPA at W/P ratios of 12, 24, 48, 144

* $C_{H_2PO_4^{-}} = 5.0 \times 10^{-5}$ M and was held constant in these experiments.

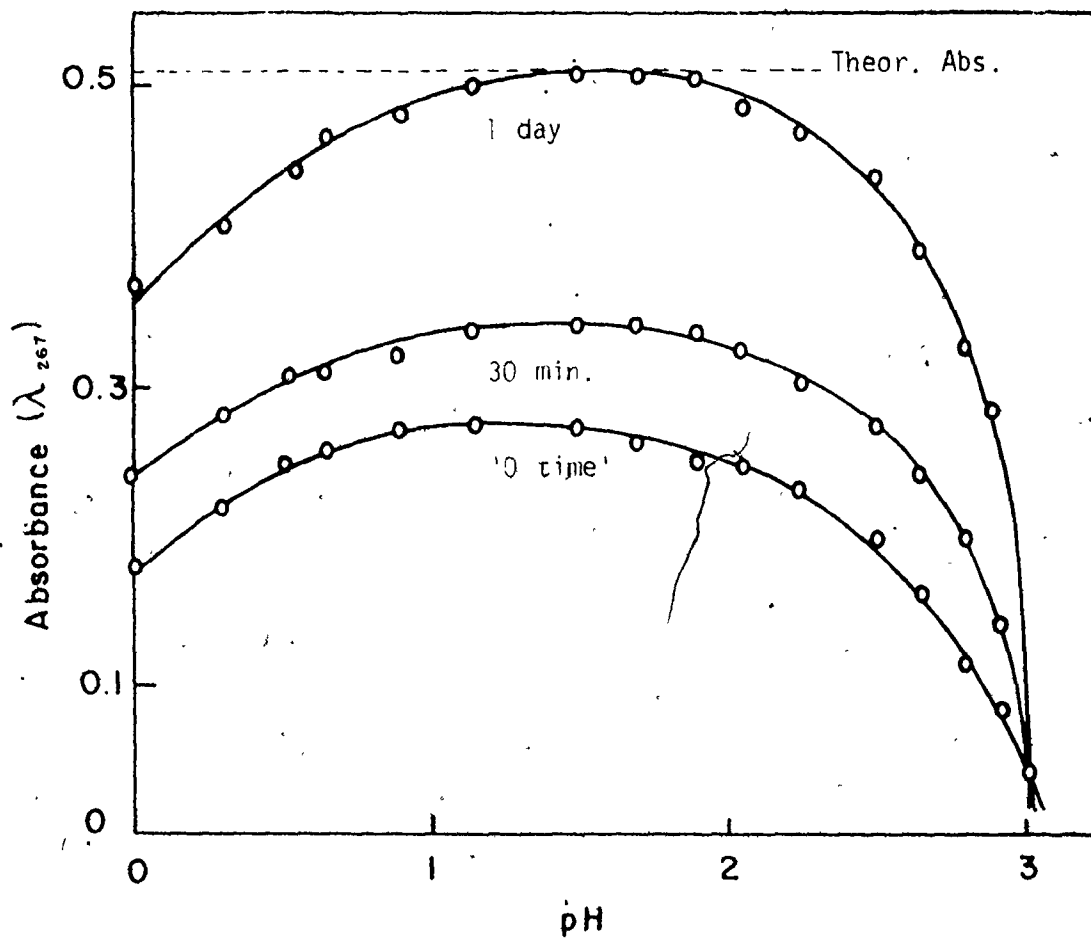


Figure 28. formation/Extraction of TPA as a function of pH
 $W_4^{-2} = 3.4 \times 10^{-3}$ M, $H_2PO_4^- = 5.0 \times 10^{-5}$ M, W/P = 48,
 25°C, 5-mm cells, (corresponding n-amyl alcohol extract of
 blank as reference)

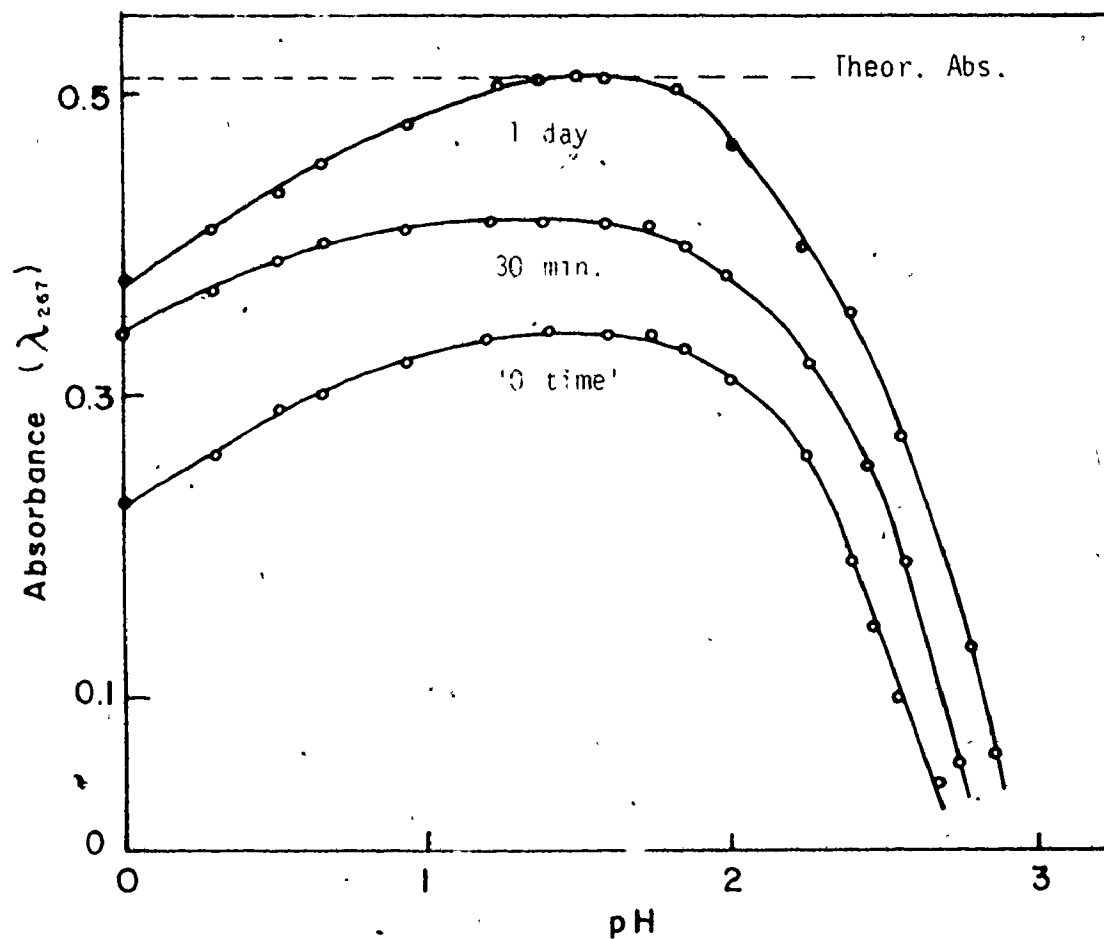


Figure 22. formation/Extraction of IPA as a function of pH

$(\text{WO}_4)^{-2} = 1.2 \times 10^{-2} \text{ M}$, $\text{H}_2\text{PO}_4^- = 5.0 \times 10^{-5} \text{ M}$, W/P = 240,

0.5%, 5-mm cells, (corresponding n-amyl alcohol extract of blank as reference)

TABLE VI

Formation/Extraction of TPA - Effect of W/P Molar Ratio and Time (25°C)

| W/P molar ratio | Max. % TPA formed (pH 1.2-1.9) | | |
|--------------------|--------------------------------|---------|-------------------|
| | '0 time' | 30 min. | 1 day |
| 12 [*] | 52 | 54 | 80 |
| 24 | 54 | 58 | 100 ^{**} |
| 48 | 56 | 68 | 100 |
| 96 | 60 | 76 | 100 |
| 144 | 64 | 80 | 100 |
| 240 | 70 | 84 | 100 |

* Stoichiometric; ** Quantitative

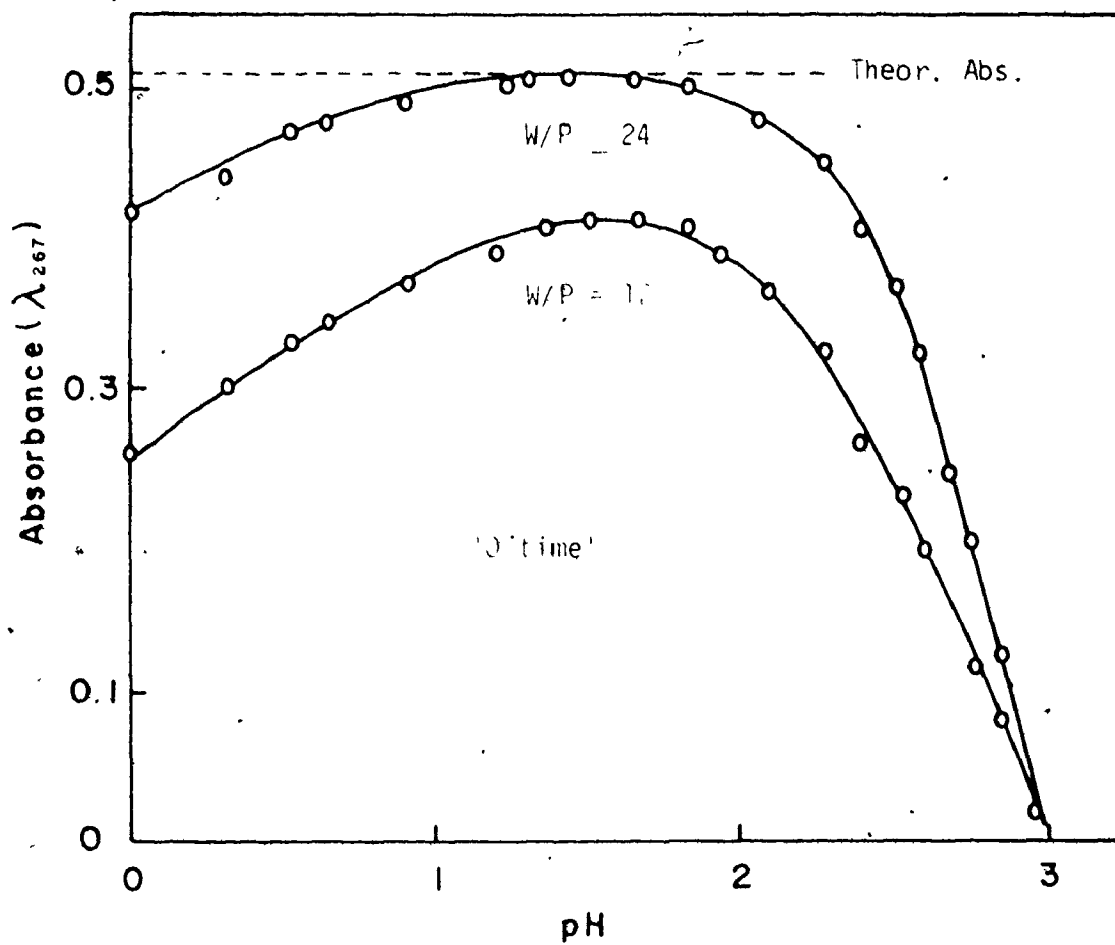


Figure 30. formation (extraction of TPA as a function of pH)

($\text{H}_2\text{PO}_4^- = 0.1 \times 10^{-5}$ M, 100 %, 5-mm cells, corresponding n-amyl alcohol extract of blank as reference)

and 240 at 100°C after '0 time' and at 25°C after one day, respectively.

In either case, the reaction is quantitative at W/P \geq 24 in the pH range 1.2-1.9.

Studies were also conducted at 45 \pm 2°C and 60 \pm 2°C. At 60°C, the reaction was found to be quantitative at W/P \geq 24* in the pH range 1.3-1.9. At 45°C, however, formation was only 90% at W/P \geq 24**.

The results are presented in TABLE VII. The fact that the formation of TPA is quantitative at 60°C should facilitate automation of the TPA method in water-pollution studies.

When the solution of phosphate was added ($C_{H_2PO_4^-} = 5.0 \times 10^{-5}$ M) to a pre-boiled solution of tungstate and acid (at W/P = 96 and 240) after it had been cooled to 25°C, the formation of TPA was found to be only 36. When measurement of the same solution was made ten hours later, formation was found to be quantitative. Although this experiment demonstrates that the reaction between phosphate and aggregated tungstate to form TPA can be quantitative without application of heat (and thus readily automated), the 10-hour time period renders this procedure impractical.

Studies similar to those for $C_{H_2PO_4^-} = 5 \times 10^{-5}$ M (0.155 ppm P) at 100°C (i.e., after the test solutions had been brought to a boil and cooled to 25°C) were repeated for $C_{H_2PO_4^-} = 5.0 \times 10^{-4}$ M (15.5 ppm P)

* Studies at 60°C were conducted at W/P = 24, 96 and 240.

** Studies at 45°C were conducted at W/P = 24 and 240.

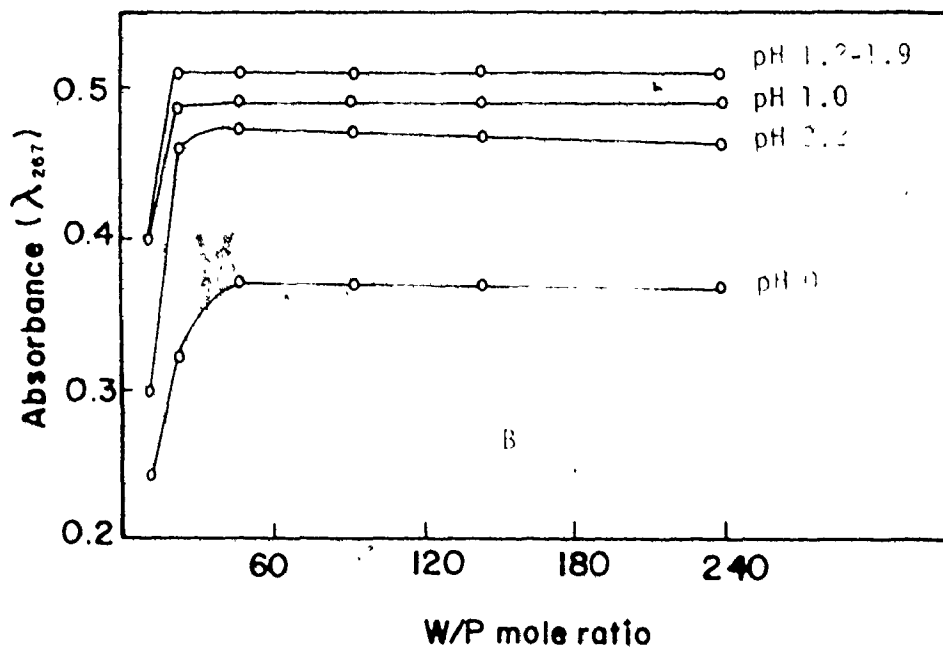
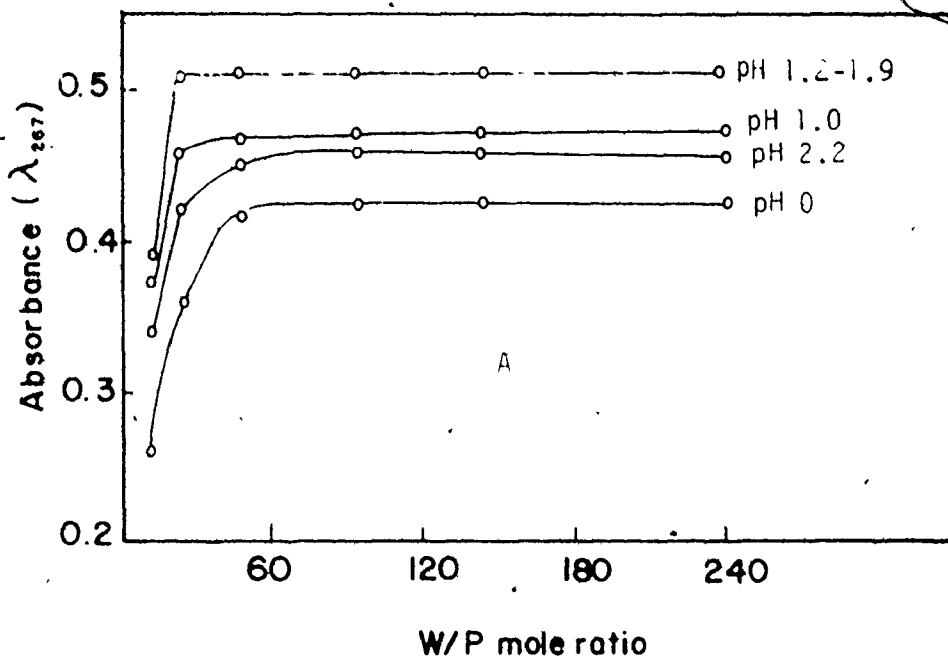


Figure 5: Formation/Extraction of TPA as a function of W/P mole ratio at various pH values

A. $(\text{H}_2\text{PO}_4^- = 5.0 \times 10^{-5} \text{ M}, 100^\circ\text{C}, 10 \text{ min})$

B. $(\text{H}_2\text{PO}_4^- = 5.0 \times 10^{-5} \text{ M}, 25^\circ\text{C}, 1 \text{ day})$

TABLE VII.

Formation/Extraction of TPA - Effect of Temperature

$[C_{WO_4}^{-2} = 1.2 \times 10^{-2} \text{ M}, C_{H_2PO_4}^{-} = 5.0 \times 10^{-5} \text{ M (1.55 ppm P}^*), W/P = 240,$
 $\lambda_{\text{max}} = 267 \text{ nm, 5-mm cells}]$

| pH | Phosphorus Found (ppm)** | | |
|-----|--------------------------|-------------|-------------|
| | 45°C | 60°C | 100°C |
| 1.2 | 1.35 ± 0.02 | 1.48 ± 0.02 | 1.50 ± 0.02 |
| 1.4 | 1.40 ± 0.03 | 1.54 ± 0.01 | 1.54 ± 0.01 |
| 1.6 | 1.41 ± 0.02 | 1.55 ± 0.02 | 1.55 ± 0.01 |
| 1.9 | 1.39 ± 0.02 | 1.54 ± 0.01 | 1.55 ± 0.02 |

* The corresponding value for phosphorus in the organic phase is 0.62 ppm

** The absorbance values have been converted to give the equivalent phosphorus concentrations. The absorbance values were measured against the n-amyl alcohol extract of the corresponding blank as reference. The data in the table represent the average of at least 3 determinations. The precision measure is the standard deviation.

and $C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ M (0.155 ppm P^{*}). The curves for 15.5 ppm (Figure 32) are essentially the same as those obtained for $C_{H_2PO_4^-} = 5.0 \times 10^{-5}$ M (Figure 30). As before, instant quantitative formation of TPA occurs at $W/P \geq 24$ in the pH range 1.2-1.9. TABLE VIII gives the absorbance values for TPA corresponding to 15.5 ppm P at W/P ratios of 48, 96, 144 and 240.

For $C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ M (0.155 ppm P), instant quantitative formation of TPA was achieved only at a W/P ratio ≥ 240 (Figure 33), although the pH range was the same (i.e., 1.2-1.9). TABLE IX gives the absorbance values for the formation of TPA at W/P ratios of 12, 48, 430, 960 and 1440. Although quantitative formation of TPA for $C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ M was expected at a ratio $W/P \geq 24$, Figure 33 shows only 33% formation at this molar ratio. For $W/P = 12$, for which $C_{WO_4^{2-}} = 6.0 \times 10^{-5}$ M, formation of TPA is even less (about 9%, TABLE IX). Indeed, the tungstate concentration 6.0×10^{-5} M is very close to the limit at which formation of isopolytungstates hardly occurs[@]. These facts suggest that the formation of TPA depends on the formation of appropriate isopoly species^{**} prior to the incorporation of the phosphate ion. If this scheme is correct in principle, an increase in $C_{WO_4^{2-}}$ should increase the rate and extent of formation of the required

* The corresponding concentrations in the 25-ml n-amyl alcohol phase are 6.20 ppm and 0.062 ppm P, respectively.

@ At $C_{WO_4^{2-}} \leq 5.0 \times 10^{-5}$ M, no isopolytungstates are formed. (172)

** By "appropriate isopoly species" is meant aggregates smaller than W_{12} .

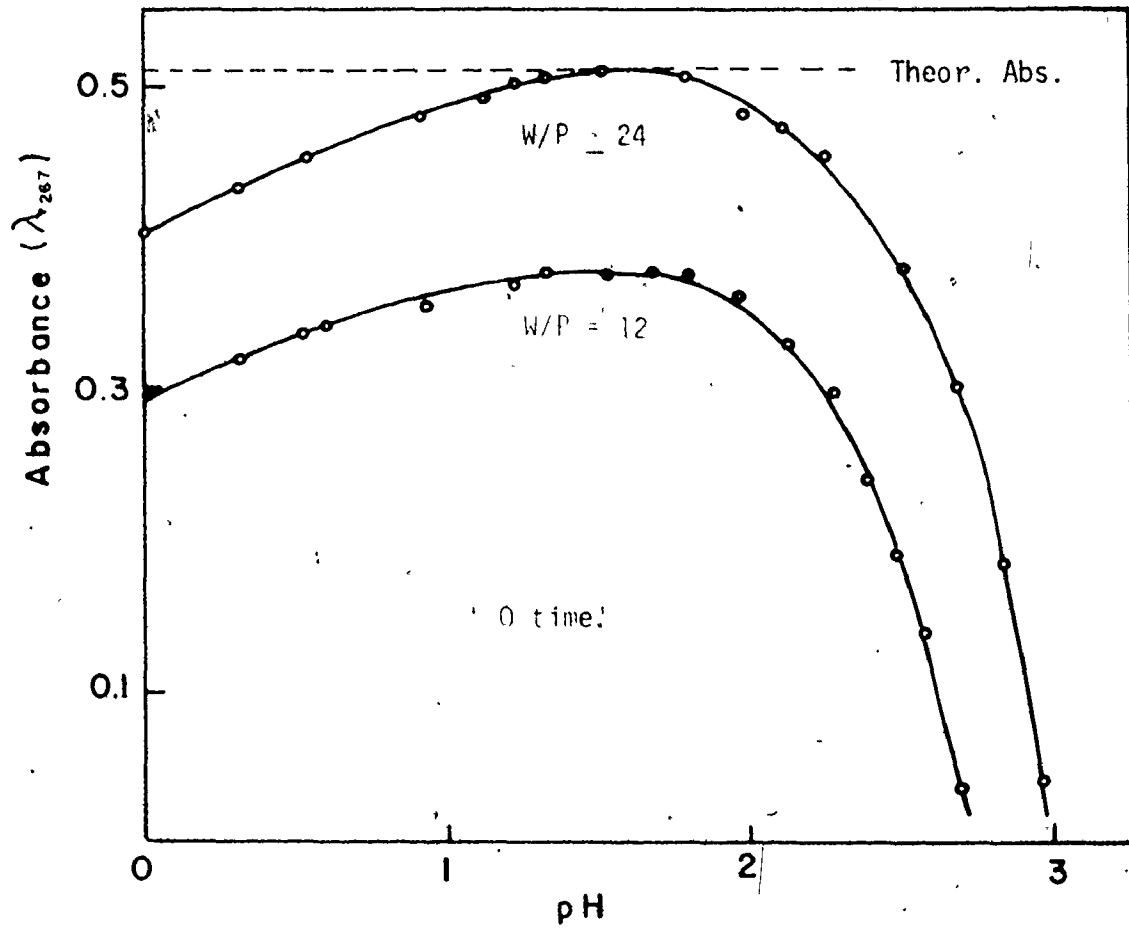


Figure 32. Formation/extraction of TPA as a function of pH
 ($[\text{H}_2\text{PO}_4^-] = 5.0 \times 10^{-2} \text{ M}$, 100°C , 5-mm cells, corresponding
 n-amyl alcohol extract of blank as reference)

TABLE VIII

Formation/Extraction of TPA - Effect of pH on Absorbance

[$C_{H_2PO_4^-} = 5.0 \times 10^{-4}$ M (15.5 ppm P^{*}), T = 100°C, $\lambda_{max} = 267$ nm, 5-mm cells]

| pH | Absorbance ^{**} | | | |
|-----|--------------------------|----------|-----------|-----------|
| | W/P = 48 | W/P = 96 | W/P = 144 | W/P = 240 |
| 0 | 0.40 | 0.41 | 0.36 | 0.38 |
| 0.3 | 0.43 | 0.43 | 0.40 | 0.42 |
| 0.5 | 0.45 | 0.44 | 0.44 | 0.44 |
| 0.9 | 0.45 | 0.48 | 0.47 | 0.46 |
| 1.2 | 0.50 | 0.50 | 0.49 | 0.49 |
| 1.4 | 0.51 | 0.51 | 0.51 | 0.51 |
| 1.6 | 0.51 | 0.51 | 0.51 | 0.51 |
| 2.0 | 0.48 | 0.49 | 0.49 | 0.49 |
| 2.3 | 0.43 | 0.42 | 0.45 | 0.45 |
| 2.5 | 0.36 | 0.38 | 0.39 | 0.38 |
| 2.7 | 0.25 | 0.27 | 0.29 | 0.30 |
| 2.8 | 0.14 | 0.14 | 0.17 | 0.18 |
| 3.0 | 0.03 | 0.04 | 0.05 | 0.05 |

* This concentration corresponds to 6,20 ppm in the 25-ml n-amyl alcohol phase.

** The absorbance values given are for the organic phase. The values will be higher by a factor of 2.5 in the aqueous phase (10-ml aqueous phase vs. 25-ml organic phase). The absorbance measurements were made by dilution of exactly one ml of the organic phase to 10 ml with alcohol (theoretical absorbance = 0.51). The n-amyl extract of the corresponding blank solution was used as the reference.

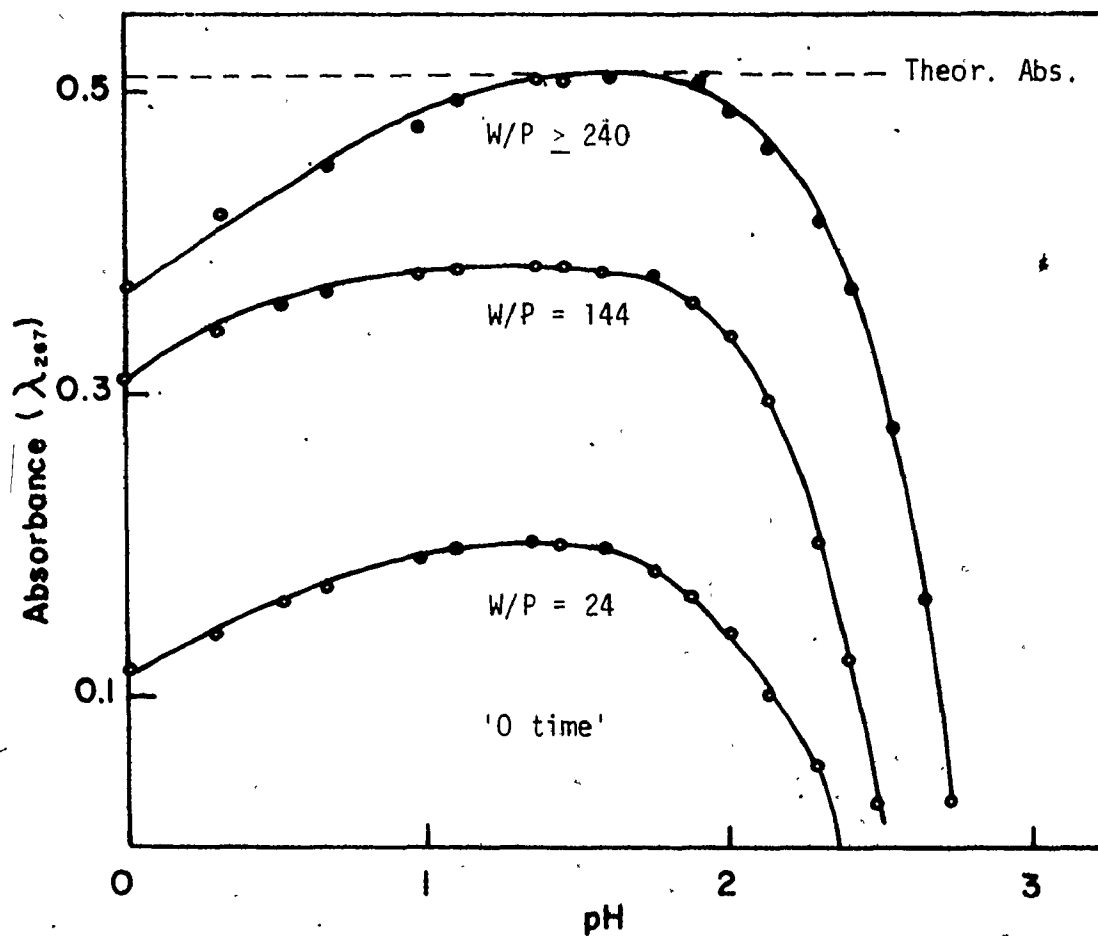


Figure 33. Formation/Extraction of TPA as a function of pH

($C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ M, 100°C , 5-cm cells, corresponding n-amyl alcohol extract of blank as reference)

TABLE IX

Formation/Extraction of TPA - Effect of pH on Absorbance

$[\text{C}_2\text{H}_2\text{PO}_4^-] = 5.0 \times 10^{-6} \text{ M (0.155 ppm P}^*)$, $T = 100^\circ\text{C}$, $\lambda_{\text{max}} = 267 \text{ nm}$, 5-cm cells]

| pH | Absorbance** | | | | |
|-----|--------------|----------|-----------|-----------|------------|
| | W/P = 12 | W/P = 48 | W/P = 480 | W/P = 960 | W/P = 1440 |
| 0 | 0.05 | 0.17 | 0.38 | 0.37 | 0.37 |
| 0.3 | 0.05 | 0.17 | 0.41 | 0.40 | 0.42 |
| 0.5 | 0.05 | 0.19 | 0.42 | 0.43 | 0.45 |
| 0.9 | 0.05 | 0.22 | 0.44 | 0.47 | 0.48 |
| 1.1 | 0.05 | 0.24 | 0.48 | 0.49 | 0.49 |
| 1.4 | 0.05 | 0.26 | 0.51 | 0.51 | 0.51 |
| 1.6 | 0.04 | 0.26 | 0.51 | 0.51 | 0.51 |
| 1.9 | 0.04 | 0.25 | 0.51 | 0.51 | 0.51 |
| 2.1 | 0.02 | 0.20 | 0.45 | 0.46 | 0.49 |
| 2.2 | ---- | 0.12 | 0.43 | 0.43 | 0.46 |
| 2.4 | ---- | 0.08 | 0.32 | 0.32 | 0.37 |
| 2.6 | ---- | 0.04 | 0.24 | 0.25 | 0.28 |
| 2.7 | ---- | ---- | 0.16 | 0.16 | 0.17 |
| 2.8 | ---- | ---- | 0.03 | 0.03 | 0.03 |

* This concentration corresponds to 0.062 ppm in the 25-ml n-amyl alcohol phase.

** The absorbance values given are for the organic phase. The values will be higher by a factor of 2.5 in the aqueous phase (10-ml aqueous phase vs. 25-ml organic phase). The absorbance measurements were made against the n-amyl alcohol extract of the corresponding blank solution as the reference.

isopoly species, and thus of the TPA. At $C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ M, instant quantitative formation of TPA did occur at $C_{WO_4^{2-}} = 1.2 \times 10^{-3}$ M (W/P = 240). Interestingly, this tungstate concentration is identical to that which yields 100% formation of TPA when $C_{H_2PO_4^-} = 5.0 \times 10^{-5}$ M (W/P = 24), which indicates that the analytical concentration of tungstate is more critical than that of phosphate in determining the amount of TPA formed instantly. This is consistent with the suggestion that the rate-determining step in the formation of TPA involves formation of the appropriate isopoly species.

In summary, the above studies clearly show that TPA can be formed quantitatively after one day at 25°C or instantly at 100°C from a solution containing tungstate, phosphate and acid in the pH range 1.2-1.9 and at W/P \geq 24 for P in the range 1.55-15.5 ppm ($C_{H_2PO_4^-} = 5.0 \times 10^{-5}$ M- 5.0×10^{-4} M) and W/P \geq 240 for P = 0.155 ppm ($C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ M) or less.

(iii) X-ray diffraction analysis of TPA after its isolation as a solid from solution containing tungstate, phosphate and acid. To ensure that the species formed in aqueous solution (100°C, W/P = 24, $C_{H_2PO_4^-} = 2.0 \times 10^{-3}$ M) and extracted into n-amyl alcohol is indeed TPA, the X-ray powder patterns of the solid isolated from n-amyl alcohol were compared with those of the anhydrous TPA (prepared from commercially-available hydrated TPA). As seen from TABLE X, the d-spacings are in good agreement. It is concluded that the compound formed in solution from tungstate, phosphate and acid under the conditions required for its quantitative formation is $H_3PW_{12}O_{40}$ (in a hydrated form).

TABLE X

X-ray Powder Data for TPA

| <u>TPA, isolated^b</u> | | <u>TPA, commercial grade</u> |
|-----------------------------------|------------------------|------------------------------|
| <u>d-Spacings^a (Å)</u> | <u>hkl^c</u> | <u>d-Spacings (Å)</u> |
| 8.70(I) | 200 | 8.70(I) |
| 5.00(W) | 211 | 5.00(W) |
| 4.30(W) | 220 | 4.30(W) |
| 3.85(W) | 310 | 3.85(W) |
| 3.50(I) | 222 | 3.50(I) |
| 3.02(I) | 400 | 3.02(I) |
| 2.85(W) | 300,411 | 2.85(W) |
| 2.70(W) | 420 | 2.71(W) |
| 2.59(I) | 332 | 2.59(I) |
| 2.37(I) | 510,431 | 2.37(I) |
| 2.21(V.W) ^{***} | 521 | 2.22(V.W) |
| 2.15(W) | 440 | 2.15(W) |
| 2.02(W) | 600 | 2.02(W) |
| 1.97(I) | 611,532 | 1.97(I) |
| 1.87(W) ^{**} | 622,541 | 1.86(I) |
| 1.72(I) | 550,710 | 1.72(I) |
| 1.54(I) [*] | 732,651 | 1.54(I) |

a. The d-spacings are based on $\text{CuK}_{\alpha} = 1.5418 \text{ \AA}$ for $d > 1.09 \text{ \AA}$ and $\text{CuK}_{\alpha} = 1.5405 \text{ \AA}$ for $d < 1.0 \text{ \AA}$.

b. The TPA was isolated and prepared for X-ray powder diffraction as described in the EXPERIMENTAL SECTION.

c. cubic system, $a_0 = 12.12 \pm 0.03 \text{ \AA}$; space group $\text{Pn}3\text{m}$ (see reference 205).

* I = Intense; ** W = Weak; *** V.W. = Very weak.

(e) Formation of TPA in solution from paratungstate Z, phosphate and acid

The reaction of paratungstate Z (obtained commercially), also leads to quantitative formation of TPA. The data are presented in Figure 34. The studies were made at $C_{H_2PO_4^-} = 5.0 \times 10^{-5} M$ (1.55 ppm P) for W/P ratios of 19 ($C_{para Z} = 8.02 \times 10^{-5} M$), 38, 76 and 190. Quantitative formation of TPA occurs after one day at $W/P \geq 19$ at room temperature in the pH range 1.1-1.9, and instantly when the solution containing para Z, phosphate and acid are brought to a boil at $W/P \geq 19$ in the pH range 1.3-1.8 (Figure 35). The decrease in the formation of TPA below and above the range of pH 1.3-1.8 (or pH 1.1-1.9 at 25°C) is caused by the same factors as for the tungstate system.

From these studies, it is apparent that the formation of TPA from the para Z ($H_2W_{12}O_{42}^{-10}$) resembles its formation from the tungstate. For analytical purposes, formation from tungstate is preferred since its unacidified solutions (e.g., a 0.1 M stock solution of tungstate) are stable whereas solutions of the para Z are not (see discussion on isopolytungstates).

(f) Formation of TPA in solution from metatungstate, phosphate and acid

The metatungstate species ($H_2W_{12}O_{40}^{-6}$) does not react with phosphate to form TPA, at least under any of the conditions described in the EXPERIMENTAL section. The metatungstate-phosphate-acid system has the same absorbance as the metatungstate-acid system, i.e., the absorbance of the test solution is the same as that of the blank.

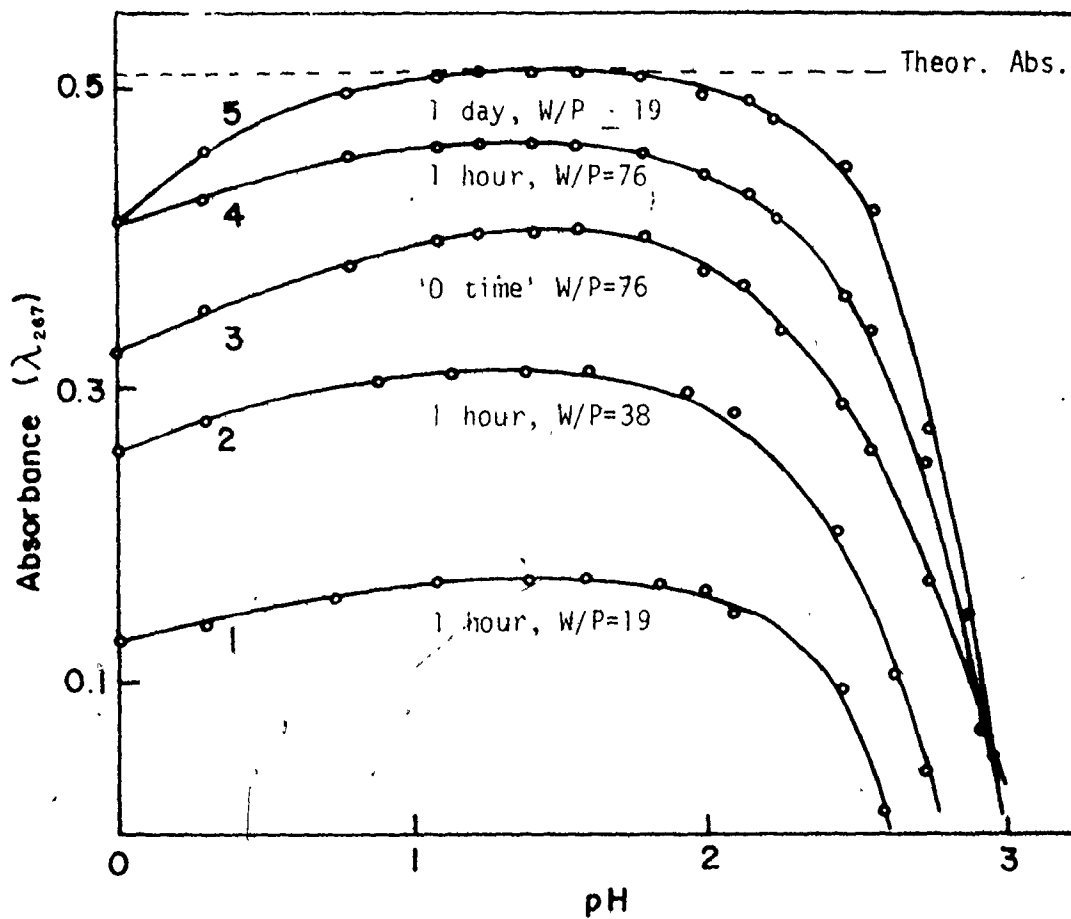


Figure 3. Formation/Extraction of TPA (from paratungstate Z) as a function of pH. ($\text{C}_2\text{H}_2\text{PO}_4^- = 5.0 \times 10^{-5}$ M, 25°C, 5-mm cells, corresponding n-amyl alcohol extract of blank as reference)

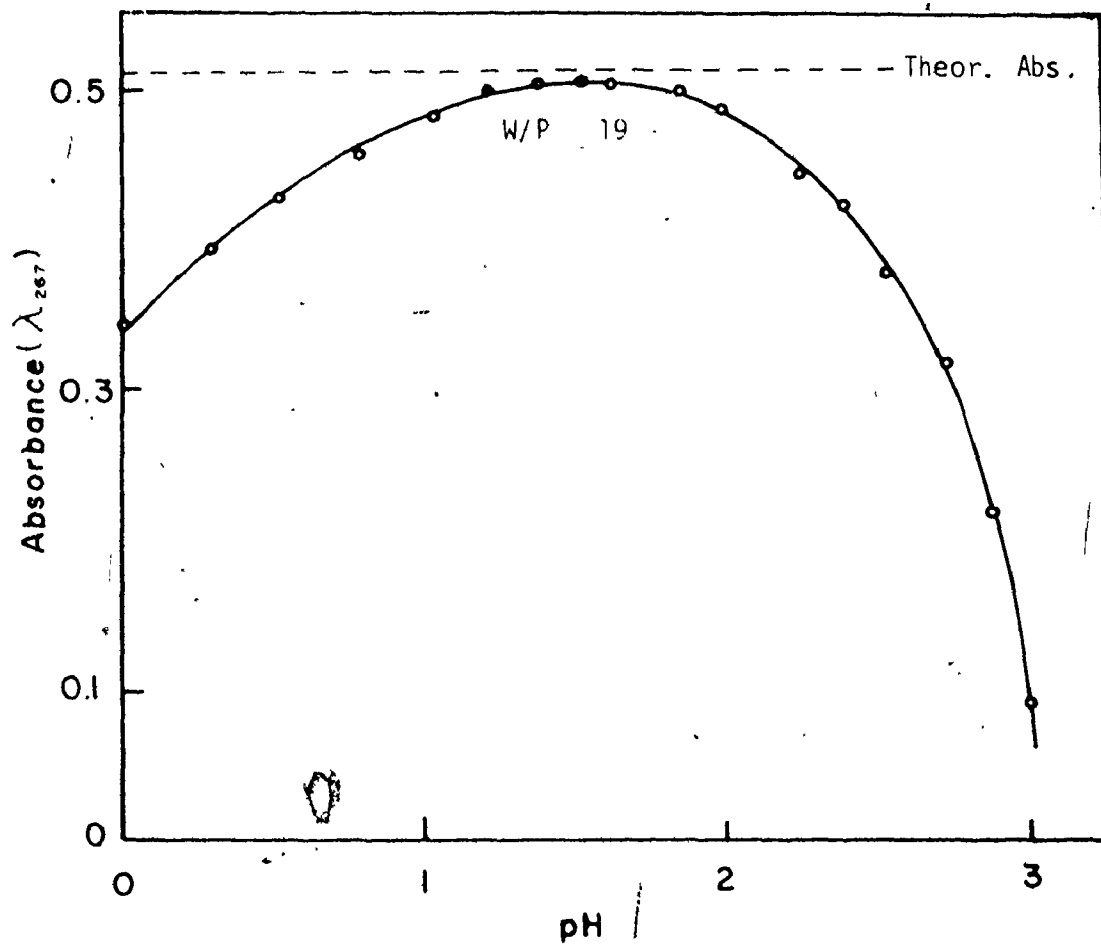


Figure 35. Formation/Extraction of TPA (from paratungstate Z) as a function of pH ($\text{C}_2\text{H}_2\text{PO}_4^- = 5.0 \times 10^{-5}$ M, 100°C , 5-mm cells; corresponding n-amyl alcohol extract of blank as reference)

(g) Formation of TPA in solution from tungstic oxide, phosphate and acid

(i) From yellow tungstic oxide ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$). As in the case of the metatungstate, $\text{WO}_3 \cdot \text{H}_2\text{O}$ does not react with KH_2PO_4 or H_3PO_4 to form TPA in solution under the conditions described in the EXPERIMENTAL section.

(ii) From white tungstic oxide ($\text{WO}_3 \cdot \text{H}_2\text{O}$): Preliminary qualitative studies showed that the reaction between freshly-precipitated white tungstic oxide and phosphate (both KH_2PO_4 and H_3PO_4) yields TPA (absorption maximum at 267 nm). This interesting reaction could be analytically useful and further study should be given it.

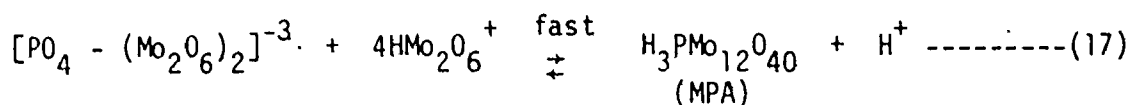
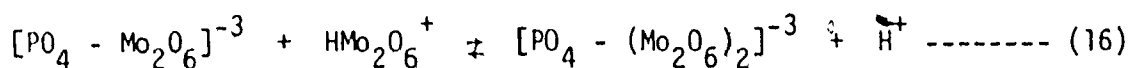
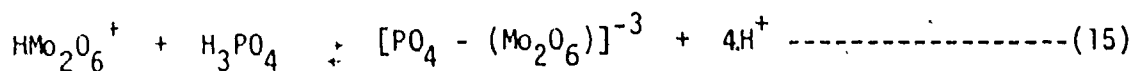
From the foregoing observations, it is interesting to speculate on the mechanism for the formation of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. In summary, these observations are as follows. (i) TPA is formed from an initial solution of simple tungstate ion and phosphate which has been acidified to $\text{pH} < 2$. At 25°C , formation is quantitative only after one day. The predominant isopoly species present are the ψ -meta, the poly Y and white tungstic oxide. Whereas the ψ -meta converts to the meta within about 2 hours and the poly Y species disappears after about 5 hours, the oxide continues to form slowly, together with the TPA. When the solution is heated to 60 - 100°C , the ψ -meta converts rapidly to the meta species, the poly Y disappears instantly and the formation of the tungstic oxide is accelerated. In this temperature range, the formation of TPA is instant. (ii) TPA is also formed from an initial solution of paratungstate^Z and phosphate, acidified to $\text{pH} < 2$. The observations are essentially as in (i). In addition, an acid solution of the paratungstate in the

absence of phosphate precipitates the white oxide. In the presence of phosphate, the oxide is not precipitated. (iii) TPA is not formed in a solution of metatungstate and phosphate in the range pH 2 to 4 M HClO_4 . The metatungstate ion itself is very stable and decomposes to the white oxide only in very concentrated acid solution (7 M HClO_4). The decomposition is instant. On addition of phosphate to this solution and warming, the oxide dissolves and TPA is formed instantly. (iv) When a freshly prepared precipitate of white tungstic oxide is treated with phosphate and warmed at pH < 2, dissolution occurs and TPA is formed. (TPA is not formed from aged white tungstic oxide, or from yellow tungstic oxide.)

From these observations, it is almost certain that TPA is not formed by direct reaction of phosphate with a dodecameric species (i.e., metatungstate or paratungstate Z), but from smaller isopoly species formed in the degradation of the dodecameric species. In the observations above, the white tungstic oxide is implicated very strongly. The structure of the solid is unknown,⁽¹⁷⁰⁾ but if it were trimeric or, more important, if the solution species with which the solid was in equilibrium in a saturated solution were trimeric, then a relatively tidy mechanism for the formation of TPA can be envisaged. For example, in such a scheme, the tetrahedral phosphate ion could serve as a central template gathering, in succession, a W_3O_9 unit at each of its corners to give the structure for $\text{PW}_{12}\text{O}_{40}^{-3}$ shown in Figure 2, in the INTRODUCTION. To the author's knowledge, no detailed study of the mechanism of TPA formation has yet been reported. There have been studies with regard to the formation of isopolytungstate species

(e.g., the paratungstate A ion⁽¹⁷⁷⁻¹⁷⁹⁾). Also, some evidence for small isopoly units in solution such as the tetratungstate ion, $H_5W_4O_{16}^{-3}$, has been found,^(172,175,176) but the existence of the trimeric species has not been proved unequivocally.⁽¹⁰⁹⁾ The main thesis that the reactive phosphate species must await the build-up of an unidentified isopoly species is supported by the observation reported in an earlier section that the initial rate of TPA formation seems dependent more on $C_{WO_4}^{-2}$ than on $C_{H_2PO_4}^{-}$.

Quantitative experimental evidence is required to provide definitive insight into the stepwise formation of TPA. In this regard, the work of Malmstadt et al. on the mechanism for the formation of 12-molybdophosphoric acid, $H_3PMo_{12}O_{40}$ (MPA), is of special interest.^(89,255) These investigators used a stopped-flow high-precision spectrophotometric technique to measure initial reaction rates and concluded that in acid solution (0.5-0.8 M HNO_3), Mo(VI) is appreciably dimerized. They suggested that the formation of MPA can arise by sequential reaction of the dimers with phosphate:



A similar study on the formation of TPA should be made. This study should show that small tungsten aggregates (e.g., W_2 , W_3 or W_4) are involved.

(h) Conformity to Beer's law of TPA formed in solution from tungstate, phosphate and acid and extracted into n-amyl alcohol

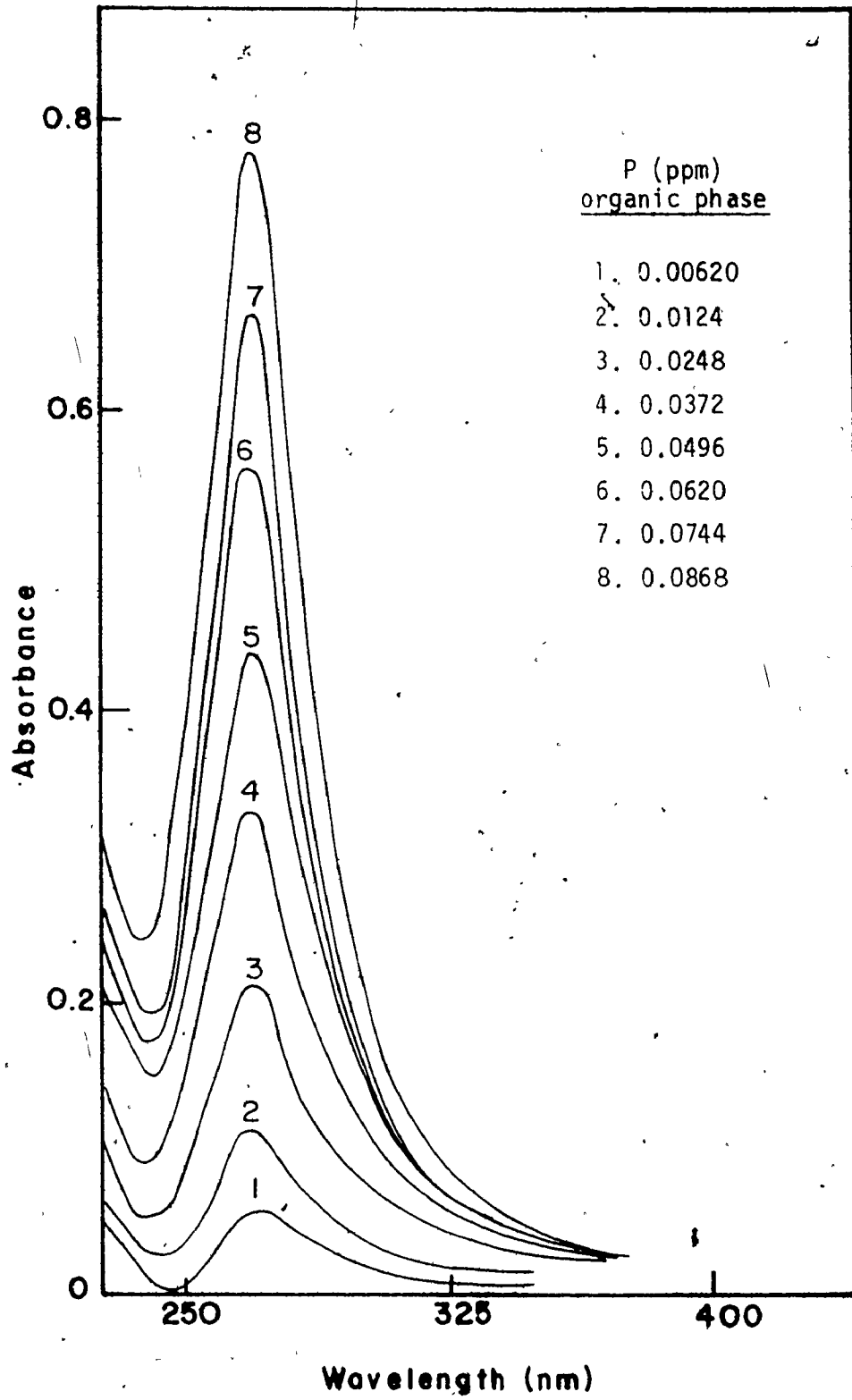
Figure 36 shows typical absorption spectra of TPA in the n-amyl alcohol phase after its formation in aqueous solution at 100°C and subsequent extraction. In terms of phosphorus concentration, the spectra range in value from 0.0155-0.217 ppm P in the aqueous phase (10 ml) and 0.00620-0.0868 ppm in the 25-ml n-amyl alcohol phase. A least-squares plot is presented for the range 0-0.0992 ppm P (0-0.248*) in Figure 37. Similar absorption curves and corresponding least-squares plots were obtained for the ranges 0-1.0 (0-2.5) and 0-10.0 (0-25.0) ppm P. For example, Figure 38 gives the least squares plot for the range 0-0.992 ppm P. Thus, Beer's law is obeyed at least up to 10.0 (25.0) ppm P.

In these tests of Beer's law, the pH range was maintained between 1.3-1.9 and $W/P \geq 24$. In those cases in which W/P was less than 24, deviations from Beer's law were evident. Figure 39, for example, represents a case where Beer's law is obeyed only up to 0.62 ppm P (1.55 ppm P in the 10-ml aqueous phase) since $C_{WO_4}^{-2}$ was only 1.2×10^{-3} M. In order to cover the entire range of ~ 0.10 (0.25) ppm P, $C_{WO_4}^{-2}$ would have to be at least 1.94×10^{-3} M. Similar comments apply to the range 0-10 (0-25) ppm P.

Beer's law was also tested for the formation of TPA in aqueous solution at 60°C, followed by extraction. According to Figure 40;

* Bracketed values correspond to concentrations of phosphorus in the 10-ml aqueous phase.

Figure 36. Absorption spectra of TPA in the n-amyl alcohol phase (25 ml) after its formation in aqueous solution (10 ml) and subsequent extraction. ($C_{WO_4^{2-}} = 4.8 \times 10^{-3}$ M, $C_{H_2PO_4^-} = 5.0 \times 10^{-7} - 7.0 \times 10^{-6}$ M, pH 1.3-1.9, 100°C, 5-cm cells, corresponding n-amyl alcohol extract of blank solution as the reference). Concentrations in Figure are for equivalent ppm P in organic phase; ppm P in aqueous phase are 2.5 times greater.



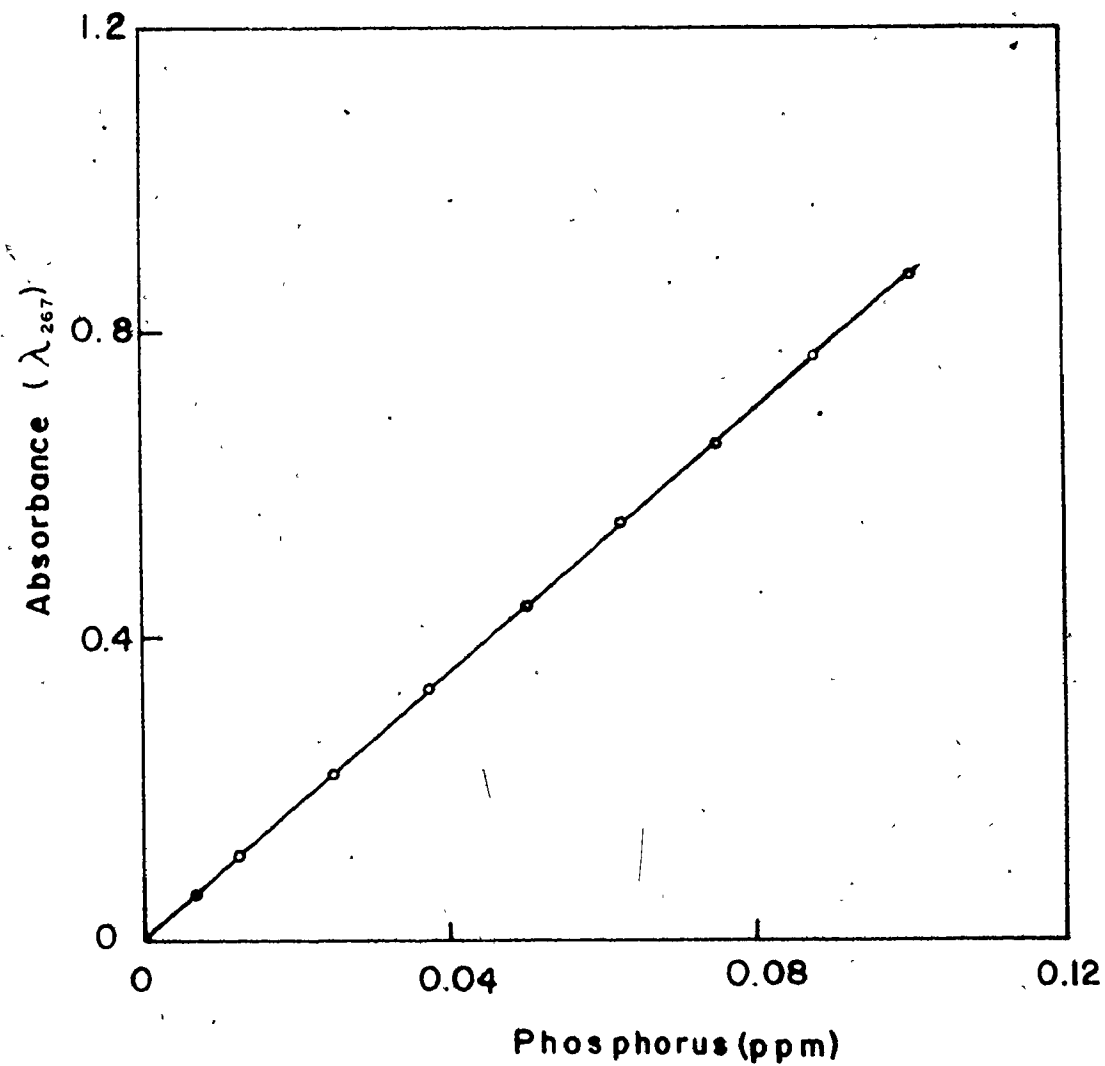


Figure 37. Least-squares Beer's Law plot for the estimation of phosphorus by the TPA Method. (Conditions same as for Figure 36). Concentrations in aqueous phase are 2.5 times greater.

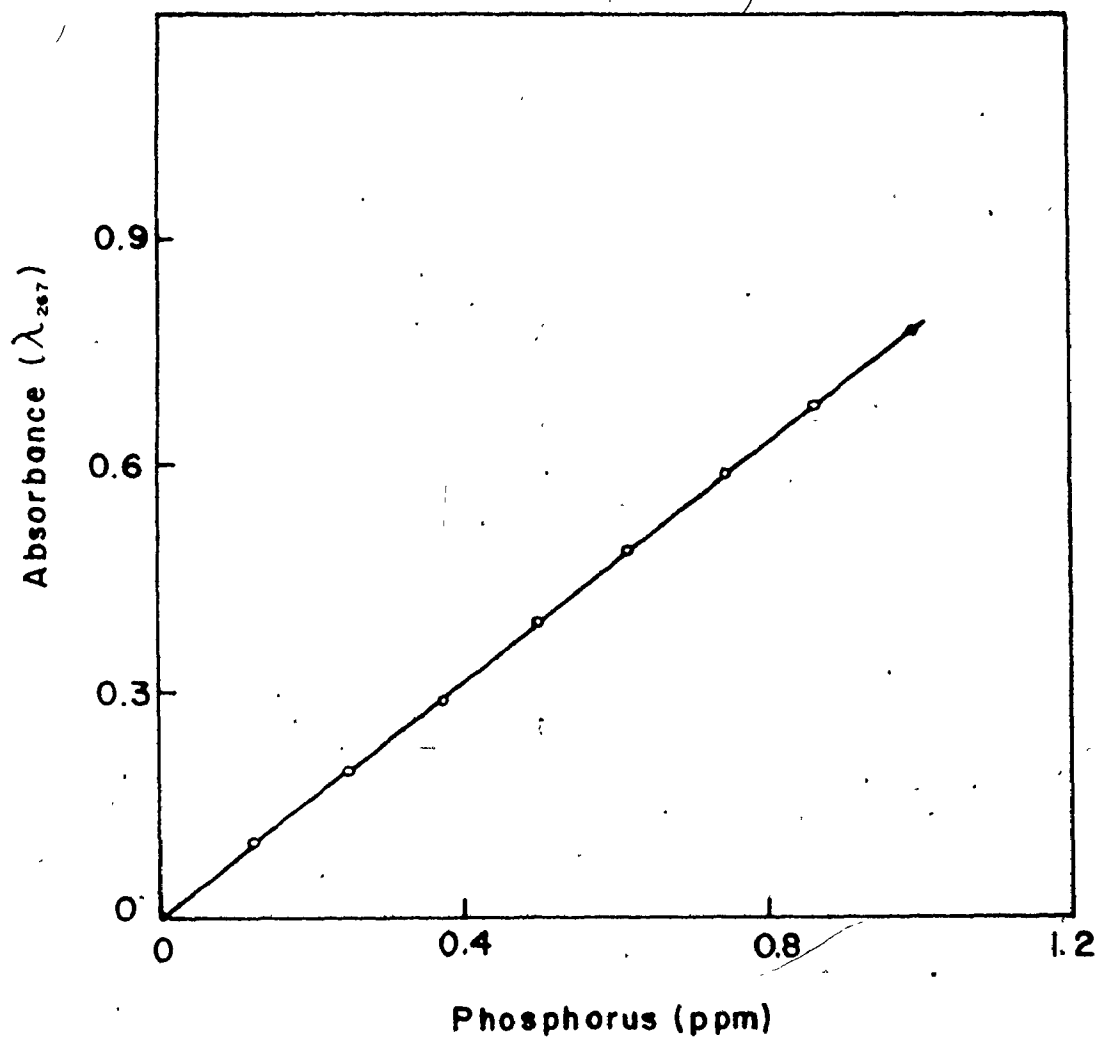


Figure 53. Least-squares Beer's Law plot for the estimation of phosphorus by the TPA Method. ($C_{WO_4^{2-}} = 2.4 \times 10^{-3}$ M, $C_{H_2PO_4^-} = 5.0 \times 10^{-6}$ - 8.0×10^{-5} M, pH 1.3-1.9, 100°C, 5-mm cells, corresponding n-amyl alcohol extract of blank solution as the reference; ppm P in aqueous phase are 2.5 times greater.)

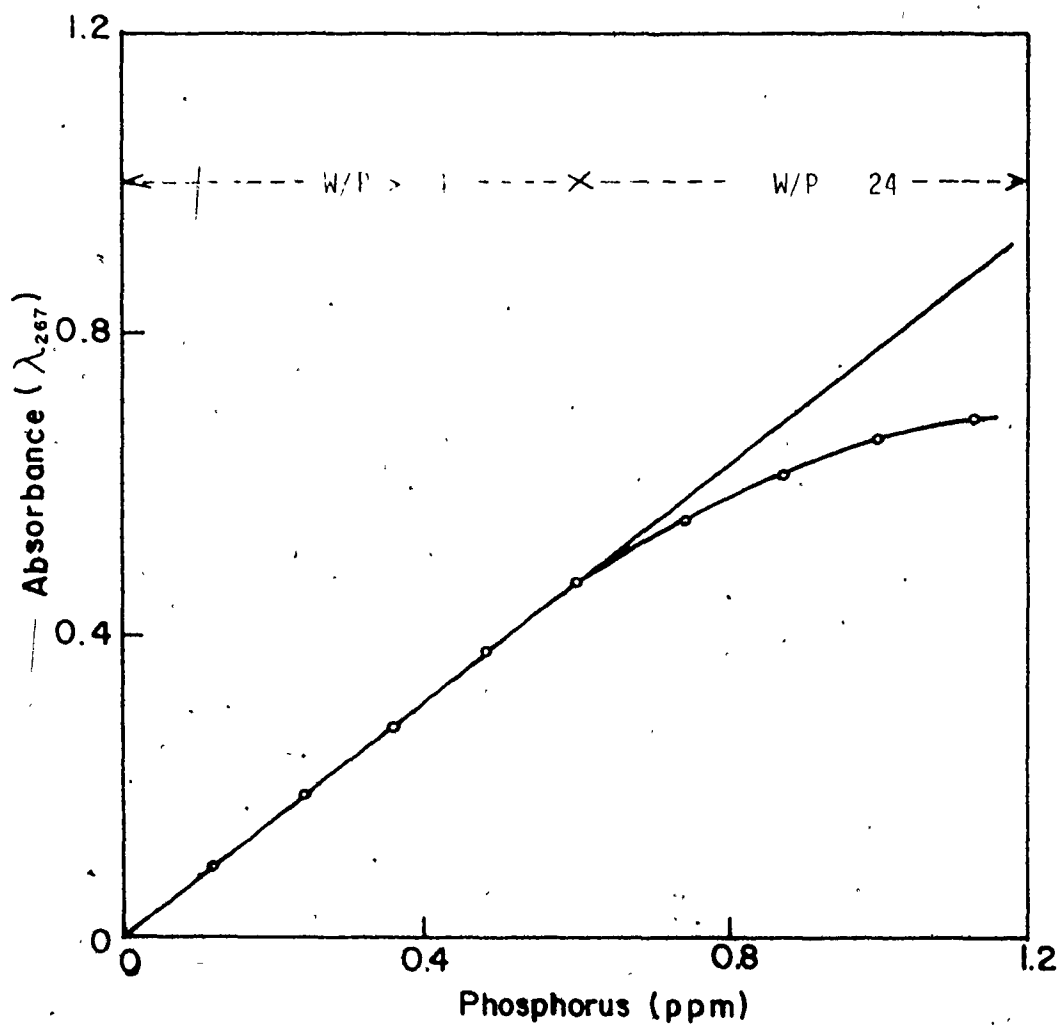


Figure 39. Deviation of Beer's Law for the estimation of phosphorus by the TPA Method. ($C_{WO_4^{-2}} \approx 1.2 \times 10^{-3}$ M, pH 1.5, 100°C , 5-mm cells, corresponding *n*-amyl alcohol extract of blank solution as the reference). For 1.0 ppm P in organic phase, $C_{H_2PO_4^-} = 8.1 \times 10^{-5}$ M in aqueous phase; i.e. W:P = 15.

Beer's law is obeyed at least up to 0.992 (2.48) ppm P.

Beer's law was tested for conformity with a synthetic sea-water sample* containing 35 parts per thousand salinity and up to 25 ppm P. The absorption curves and calibration plots were essentially identical to those obtained in aqueous solution. A decrease in sensitivity of about 17% occurs when the molybdenum-blue procedure (SnCl_2 as reductant) is applied to synthetic sea-water samples,⁽¹²⁾ although the Murphy-Riley method suffers only a 1% decrease in sensitivity.⁽⁶⁵⁾ This decrease has been referred to as the "salt error".⁽⁵⁾ In the TPA method, the decrease in sensitivity in the determination of phosphate was < 1% relative to non-seawater samples. The negligible decrease is due to the facts that the ionic strength of the aqueous phase in the formation of TPA is already high relative to that of sea water and that once formed, the TPA is removed from the aqueous phase for measurement.

In conclusion, the TPA method for phosphate determinations has been found to obey Beer's law for phosphate concentrations corresponding to as high as 25 ppm P in a water sample. In these studies, $C_{\text{WO}_4^{-2}}$ ranged from 6.0×10^{-4} to 4.8×10^{-2} M, and the pH values from 1.3 to 1.9. In all cases, the absorbance values of the TPA in the alcohol phase remained constant for at least two days. This stability is a decided advantage over the popular molybdenum-blue methods^(54,55) and the molybdovanadophosphate method.⁽⁴⁵⁾

* The composition of the synthetic sea water is given in the EXPERIMENTAL section.

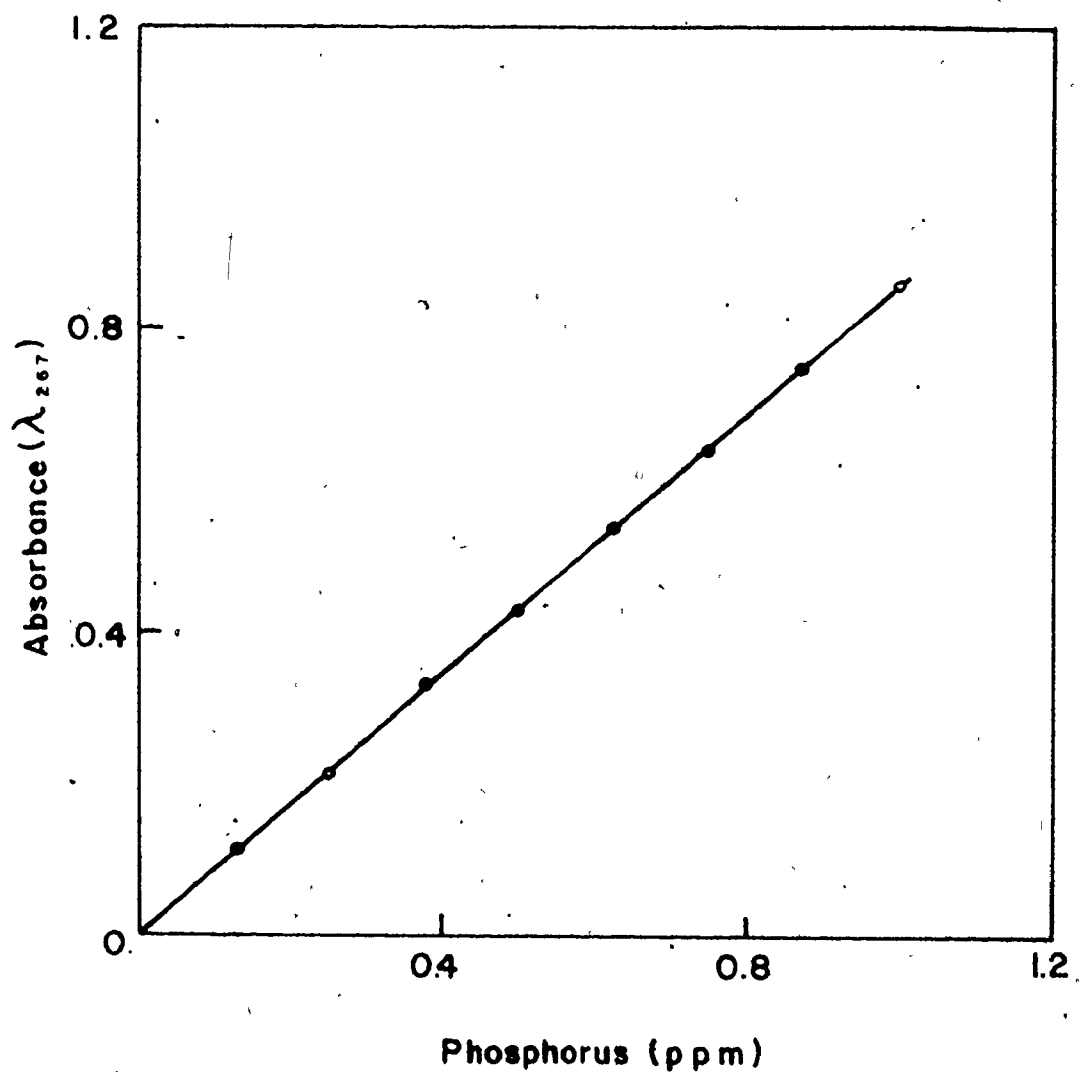


Figure 40. Least-squares Beer's Law plot for the estimation of phosphorus by the TPA Method. ($C_{\text{WO}_4^{2-}} = 4.8 \times 10^{-3}$ M, $C_{\text{H}_2\text{PO}_4^-} = 5.0 \times 10^{-6} - 8.0 \times 10^{-5}$ M, pH 1.3-1.9, 60°C, 5-mm cells, corresponding n-amyl alcohol extract of blank solution as the reference; ppm P in aqueous phase are 2.5 times greater.)

(i) Test of precision

The precision of the TPA method for the determination of phosphate in both aqueous solution and synthetic sea-water has been analysed statistically. ⁽²⁵⁶⁾ The results are presented in TABLE XI for phosphorus concentrations of 0.0062, 0.062, 0.62 and 6.2 ppm P in the n-amy1 alcohol phase. Since the molar absorptivity of TPA in both the aqueous and organic phase is the same, these values of precision in the organic phase should be equally applicable in the aqueous phase. The data are given in terms of the 95% confidence limit for the average and the percentage coefficient of variation. TABLE XI shows that the results for phosphate determination are precise to $\pm 4.8\%$ at the 0.0062, 2.3% at the 0.062, 1.6% at the 0.62 and $< 1\%$ at the 6.2 ppm P levels. The corresponding values for synthetic sea-water are $\pm 6.8\%$, 3.3%, 1.6% and $< 1\%$ at the 0.0062, 0.062, 0.62 and 6.2 ppm P levels.

(j) Effect of foreign ions

The results of the study regarding potential cationic and anionic interferences in the determination of phosphate based on TPA are presented in TABLE XII. The study was carried out at only one phosphorus concentration, 1.55 ppm P (0.62 ppm P in the organic phase). The following ions, Na^+ , K^+ , Cl^- , SO_4^{-2} and NO_3^{-*} do not interfere at least at levels $< 5,000$ ppm; Ca(II) , Mg(II) , Ni(II) , Co(II) , Mn(II) , Mo(VI) , ^{**}

* This ion interferes seriously in the molybdenum blue method [see INTRODUCTION]

** In the molybdenum blue procedure, a relative error of 29% occurs at 4.0 ppm W(VI). ⁽⁶⁶⁾

TABLE XI

Precision of the IPA Method for the Determination of Phosphate

(W/P \geq 24; λ_{max} = 267 nm, 100°C, n-amy1 alcohol extract of corresponding blank reference)

| Number of observations | Phosphorus taken* (ppm) | 95% Confidence limit** | | % Coefficient of variation | |
|------------------------|-------------------------|------------------------|---------------------|----------------------------|---------------------|
| | | fresh water | synthetic sea water | fresh water | synthetic sea water |
| 25 | 0.0062 | 0.0060 \pm 0.0003 | 0.0059 \pm 0.0004 | 4.8 | 6.8 |
| 20 | 0.062 | 0.061 \pm 0.0014 | 0.060 \pm 0.002 | 2.3 | 3.3 |
| 20 | 0.62 | 0.61 \pm 0.01 | 0.61 \pm 0.01 | 1.64 | 1.64 |
| 10 | 6.20 | 6.15 \pm 0.04 | 6.15 \pm 0.05 | 0.65 | 0.81 |

* The concentrations of phosphorus given are for the organic phase.

** Since the molar absorptivity values for TPA are the same in both aqueous and organic phases, these precision measures are same for both phases.

Cr(VI), and F^- do not interfere at levels $< 1,000$ ppm; $Hg(II)^*$, $Al(III)$, $Si(IV)$, Br^- , I^- , NO_2^-* , S^{2-} , SO_3^{2-} , SeO_3^{2-} and CN^- do not interfere at levels up to 400-700 ppm; $Ag(I)$, $Ba(II)$, $Cd(II)$, $U(VI)$ and $As(III)$ are tolerated up to 150-300 ppm; $Cu(II)^*$, $Be(II)$, $Zn(II)$, $Pb(II)$, $Ge(IV)$ and $Sn(IV)$ up to levels of 50-100 ppm; and $Ti(IV)$ and $Zr(IV)$ up to levels of 20-50 ppm.

Serious interferences result from $Fe(III)$, $Th(IV)$, $As(V)$, $V(V)$ and $Sn(II)$. The interference of $Fe(III)$ is due to its reaction with PO_4^{3-} to form insoluble $FePO_4$ [$pK_{sp} = 21.9$ at $25^\circ C$ ⁽²⁴¹⁾]. Complexation with F^- , CN^- and other ligands to remove the $Fe(III)$ interference failed because of the acidity of the solution. Separation of $Fe(III)$ by extraction into ether also failed because of the co-extraction of phosphate as H_3PO_4 . Removal of the $Fe(III)$ by ion-exchange was successful as demonstrated later.

There is no definitive study on the interference of $Fe(III)$ in the molybdenum-blue method. Burton et al.⁽⁵⁴⁾ however, pointed out that $Fe(III)$ does not interfere in the molybdenum-blue procedure ($SnCl_2$ reductant) at levels found in sea-water [i.e., 3.4 ppb⁽⁷⁰⁾]. In the Murphy-Riley procedure, no more than 50 ppm $Fe(III)$ can be tolerated at a phosphorus concentration of 10 ppm. The $Fe(III)/P(V)$ ratio (ppm basis) for the Murphy-Riley procedure is 5 whereas it is 2 for the TPA method.

The following ions $V(V)$, $Th(IV)$, $Ti(IV)$ and $Zr(IV)$ interfere most

* These ions interfere seriously in the molybdenum blue method [see INTRODUCTION].

TABLE XII

Interference of Foreign Ions in the Formation/Extraction of TPA

[$C_{\text{WO}_4^{-2}} = 4.8 \times 10^{-3}$ M, $C_{\text{H}_2\text{PO}_4^{-}} = 5.0 \times 10^{-5}$ M (1.55 ppm P, aqueous phase),
 pH 1.3-1.9, $T = 100^\circ\text{C}$, $\lambda_{\text{max}} = 267$ nm, 5-mm cells, corresponding n-amyl
 alcohol extract of blank solution as the reference]

| Ion | Added as | Max. tolerance limit* (as ppm of the ion) |
|-----------------|---|--|
| Li ⁺ | LiClO ₄ ·3H ₂ O | > 5 × 10 ² |
| Na ⁺ | NaCl | > 1 × 10 ⁴ |
| K ⁺ | KCl | ≤ 5 × 10 ³ |
| Ag(I) | AgNO ₃ | ≤ 1.8 × 10 ² |
| Be(II) | BeSO ₄ ·4H ₂ O | ≤ 50 |
| Mg(II) | MgSO ₄ ·7H ₂ O | > 2.5 × 10 ³ |
| Ca(II) | CaCl ₂ | ≤ 2.5 × 10 ³ |
| Ba(II) | BaCl ₂ | ≤ 3 × 10 ² |
| Cu(II) | Cu(NO ₃) ₂ ·3H ₂ O | ≤ 1 × 10 ² |
| Zn(II) | Zn(ClO ₄) ₂ ·6H ₂ O | ≤ 1 × 10 ² |
| Cd(II) | CdCl ₂ ·2½H ₂ O | ≤ 2.5 × 10 ² |
| Hg(II) | Hg(NO ₃) ₂ ·H ₂ O | ≤ 4 × 10 ² |
| Sn(II) | SnCl ₂ ·2H ₂ O | ≤ 2 |
| Pb(II) | Pb(NO ₃) ₂ | ≤ 1 × 10 ² |
| Co(II) | CoCl ₂ ·6H ₂ O | ≤ 1 × 10 ³ |
| Ni(II) | NiSO ₄ ·6H ₂ O | ≤ 1 × 10 ³ |
| Mn(II) | Mn(ClO ₄) ₂ ·6H ₂ O | ≤ 1 × 10 ³ |

TABLE XII (Continued)

| Ion | Added as | Max. tolerance limit* (as ppm of the ion) |
|-----------------|--|--|
| Al(III) | $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | $\leq 4 \times 10^2$ |
| Fe(III) | $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ | ≤ 3 |
| As(III) | NaAsO_2 | $\leq 1.5 \times 10^2$ |
| Ge(IV) | Na_2GeO_3 | $\leq 1 \times 10^2$ |
| Si(IV) | $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ | $\leq 7 \times 10^2$ |
| Sn(IV) | $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ | ≤ 50 |
| Th(IV) | $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ | ≤ 2 |
| Ti(IV) | $\text{Ti}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ | ≤ 50 |
| Zr(IV) | $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ | ≤ 20 |
| As(V) | $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ | see Table XIII |
| V(V) | NH_4VO_3 | ≤ 2 |
| Cr(VI) | K_2CrO_4 | $\leq 1 \times 10^3$ |
| Mo(VI) | $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ | $\leq 1 \times 10^3$ |
| U(VI) | $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | $\leq 2 \times 10^2$ |
| F^- | NH_4F | $\leq 2 \times 10^3$ |
| Cl^- | NaCl | $> 1.5 \times 10^4$ |
| Br^- | NH_4Br | $\leq 5 \times 10^2$ |
| I^- | NH_4I | $\leq 5 \times 10^2$ |
| NO_2^- | NaNO_2 | $> 5 \times 10^2$ |
| NO_3^- | NaNO_3 | $> 5 \times 10^4$ |
| CN^- | NaCN | $> 5 \times 10^2$ |

TABLE XII (Continued)

| Ion | Added as | Max. tolerance limit* (as ppm of the ion) |
|--------------|----------------------|--|
| S^{-2} | Na_2S | $< 5 \times 10^2$ |
| SO_3^{-2} | Na_2SO_3 | $> 5 \times 10^2$ |
| SO_4^{-2} | $MgSO_4 \cdot 7H_2O$ | $> 1 \times 10^4$ |
| SeO_3^{-2} | H_2SeO_3 | $> 5 \times 10^2$ |

* The maximum tolerance limit is given for the recovery of phosphorus corresponding to 1.55 ± 0.02 ppm P.

likely by their reaction with TPA to form mixed heteropolytungstates ($\text{PVW}_{11}\text{O}_{40}^{-4}$ and $\text{PTiW}_{11}\text{O}_{40}^{-5}$, for example, are known at least in the solid state⁽¹⁸⁶⁾). Th(IV) might also react with the phosphate to form insoluble $\text{Th}_3(\text{PO}_4)_4$ ($\text{pK}_{\text{sp}} = 78.6$ at 25°C ⁽²⁴¹⁾). Since the effects of these interferences have not been examined in the molybdenum-blue procedure, valid comparisons with the TPA method cannot be made. But V(V) is known to react with Mo(VI) to form the molybdovanadophosphoric acid, $\text{PVMo}_{11}\text{O}_{40}^{-4}$ (see INTRODUCTION). Similarly, mixed heteropoly-molybdates of Th(IV), Ti(IV) and Zr(IV) are known in the solid state.⁽¹⁸⁶⁾

The effect of Sn(II) on the TPA system is not known. Perhaps reduction of TPA to "tungsten blue" occurs. In the Murphy-Riley procedure, the peak due to the molybdenum-blue [ascorbic acid/Sb(III)] is blocked by Sn(II).⁽¹⁷⁵⁾

Excessive amounts of Be(II) and Sn(IV) interfere, probably by formation of their corresponding heteropolytungstates in solution. The heteropolytungstates of Be(II) and Sn(IV) are known in the solid state (e.g., $\text{BeW}_{12}\text{O}_{40}^{-6}$ and $\text{SnW}_{12}\text{O}_{40}^{-4}$ ⁽¹⁸⁶⁾). Excessive amounts of Pb(II) yields $\text{Pb}_3(\text{PO}_4)_2$ [$\text{pK}_{\text{sp}} = 42.1$ at 25°C].⁽²⁴¹⁾ These species have not been examined in the molybdenum-blue procedure for their interference. However, Sn(IV) is known to retard the colour development in the Murphy-Riley procedure.⁽⁷⁵⁾

Interference from As(V), Si(IV), Ge(IV) and isopolytungstates are special cases and are discussed separately below.

(i) Effect of arsenic. As(V) is potentially the most serious interference in the TPA method. Its interference arises from absorption at 267 nm, probably due to the acid, $\text{H}_3\text{AsW}_{12}\text{O}_{40}$, or an ion-association

complex of $\text{AsW}_{12}\text{O}_{40}^{-3}$. The acid has not been isolated and characterized* but the ammonium, potassium and thallium salts of the anion have been obtained and their crystal structures determined by X-ray diffraction. (258) The anion is isostructural with $\text{PW}_{12}\text{O}_{40}^{-3}$.

A detailed study of the recovery of phosphorus in the presence of As(V) was made and the results are presented below. Figure 41, A and B, shows typical absorption spectra in n-amyl alcohol of the 12-tungstoarsenate species extracted from aqueous solution in the pH range 0-2 with $C_{\text{HAsO}_4}^{-2} = 5.0 \times 10^{-5}$ and 3.0×10^{-5} M and $C_{\text{WO}_4}^{-2} = 4.8 \times 10^{-3}$ M. The formation and extraction of $\text{AsW}_{12}\text{O}_{40}^{-3}$ (as the acid or ion-associated complex) at concentrations ranging from 0.75-15 ppm As** (aqueous phase, $C_{\text{HAsO}_4}^{-2} = 1.0 \times 10^{-5}$ - 2.0×10^{-4} M) and at pH 0-2 are presented in Figure 42. Superimposed is the curve for the formation of TPA equivalent to 1.55 ppm P^{O} (aqueous phase). These curves show that if the pH is set between 1.5-1.9, the interference from As(V) is minimal at concentrations of As(V) \leq 15 ppm. The interference is substantial at pH 1.5 (8% at 15 ppm As) and insignificant at pH 1.9 (0.02% at 15 ppm As). Such high concentrations of As are rarely encountered, however, in samples. The recovery of phosphate in solutions containing AsO_4^{-3} is given in

* A recent claim for the formation of $\text{H}_3\text{AsW}_{12}\text{O}_{40}$ in solution at pH 2 has been made. (257)

** This concentration corresponds to 0.3-6 ppm As in the 25-ml n-amyl alcohol phase.

@ The corresponding concentration in the alcohol phase is 0.62 ppm P.

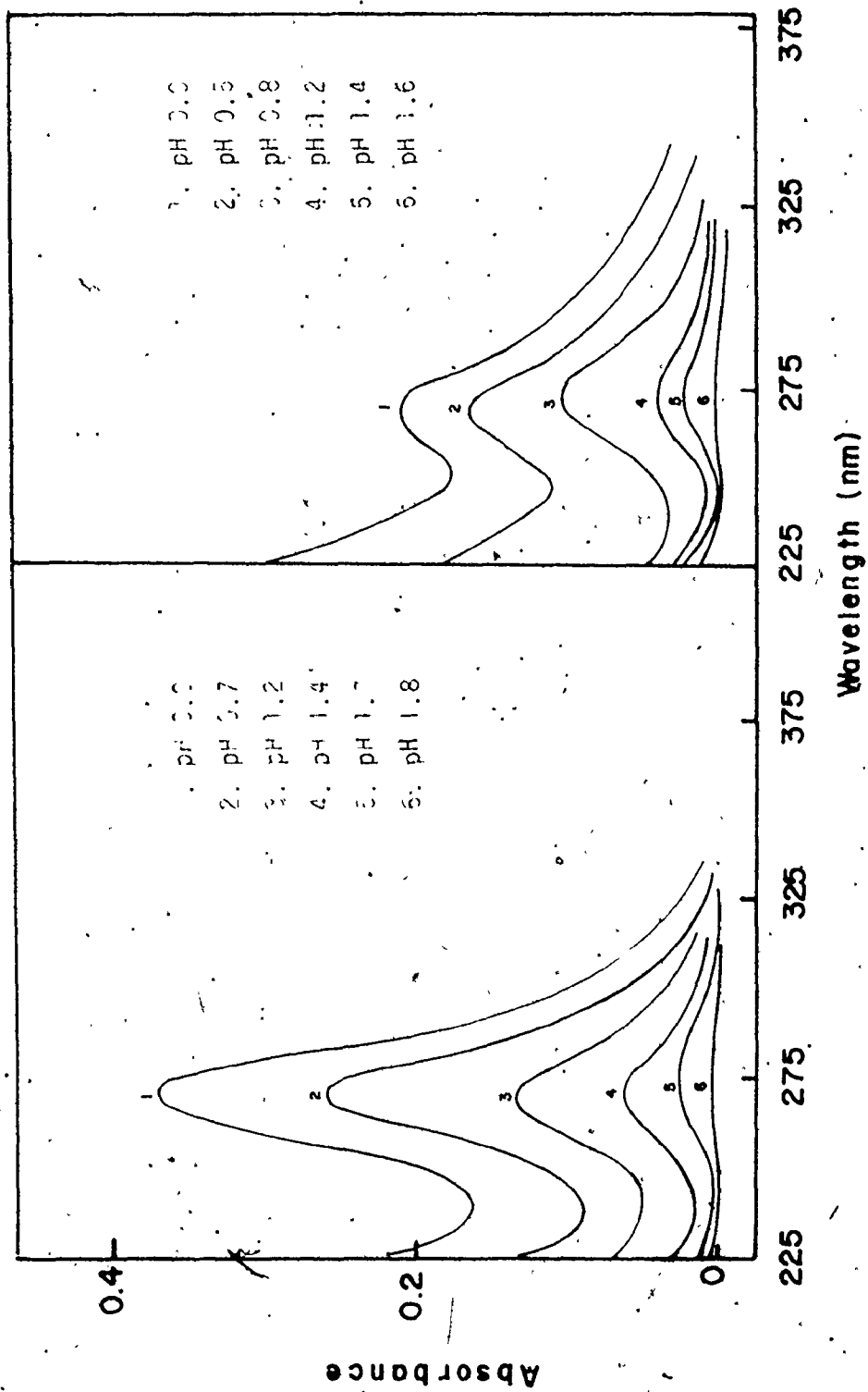


Figure 4. Absorption spectra for the formation/extraction of TAA. ($^{14}\text{O}_4^{-2} = 4.8 \times 10^{-3} \text{ M}$, 100°C , 5-mm cells, corresponding n-amy) alcohol extract of blank as reference).

- A. $\text{CHAsO}_4^{-2} = 5.0 \times 10^{-5} \text{ M}$ (3.75 ppm As);
- B. $\text{CHAsO}_4^{-2} = 3.0 \times 10^{-5} \text{ M}$ (2.25 ppm As)

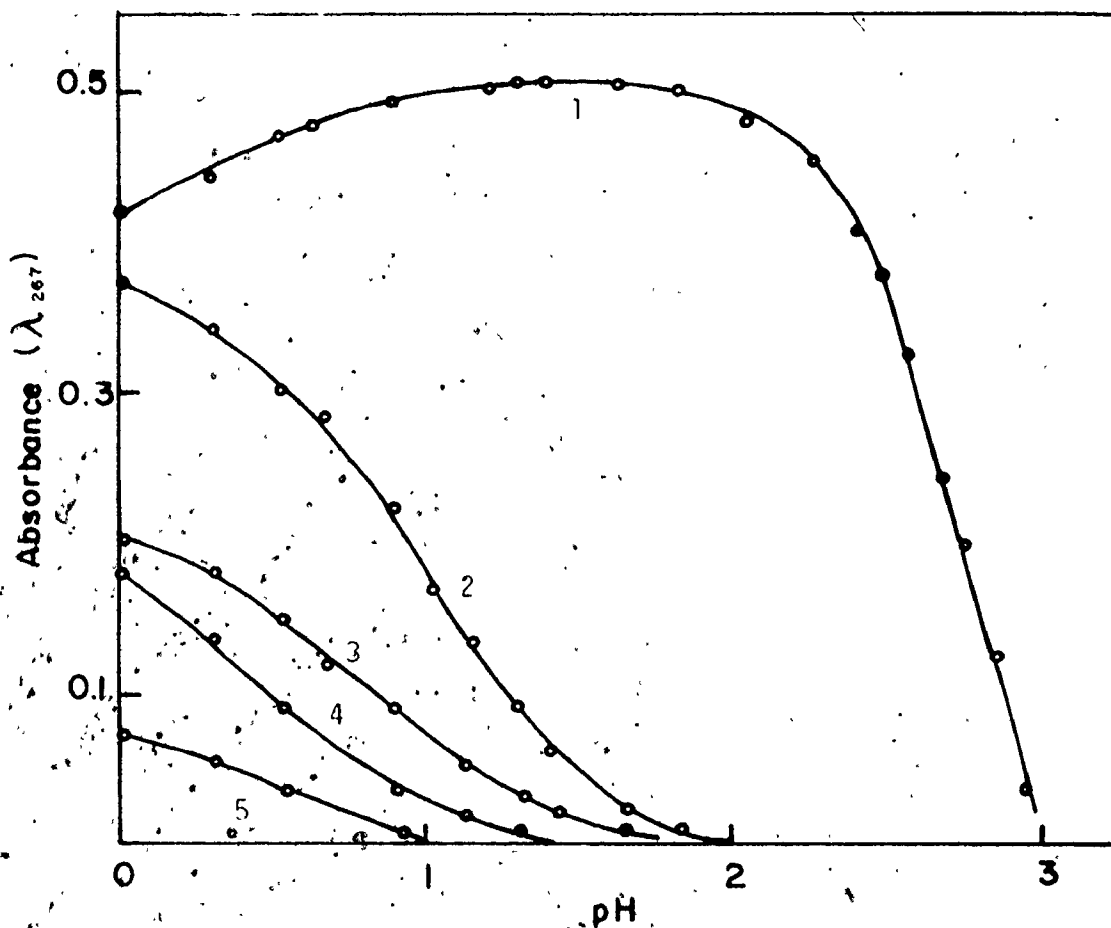


Figure 12. Formation/Extraction of $AsW_{12}O_{40}^{-3}$ as the acid or ion-pair; (comparison to Formation/Extraction of TPA. (W/P \geq 24, W/As \geq 24, T = 100°C, 5-mm cells, corresponding n-amyl alcohol extract of blank solution as the reference)

1. 0.62 ppm P; 2. 6.0 ppm As; 3. 3.8 ppm As; 4. 1.5 ppm As
5. 0.75 ppm As. Concentration are for organic phase. Concentrations in aqueous phase are 2.5 times greater.

TABLE XIII. Note that even for rather high As/P ratios, satisfactory recovery is still achieved in the pH range 1.5-1.9. This relative freedom from interference of As in the pH range 1.5-1.9 is very significant, especially in view of the fact that in the molybdenum-blue procedure (SnCl_2 as reductant), As(V) interferes as its equivalent of P(V).⁽¹²⁾ With ascorbic acid as the reductant, freedom from As(V) - interference requires stringent conditions ($\text{C}_2\text{MoO}_4^{-2} = 4.1 \times 10^{-3}$ and 0.4 N H_2SO_4).⁽¹⁴⁶⁾ In the Murphy-Riley procedure (ascorbic acid/Sb(III) as reductants) no more than 0.01 ppm As can be tolerated for 1.0 ppm P.⁽⁶⁵⁾

Since As(III) does not react with tungstate ion in acid solution to form the $\text{AsW}_{12}\text{O}_{40}^{-5}$ anion or a P-As(III)-W complex, initial efforts in this work to overcome the interference from As(V) were based on selective reduction to As(III). Such reductants as oxalic acid, urea, ascorbic acid, thiosulphate, and a reducing solution made up of sodium thiosulphate (40 ml, 1.4% W/V), sodium metabisulphite (40 ml, 14% W/V) and H_2SO_4 (20 ml, 1.5 M)^(75,76) were used. All reducing agents failed for one reason or another. With oxalic acid, As(V) was converted completely to As(III), but quantitative formation of TPA was not achieved (~60-75% only). Sodium thiosulphate proved to be an effective reducing agent but sulphur formed in the acid solutions, was extracted into n-amyl alcohol, and gave a broad band at ~265-270 nm.* The reducing solution also led to extraction of sulphur. Ascorbic acid was extracted and found to absorb at 267 nm. Urea (0.01 M) did not reduce As(V) quantitatively. Ultimately, the above procedure of extraction in the

* Sulphur dissolved in n-amyl alcohol gives the same band.

TABLE XIII

Recovery of Phosphorus (as Phosphate) in the Presence of Arsenic (as Arsenate) by the TPA Method

(T = 100°C, λ_{max} = 267 nm, corresponding n-amyl alcohol extract of blank solution as the reference)

| Taken (ppm) | | P _{found} (ppm) |
|-------------|------------------|--------------------------|
| P | As | pH 1.5-1.9 |
| 0.0155 | 3.75 | 0.0230 ± 0.0020 |
| | 1.50 | 0.0170 ± 0.0020 |
| | 0.75 | 0.0153 ± 0.0002 |
| 0.155 | 15.0 | 0.212 ± 0.003 |
| | 3.75 | 0.180 ± 0.001 |
| | 1.50, 0.75 | 0.156 ± 0.002 |
| 1.55 | 15.0 | 1.75 ± 0.02 |
| | 3.75, 1.50, 0.75 | 1.54 ± 0.002 |
| 15.50 | 15.0 | 16.10 ± 0.02 |
| | 3.75, 1.50, 0.75 | 15.53 ± 0.02 |

NOTE. For the range 0.01-0.02 ppm P, an As/P ratio (based on ppm) of at least 50 is tolerable. For the ranges 0.1-0.2 and 1-2, ratios of at least 10 and 2, respectively, are tolerable.

pH range 1.5-1.9 was adopted for minimization of the As(V) interference.

(ii) Effect of silicon and germanium. According to TABLE XII, high levels of Si(IV) and Ge(IV) can be tolerated, i.e., 700 ppm and 100 ppm, respectively, for 1.55 ppm P. In the molybdenum-blue method,* no more than 3.0 ppm Si(SnCl₂ reduction)⁽¹²⁾ and 10 ppm Si [ascorbic acid/Sb(III) reduction]⁽⁶⁵⁾ can be tolerated for 10 ppm P. Such high tolerance levels in the TPA method arise for one or both of the following reasons: the formation of both tungstosilicic (TSA, H₄SiW₁₂O₄₀) and tungstogermanic (TGA, H₄GeW₁₂O₄₀) acids is negligible in the pH range (pH 1-2) of quantitative formation of TPA; or, their anions may be present in the pH range 1-2 but are not extracted into n-amyl alcohol.

Experiments with the commercially-available TSA and TGA compounds showed that both had constant absorbances at 270 nm (0.48 and 0.42 units, respectively, for $C_{TSA} = 2.0 \times 10^{-5} \text{ M} = C_{TGA}^{\text{⑥}}$) in the acid range 4 M HClO₄ - pH 2. The absorbance remained constant at least for 10 hours. (At pH > 2, both acids dissociated, and ultimately to WO₄⁻² above pH 7.). Thus, the acid anions may well be present in the pH range (1-2) of quantitative formation of TPA but not be extractable at these acidities. A subsequent experiment showed that extraction into

* Although Ge(IV) is known to form the 12-molybdogermanic acid (H₄GeMo₁₂O₄₀) in the same region of acidity as H₃PmO₁₂O₄₀, information is not available on its extent of interference.

⑥ $\epsilon_{TSA} = 4.8 \times 10^4 \text{ litre mol}^{-1} \text{ cm}^{-1}$ at 270 nm; $\epsilon_{TGA} = 4.2 \times 10^4 \text{ litre/mol-cm}$ at 270 nm ($\mu = 1, 25^\circ\text{C}$).

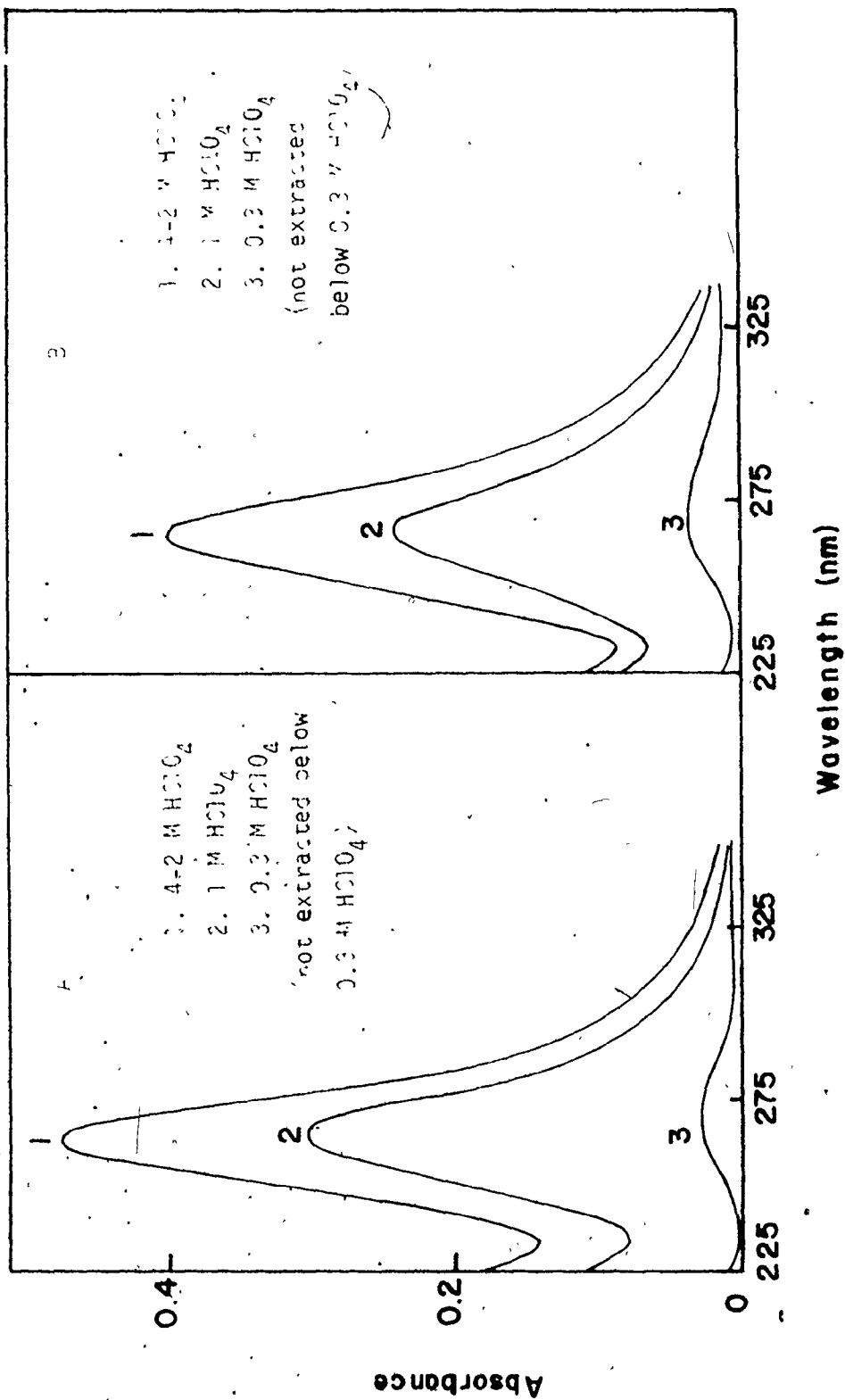


Figure 43. Extraction of 12-heteropolytungstates into *n*-amyl alcohol. (25°C, 5-mm cells, corresponding *n*-amyl alcohol extract of blank solution as reference)

A. 12-tungstosilicic acid ($[\text{TSA}] = 2.0 \times 10^{-5} \text{ M}$).

B. 12-tungstogermanic acid ($[\text{TGA}] = 2.0 \times 10^{-5} \text{ M}$)

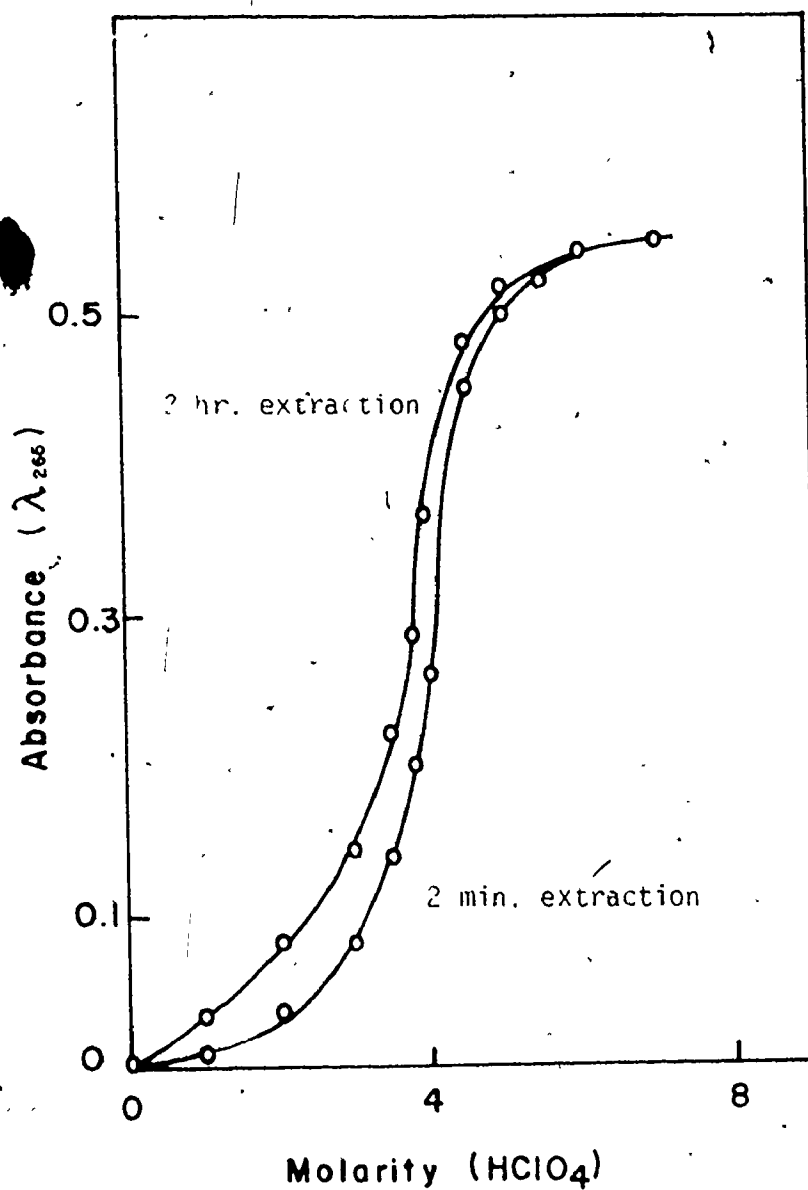


Figure 44. Extraction of metatungstate into *n*-amyl alcohol as a function of acidity ($C_{\text{meta}} = 1.97 \times 10^{-5}$ M, 25°C ; 5-mm cells, corresponding *n*-amyl alcohol extract of blank solution as the reference)

n-amy] alcohol occurs at acidities $> 0.3 \text{ M HClO}_4$ (Figure 43).

(iii) Effect of isopolytungstates. As has been already discussed, the predominant isopoly species that exist below pH 2 on heating an acid solution of tungstate to 60-100°C are tungstic oxide hydrates and metatungstate. The former is not extracted while the latter is extracted only above $1 \text{ M H}_3\text{O}^+$ (Figure 44). Thus, the isopolytungstates do not interfere under the conditions of the TPA method.

III. B. ANALYTICAL APPLICATION OF THE TPA METHOD TO PHOSPHORUS - CONTAINING MATERIALS

1. Application to total soluble phosphate in water samples

The results for the determination of total soluble phosphorus in six water samples obtained from the International Reference Group on Upper Lakes Pollution (Windsor, Ontario) are presented in TABLE XIV. The results obtained by the TPA method are compared with the average values obtained by 17 different laboratories which participated in the round-robin analysis. All laboratories used the molybdenum-blue method but the reduction of the molybdophosphoric acid to the "blue" was effected by the use of different reductants such as stannous chloride, 1-amino-2-naphthol sulphonic acid, ascorbic acid and a combination of ascorbic acid and Sb(III).

The data obtained by the TPA method agree well with those obtained by the molybdenum-blue procedures. The precision of the TPA method is apparently better but the comparison is not valid since the ULPG data represent several different analysts. In the INTRODUCTION, drawbacks of the molybdenum-blue procedure were discussed [e.g., As(V) interference,

TABLE XIV

Determination of Phosphorus in Water Samples* by the TPA Method

| Sample No. | Source | Total Phosphorus (mg/l) | |
|------------|---------------|-------------------------|-------------------------|
| | | Molybdenum-blue** | TPA Method [@] |
| 41 | Lake Michigan | 0.010 ± 0.003 (17) | 0.008 ± 0.001 |
| | | 0.010 ± 0.001 (11) | |
| 42 | Lake Michigan | 0.009 ± 0.004 (17) | 0.008 ± 0.001 |
| | | 0.007 ± 0.003 (11) | |
| 43 | S&S Canal | 1.61 ± 0.07 (17) | 1.61 ± 0.03 |
| 44 | S&S Canal | 1.83 ± 0.15 (16) | 1.85 ± 0.01 |
| | | 1.85 ± 0.12 (15) | |
| 45 | STP-Effluent | 0.174 ± 0.028 (17) | 0.167 ± 0.001 |
| | | 0.179 ± 0.021 (16) | |
| 46 | STP-Effluent | 0.174 ± 0.024 (17) | 0.170 ± 0.001 |
| | | 0.179 ± 0.015 (16) | |

* The water samples were obtained from the Upper Lakes Pollution Group (ULPG).

** The precision measure is the standard deviation. The numbers in brackets represent the number of laboratories included in the average. The averages based on less than 17 results were recalculated by ULPG after deletion of suspected data.

@ Each result represents the average of three determinations. The precision measure is the standard deviation.

the slow rate and instability of colour development, and sensitivity to reagent concentrations]. These drawbacks can be overcome but at the expense of exercising strict control over the procedure. In this connection, the TPA procedure is superior, despite the fact that it requires an extraction.

In TABLE XV are reported the values of total phosphorus by the TPA method for water samples obtained from the Canada Centre for Inland Waters (Burlington, Ontario). The values are compared with those obtained by the CCIW laboratory which used the automated molybdenum-blue method with SnCl_2 as the reductant. A critical evaluation of the results cannot be made since only a single value was obtained from CCIW for each sample; however, one can say that the values are not in bad disagreement.

The phosphorus content in the two Nutrient Reference Samples, supplied by the US Environmental Protection Agency (Cincinnati, Ohio) have been determined by the TPA method. These samples were prepared by the EPA as concentrates by dissolution of known amounts of analytical reagent-grade chemicals in distilled water. Concentrate 1 contains inorganic phosphorus (orthophosphate) and nitrogen and Concentrate 3 contains organically-bound forms of phosphorus and nitrogen. The former was analysed for orthophosphate and the latter for total phosphorus. The results are given in TABLE XVI. While the result for Concentrate 1 agrees well with the given EPA value, the result for Concentrate 3 is significantly lower ($\sim 5\%$). Since the TPA data is precise, it is likely that the low result was introduced by a systematic error.

TABLE XV

Determination of Phosphorus in Water Samples* by the TPA Method

| Sample No. | Source | Total Phosphorus (mg/l) | |
|------------------------|------------------|--------------------------|---------------|
| | | molybdenum-blue Method** | TPA Method*** |
| 1806 (F) ^① | St. Mary's River | 0.001 | 0.002 |
| 1806 (UF) ^① | St. Mary's River | 0.002 | 0.002 |
| 2982 (F) | not known | 0.008 | nil |
| 2982 (UF) | not known | 0.019 | 0.021 ± 0.001 |
| 4907 (F) | Welland Canal | 0.005 | 0.003 |
| 38-1-N-C/H(F) | CCIW | 0.062 | 0.057 ± 0.002 |
| 2302 (UF) | Well-Site | 0.026 | 0.020 ± 0.001 |
| 2412 (UF) | Well-Site | 0.038 | 0.042 ± 0.001 |
| 2413 (UF) | Well-Site | 0.10 | 0.085 ± 0.002 |
| 2793 (UF) | Well-Site | 0.003 | 0.004 |

* The water samples were obtained from the Canada Centre for Inland Waters (CCIW), Burlington, Ontario.

** Each result is based on only a single determination by CCIW (SnCl₂ method, automated).

*** Average of at least two determinations. Precision measure is standard deviation.

① (F) - filtered sample; (UF) - unfiltered sample.

TABLE XVI

Determination of Phosphorus in EPA Concentrates by the TPA Method

| Concentrate No. | Total phosphorus (mg/l) | |
|--------------------|-------------------------|------------------|
| | TPA Method* | Calculated value |
| 1 | 0.019 ± 0.002 | 0.021 |
| 3 | 0.135 ± 0.002 | 0.142 |

The error cannot have originated in incomplete oxidation since it is known that organophosphorus compounds containing P-C and P-O-C linkages are completely oxidised by the persulphate/H₂SO₄ digestion technique. (244) No interference is expected from the organic nitrogen compounds, provided they are not in the cationic form in which case, they might interact with the tungstophosphate anion. Since the test solution is acidic, it is conceivable that a cationic organonitrogen compound could have interfered, but it is more likely that the persulphate/H₂SO₄ digestion rendered the nitrogen as NH₄⁺, which does not interfere. A further possible explanation could be that the Concentrate has undergone partial decomposition in spite of the fact that it was preserved. It is known that the Concentrate is stable for a period of months, but the age of the tested sample is not known. As shown later, the application of the

* Average of at least 5 determinations. The precision measure is the standard deviation.

TPA method to a NBS organophosphorus standard yielded excellent results.

The literature contains several methods for the determination of phosphorus in natural waters but few for its determination in waste water. (14,66) Furthermore, Heinke⁽¹⁴⁾ has stated that many investigators are using methods developed for natural waters for the determination of phosphorus in waste waters without showing that materials in sewage do not interfere. In this regard, the TPA method was tested by application to raw-sewage influent (and its effluent) from the Hamilton sewage treatment plant. The samples, as obtained, had not been preserved and so their phosphorus content as determined by the TPA method are not representative of the sewage-water sample. To ascertain the effect of possible interferences, however, a standard addition was made to both the influent and effluent and the phosphate in these 'spiked' systems and the natural systems (i.e., the unspiked influent and effluent) was determined. Results for recovery of the spike were then compared to the calculated amounts (TABLE XVII).

The raw-sewage sample was very turbid and dark, with a non-uniform distribution of particulate matter. The final effluent, although clear, still contained suspended solids. Therefore, the determination of the phosphorus content in both the influent and effluent were carried out on filtered (0.45 μ Millipore filter) and unfiltered samples. This procedure, incidentally, yielded information regarding the amount of phosphorus present in particulate matter, within the limitations of the filter pore-size. (259) The last three columns of TABLE XVII show that the experimental and calculated values for the spike are in excellent agreement. Therefore, it is concluded that the TPA method is applicable

TABLE XVII

Determination of Phosphate in Raw and Treated Sewage water by the TPA Method

| Sample + Spike | | Total Phosphorus (mg/l), Influent | | Spike | |
|-----------------------------------|---------------|-----------------------------------|---------------|---------------|------------|
| *** UF | ** | *** UF | F | Experimental | Calculated |
| 4.44 ± 0.04 | 3.84 ± 0.03 | 1.21 ± 0.02 | 1.22 ± 0.01 | 1.22 ± 0.01 | 1.24 |
| 5.69 ± 0.02 | 5.07 ± 0.02 | 2.46 ± 0.03 | 2.45 ± 0.02 | 2.45 ± 0.02 | 2.48 |
| 6.22 ± 0.02 | 5.62 ± 0.04 | 2.99 ± 0.03 | 3.00 ± 0.01 | 3.00 ± 0.01 | 3.10 |
| 6.90 ± 0.04 | 6.31 ± 0.02 | 3.67 ± 0.04 | 3.70 ± 0.01 | 3.70 ± 0.01 | 3.72 |
| Total Phosphorus (mg/l), Effluent | | | | | |
| 0.668 ± 0.004 | 0.614 ± 0.005 | 0.242 ± 0.004 | 0.245 ± 0.005 | 0.245 ± 0.005 | 0.248 |
| 0.796 ± 0.003 | 0.737 ± 0.002 | 0.370 ± 0.004 | 0.368 ± 0.004 | 0.368 ± 0.004 | 0.372 |
| 1.042 ± 0.003 | 0.983 ± 0.005 | 0.616 ± 0.004 | 0.614 ± 0.005 | 0.614 ± 0.005 | 0.620 |

(Continued on next page)

* The sewage water was obtained from the Hamilton sewage treatment plant. The sewage water was treated by both the primary and secondary processes.

** The spike was added as a volume of standard phosphate solution. Measurements were made at both 60 and 100°C. The results obtained at both temperatures were essentially the same. The values in the TABLE represent the average of 6 determinations. The precision measure is the standard deviation.

*** UF : unfiltered sample; F - filtered sample. For the influent, the unfiltered sample had a phosphorus content of 3.23 ± 0.05 ppm; the filtered sample had a phosphorus content of 2.62 ± 0.04 ppm. For the effluent, the corresponding values were 0.426 ± 0.005 and 0.369 ± 0.006 ppm P, respectively. The values in each case represent the average of 6 determinations. The precision is the standard deviation.

of waste waters, as well as, natural waters. The results also show that about 81% of the phosphorus is in soluble form and 19% in particulate form for the influent. The corresponding figures for the effluent are 87% and 13%, respectively. Finally, samples heated to 60°C gave the same results as samples heated to 100°C.

2. Application to the determination of phosphorus in steels

The applicability of the TPA method has been tested on standard steel samples supplied by the National Bureau of Standards. The results of triplicate determinations for %P are presented in TABLE XVIII. They are in good agreement with the certified values. The interference of iron was overcome by ion-exchange separation (sub-section-2, Section II.D).

3. Application to phosphor bronzes

The results for the phosphorus content in three standard phosphor-bronze samples, obtained from the Canada Centre for Mineral and Energy Technology, are given in TABLE XIX, and are in excellent agreement with the certified values.

In addition to phosphorus, the samples contain Cu (86-95%), Sn (5-9%) and small amounts of iron, lead and zinc. Iron did not interfere since it was present at levels less than 3 ppm* for the amount of sample taken. Other elements present (e.g., Ni, Al) caused no interference. A direct analysis was, therefore, possible.

* Fe interferes in the TPA method only at levels above ~ 3 ppm [see TABLE XII, Section III. A. 2].

TABLE XVIII

Determination of Phosphorus in NBS Steels by the TPA Method

| Sample No. * | % Phosphorus | |
|--------------|------------------------|-------------------------|
| | Certified Value ** | TPA Method [ⓐ] |
| 170A | 0.005 (0.004-0.007) | 0.0053 ± 0.0001 |
| 15f | 0.006 (0.004-0.007) | 0.0065 ± 0.0005 |
| 14e | 0.008 (0.007-0.010) | 0.008 ± 0.001 |
| 8j | 0.095 (0.094-0.098) | 0.093 ± 0.002 |

* Samples 170A, 15f and 14e are open-hearth steels and sample 8j is a Bessemer steel.

** The numbers in brackets give the range of values from which the certified value was obtained as an average. The methods of analysis included gravimetry (as MgP_2O_7), titrimetry (alkali-molybdate method), and spectrophotometry (molybdenum blue).

[ⓐ] The results are the average of 3 determinations. Precision measure is standard deviation.

TABLE XIX

Determination of Phosphorus in Phosphor Bronzes* by the TPA Method

| Sample No. | % Phosphorus | |
|------------|-------------------------|-------------------------|
| | Certified Value** | TPA Method [ⓐ] |
| 304 | 0.007 (0.0045-0.011) | 0.0063 ± 0.0002 |
| 293 | 0.030 (0.028-0.032) | 0.029 ± 0.002 |
| 477 | 0.43 (0.40-0.45) | 0.422 ± 0.002 |

* The phosphor-bronze samples are spectrographic standards and were obtained from the Canada Centre for Mineral and Energy Technology.

** The certified values are based on the molybdovanadophosphate method. The numbers in brackets give the range of values from which the certified value was obtained as an average. No precision measure was calculated by the Centre.

[ⓐ] Each value represents the average of three determinations. The precision measure is the standard deviation.

4. Application to ores and a mineral

(a) Nickel-Copper-Cobalt ore, SU-1

The ore was supplied as a Standard Reference Material by the Mineral Sciences Division, Canada Centre for Mineral and Energy Technology.

SU-1 is a sample from the Falconbridge Nickel Mines and is representative of the Sudbury nickel-copper ores. The major constituents are oxygen (31.2%), iron (22.9%), silicon (16.2%), sulphur (12.1%), calcium (2.86%), magnesium (2.47%) and nickel (1.51%), with smaller amounts of other elements such as Cu, Co, Ti, Na and Ni. Since iron is a major constituent in this ore, it would interfere with the TPA method and so it was removed by ion-exchange prior to analysis. The result for phosphorus, reported as %P₂O₅, is given in the first line of TABLE XX. The result by the TPA method is in excellent agreement with the provisional value.

(b) Manganese ore (NBS Reference Material, 25c)

The manganese ore supplied by NBS contains MnO₂ (90.73%), SiO₂ (2.36%) and P₂O₅ (0.22%). Manganese and silicon do not interfere in the TPA method and no previous separation was made. The result for the direct analysis (TABLE XX) is in good agreement with the provisionally reported value.

(c) Feldspar (NBS Reference Material, 99a)

The mineral, supplied by NBS contains SiO₂ (65.2%), Al₂O₃ (20.5%) and oxides of sodium, potassium and calcium (13.5%). None of these interfere in the TPA method. Therefore, direct determination was

TABLE XX

Determination of Phosphorus in Ores and a Mineral by the TPA Method

| Sample No. | Type of Ore/Mineral | Source | % P ₂ O ₅ | |
|------------|---------------------|------------------|---------------------------------|---------------|
| | | | Provisional value* | TPA Method** |
| SU-1 | Ni-Co-Cu | Canada Reference | 0.10 ^① | 0.099 ± 0.002 |
| 25c | Mn | NBS | 0.22 | 0.204 ± 0.003 |
| 99a | Feldspar | NBS | 0.02 | 0.019 ± 0.001 |

* The methods by which the provisional values were obtained have not been reported.

** The results are the average of 3 determinations. The precision measure is the standard deviation.

① This value is based on the average results ranging from 0.092 to 0.12.

possible and the result for P (as %P₂O₅) is presented in TABLE XX.

It is in good agreement with the provisionally reported value.

5. Application to an organophosphorus compound (triphenyl phosphate)

Triphenyl phosphate is supplied by NBS as a standard for the determination of phosphorus in petroleum products. The %P determined by the TPA method is in excellent agreement with the certified value (TABLE XXI).

TABLE XXI

Determination of Phosphorus in an Organophosphorus Compound (Triphenyl Phosphate).

| Sample No. | Source | % Phosphorus | |
|------------|--------|--------------|-------------------|
| | | TPA Method | Certified Value** |
| 1071 a | NBS | 9.43 ± 0.02* | 9.5 |

* Average of 4 results. Precision measure is standard deviation

** The certified value for phosphorus was obtained through the gravimetric determination of the element as quinolinium molybdophosphate.

In conclusion, the foregoing results reported for the determination of phosphorus by the TPA method are very gratifying. The method was tested on a wide variety of samples (i.e., natural waters, waste water, standard water references, steels, phosphor bronzes, ores and a mineral, and a standard organophosphorus compound). The good agreement of the results with certified and provisional values and the satisfactory precision lend confidence to the successful wide

applicability of the method.

III. C. AN ANALYSIS OF THE TPA METHOD

As with other analytical methods, the reliability of the TPA method is characterized by its accuracy, precision, sensitivity and specificity. These properties are discussed in turn below.

1. Accuracy

An accurate result is one that agrees closely with the true value of a measured quantity. For an analytical method in which determinate errors have been confidently eliminated, the true value is obtained from the normal error curve,

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

which applies to an infinite population. Here μ is the mean of the infinite population and σ , the standard deviation. For a finite number of measurements, the central tendency of the group is given by \bar{x} , the mean of the finite number, which approaches μ as the number of measurements approaches infinity. The standard deviation is designated S for the finite population and is calculated from the well-known equation. The coefficient of variation is the standard deviation expressed as a percentage of the mean. The Student's t takes into account the fact that \bar{x} and S are not, in general, the same as μ and σ and allows calculation of the limits on either side of \bar{x} to which one must go in order to embrace μ , within an acceptable probability. For this purpose,

$$\mu = \bar{x} \pm \frac{tS}{\sqrt{n}}$$

In TABLE XXII, the 95% and 99% confidence intervals of the mean phosphorus content are calculated for several of the samples analyzed by the TPA method. Both the 95 and 99% intervals are satisfactory, as judged from experience and common sense, for the small number of replicate determinations made. In retrospect, larger numbers of determinations (e.g., 15-20) on 2 or 3 samples should have been made to gauge the confidence intervals at the higher levels of replication.

Another useful experiment would have been the direct comparison of the TPA method with the molybdenum-blue and the molybdovanadophosphate methods for the determination of phosphorus in several samples, followed by statistical testing of the significance between the \bar{x} values (e.g., t-test; null hypothesis) and S values (e.g., F-test).

Often, in the development of an analytical procedure, the accuracy is gauged by comparison of the results to those considered a priori to be highly reliable. For example, the mean result of analyses of an NBS sample compared with the certified value provides a good test. Similarly, the results of analyses of stable standard samples prepared by weighing and dissolution of pure materials is also a good test. In this regard, application of the t-test at the 95 and 99% probability levels showed that the results (i.e., the average values) for NBS samples (organically-bound phosphorus, steels, ores) and for the EPA Concentrate 1 (orthophosphate) were not significantly different.* A significant difference was obtained for the EPA Concentrate 3 (organic P) but this sample may have undergone prior decomposition as previously discussed (An excellent result was obtained on the NBS organically-bound phosphorus sample).

i.e. di from the cert values.

TABLE XXII

Accuracy of the TPA Method

| Sample No. * | n | \bar{x} (ppm or %P) | S (ppm or %P) | Confidence Interval ** | |
|-----------------|---|--------------------------|------------------|------------------------|---------------|
| | | | | 95% | 99% |
| 41 | 3 | 0.009 | 0.001 | 0.009+0.003 | 0.009+0.006 |
| 42 | 3 | 0.008 | 0.001 | 0.008+0.003 | 0.008+0.006 |
| 43 | 3 | 1.61 | 0.03 | 1.61 + 0.075 | 1.61 + 0.172 |
| 44 | 3 | 1.85 | 0.01 | 1.85 + 0.025 | 1.85 + 0.057 |
| 45 | 3 | 0.167 | 0.001 | 0.167+0.003 | 0.167+0.006 |
| 46 | 3 | 0.170 | 0.001 | 0.170+0.003 | 0.170+0.006 |
| EPA(1) | 5 | 0.019 | 0.002 | 0.019+0.003 | 0.019+0.004 |
| 1071a | 4 | 9.43 | 0.02 | 9.43 +0.032 | 9.43 + 0.058 |
| 25c | 3 | 0.204 | 0.003 | 0.204+0.008 | 0.204+0.017 |
| 99a | 3 | 0.019 | 0.001 | 0.019+0.003 | 0.019+0.006 |
| 170A | 3 | 0.0053 | 0.0001 | 0.0053+0.0003 | 0.0053+0.0006 |
| 14e | 3 | 0.008 | 0.001 | 0.008 + 0.003 | 0.008 + 0.006 |

* For further information, see TABLES XIV, XVI, XVIII, XX and XXI.

** The confidence interval is based on the equation,

$$\mu = \bar{x} \pm tS/\sqrt{n}.$$

In conclusion, although the testing of the TPA method has not been exhaustive, it is capable of yielding acceptably accurate results.

2. Precision

The precision obtainable with the TPA method for 0.00620, 0.0620, 0.620 and 6.20 ppm P has already been discussed [see subsection (1) in Section III. A. 2]. Based on the 95% confidence limit, the % coefficient of variation (%cv) for the determination of phosphate by the TPA method was found to be 5.0% for 0.0062 ppm P; 2.0% for 0.062 ppm P; 1.6% for 0.62 ppm P and < 1.0% for 6.2 ppm P. For the molybdenum-blue method (with SnCl_2 as the reductant) the %cv reported in one study was 8.5% at 3.2 ppm P and 19.0% at 0.16 ppm P levels.⁽⁶⁶⁾ With ascorbic acid as the reductant, the %cv was 100% at 0.81 ppb P, 11% at 0.027 ppm P and 4% at 0.050-0.10 ppm P.⁽⁶⁶⁾ According to Kolthoff et al.⁽²⁴¹⁾ the permissible precision error is $\pm 10\%$ when the percentage of the constituent determined is in the range 0.01-0.001. Thus, the precision of the TPA method, compared with that of the molybdenum-blue method, is good.

The large precision errors in the more dilute samples is largely due to the relative spectrophotometric error.⁽²⁶⁰⁾ To minimize this error to $\pm 1-2\%$, absorbance values should be kept in the range $\sim 0.2-0.7$ units.⁽²⁶⁰⁾ Although this adjustment can be accomplished normally by use of larger cells or a smaller volume of n-amyl alcohol for extraction, it was not always made in the present work and some improvement in the precision error in the measurement of low concentrations of phosphorus should be possible. In this connection, the technique of differential measurement is relevant.⁽²⁶⁰⁾

The main reason for the improved precision of the TPA method compared to that of the molybdenum-blue procedure is that the latter requires much stricter control of solution conditions to obtain adequate reproducibility. This procedure relies firstly on the quantitative formation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (MPA) and secondly on its reduction to the blue. The optimum conditions for quantitative formation of MPA do not appear to have been elaborated to the degree described in this thesis for TPA. To what extent the conditions required for the reduction of MPA affect the formation of MPA itself, are not known. The conditions for the reduction of MPA to the blue with either stannous chloride or ascorbic acid (the two most commonly used reductants) vary somewhat depending on the laboratory. With both reductants, the optimum concentration of molybdate (i.e., $\text{C}_{\text{MoO}_4}^{-2}$) appears to be $(4.0-8.0) \times 10^{-3}$ M. The optimum acidity range seems to be governed by two factors: reduction of the molybdate itself occurs at acidities $\sim 0.4 \text{ N H}_2\text{SO}_4$;⁽⁶⁶⁾ and the acidity range over which the colour development is essentially independent of acidity depends on the phosphate concentration (the range decreases with increasing phosphate concentration). For example, the range is $0.4 \text{ N}-0.8 \text{ N H}_2\text{SO}_4$ for 0.87 ppm P and $0.5 \text{ N}-0.7 \text{ N}$ for 2.18 ppm P.⁽⁴⁶⁾ Furthermore, with ascorbic acid as the reductant, to obtain a low reagent blank and relative freedom from As(V) and Si(IV) interference, the acidity and molybdate concentration are restricted to $0.4 \text{ N H}_2\text{SO}_4$ and $\text{C}_{\text{MoO}_4}^{-2} = 4.01 \times 10^{-3}$ M.⁽⁴⁶⁾ The concentrations of the reductants employed are very critical for colour stability. For example, $0.10 \text{ mg Sn}^{+2}/100 \text{ ml}$ of aqueous solution results in rapid fading of the colour.⁽⁴⁶⁾ The colour development itself is time-dependent.

Maximum colour development with ascorbic acid takes at least 24 hours. (12) In no case is the colour stable for more than two hours. (12) Also the rate of reduction is very sensitive to changes in temperature. (66)

In contrast, the range of tungstate and acid concentrations allowed in the TPA method are much wider. The main requirement is that the tungstate to phosphate molar ratio be ≥ 24 for quantitative formation of TPA, with the provision that the minimum tungstate concentration be 1.2×10^{-3} M (to cover most P ranges encountered). The pH range allowed is 1.2-1.9 in the absence of As(V) and 1.5-1.9 in the presence of As(V). The concentration of phosphate does not appear to have any effect on the pH range for quantitative formation of TPA. The method is reproducible. Once extracted, TPA is stable in n-amyl alcohol and as a consequence, the absorbance is independent of time.

One note of caution in the TPA method is the requirement that the blank alcohol reference solution be equilibrated with an aqueous test solution in which phosphate is absent. Figure 45 shows the effect on the TPA-spectrum (especially at λ_{267} nm) of the use of an unequilibrated and equilibrated n-amyl alcohol as the reference. The spectrum obtained using unequilibrated alcohol (i.e., distilled n-amyl alcohol) as the reference exhibits lower absorbance, since the reference (i.e., the alcohol) contains no water. When the reference solution is saturated with water by equilibration, the absorbance of the test solution is increased due to cancellation of the alcohol absorbance.*

* Distilled n-amyl alcohol absorbs strongly below 250 nm but has an absorbance tail beyond 250 nm (see Figure 14, Section II.I).

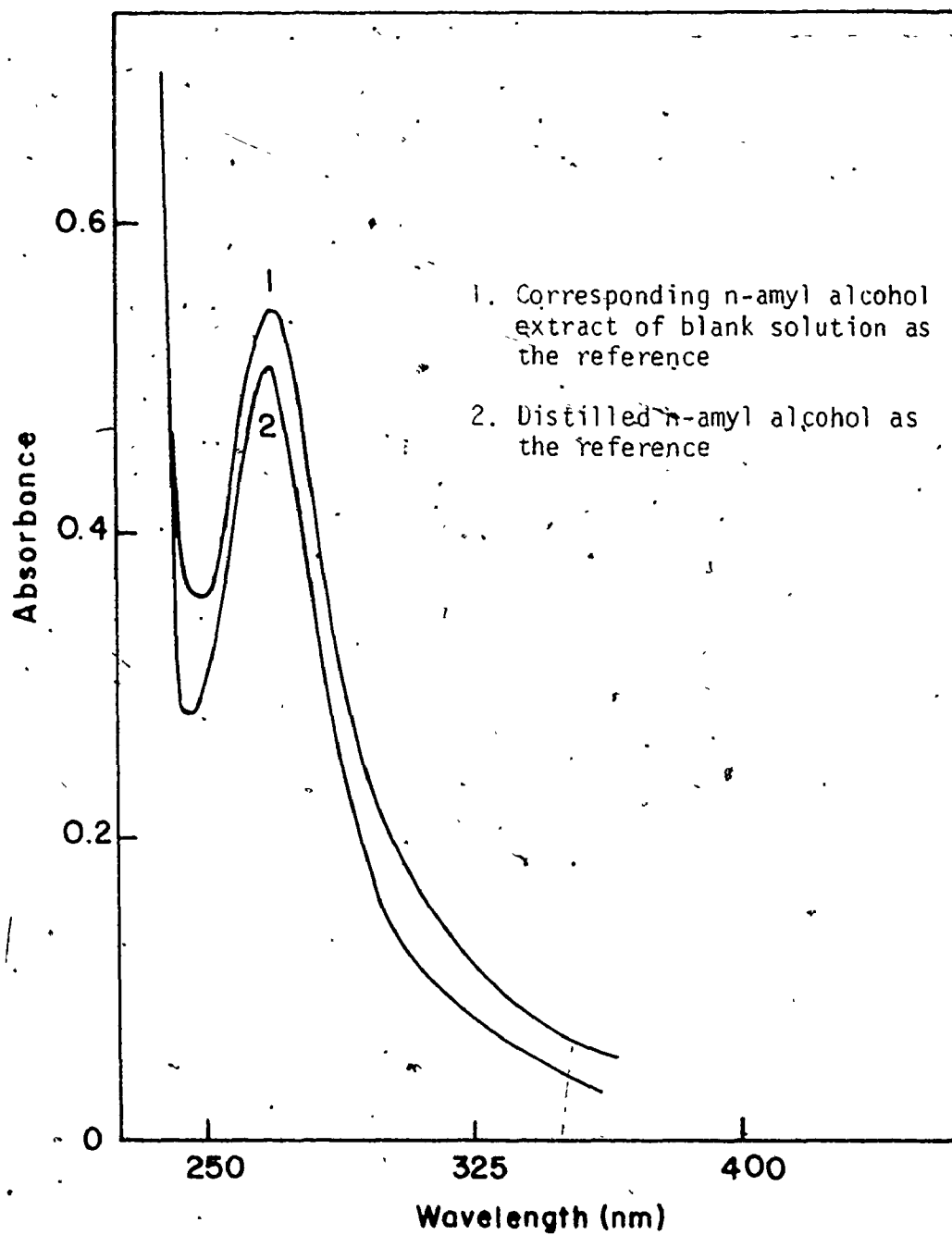


Figure 45. Absorption of TPA at 267 nm when equilibrated and non-equilibrated n-amy1 alcohol are used as references. ($C_{\text{WO}_4^{-2}} = 4.8 \times 10^{-3}$ M, $C_{\text{H}_2\text{PO}_4^-} = 5.0 \times 10^{-5}$ M, W/P = 96, 100°C, 5-mm cells)

the differential absorbance was found to be essentially constant over the pH range 1.2-1.9, so that some liberty in pH adjustment is allowable in the equilibration of the reference.

Finally, in the trace determination of phosphate, it is absolutely essential to maintain special standards of cleanliness. For example, the use of detergents and other similar materials should be avoided since they introduce phosphorus. Phosphate is more strongly adsorbed by polyethylene vessels than glass from aqueous solution. (261)

3. Sensitivity of the TPA method

The sensitivity (S) of a spectrophotometric method may be defined as the increase in the absorbance (ΔA) with respect to an increase in concentration (ΔC), i.e.,

$$S = \Delta A / \Delta C = \epsilon b$$

Thus, the minimum detectable concentration for any substance depends only on the values of ϵ (molar absorptivity) and b (cell path-length). Since the values of ϵ for MPA ($H_3PMo_{12}O_{40}$), the molybdenum-blue, and molybdovanadophosphoric acid (MPV, $H_4PVMo_{11}O_{40}$) in organic solvents* are in the range $(2.3-2.5) \times 10^4$ litre mole⁻¹ cm⁻¹ and that of TPA is

* The values of ϵ for TPA and MPV are for n-amyl alcohol; the value for MPA is for isobutanol/ $CHCl_3$ (3:1 V/V); and the value for molybdenum blue is for isobutanol. A strict comparison would have required the use of the same solvent in each case. However, the solvents selected in each case give the maximum value of ϵ for the particular compound and on this basis, the point made is deemed to be valid.

5.1×10^4 litre mole⁻¹ cm⁻¹, it is clear that the TPA method should be about twice as sensitive as the others.

The limit of sensitivity (S_{limit}) may be defined as the smallest detectable value of the quantity to be measured, i.e., absorbance (A) or concentration (C).⁽²⁶²⁾ Thus, {

$$\Delta C_{\text{limit}} = \Delta A_{\text{limit}} / \epsilon b$$

If, following Sandell,⁽²⁶³⁾ ΔA_{limit} is taken as 0.001 absorbance units,* the use of a 1-cm cell gives for TPA

$$\Delta C_{\text{limit}} = \frac{0.001}{5.1 \times 10^4 \times 1.0} \approx 2 \times 10^{-8} \text{ M}$$

i.e., a limit of detection corresponding to 0.62 ppb P. In practice, however, this sensitivity is not attainable since it is limited by the accuracy of the apparatus and the magnitude of the blank value. In the present investigation, the smallest division of the chart paper corresponded to 0.01 absorbance unit and estimates of 0.005 absorbance units could be made. The blank value in the present work corresponded to 0.005 ± 0.002 absorbance units for a total of 20 measurements. According to Kaiser,⁽²⁶⁴⁾ a signal could be considered with reasonable confidence to be different from the blank value when it is at least as great as the mean blank value plus three standard deviations of the blank value. On this basis, the practical limit of the absorbance value can be given as ~ 0.011 . Therefore, the practical limit of sensitivity of the

* With several instruments, it is possible to detect an absorbance as small as 0.001 (e.g., with the Varian Cary 118 and 118CX instruments).

TPA method is $\sim 2 \times 10^{-7}$ M in TPA, corresponding to ~ 6 to 7 ppb P for a 1-cm cell. No comparisons are possible with the molybdenum blue methods since standard deviations of the blank values have not been reported. (66)

Maximum precision is attained at an absorbance value of about 0.5 A unit. If the absorbance of the test solutions were to be maintained at this value, the practical limit of sensitivity of the TPA method for a 1-cm cell would be 0.34 ppm P. In such cases, however, the practical limit of sensitivity can be increased by the use of larger cells, a smaller organic phase or by a differential spectrophotometric technique.

4. Specificity of the TPA method

The specificity of a chemical analytical method may be defined as the degree to which the mean value of the measurements (obtained by the method) is due to the substance to be determined and not to other substances that may be present in the sample being analysed. (265) In this sense, the TPA method is more specific than the molybdenum-blue method since it has a greater degree of freedom from interferences (see section on effect of foreign ions).

III. D. SUMMARY

1. A new spectrophotometric method has been developed for the quantitative determination of phosphorus as orthophosphate. The method is based on the reaction between orthophosphate and an unspecified tungstate species in aqueous acid solution at 60-100°C to form 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$. The TPA is subsequently extracted

into n-amyl alcohol and its absorbance measured at 267 nm.

2. The method has been applied successfully to the determination of phosphorus in natural, waste and standard water samples, standard steels and phosphor bronzes, standard ores, a standard mineral and a standard organophosphorus compound. The TPA method has several advantages over the frequently used molybdenum blue and molybdovanadophosphate methods. It is not as sensitive to solution variables (e.g., pH and reagent concentrations) and the absorbance of the measured species is stable. The TPA method is freer of interferences, particularly As(V) and Si(IV), and is free of the 'salt error'. The method is competitive, and perhaps superior, with regard to accuracy, precision and sensitivity. The main disadvantages are the requirements of heating the aqueous solution to 60-100°C and of an extraction. These procedures may make automation in laboratories where this is desirable more cumbersome.

3. TPA has been shown to be intrinsically triprotic by a non-aqueous potentiometric titration.

4. The hydrolytic instability of TPA in aqueous solution above about pH 2 has been demonstrated.

5. TPA has been shown to form in aqueous acid solutions (below pH 2) of tungstate, paratungstate Z or white tungstic oxide (freshly prepared). It is not formed from the stable metatungstate species unless the solution is very acidic (e.g., 7 M HClO₄). At this acid concentration decomposition of the meta species to white tungstic oxide occurs. TPA could not be formed from yellow tungstic oxide.

6. An extension of the work described in the literature has led to contributions to knowledge regarding the chemistry of the isopolytungstates. In the point-titration of tungstate solutions, the behaviour of the titration curve between $P = 1.17-1.50$ has been re-interpreted in terms of a slow structural rearrangement of the paratungstate A species. In the presence of NaClO_4 , this rearrangement is not complete, even after 15 days. The metatungstate, paratungstate Z and polytungstate Y species are not extracted into n-amyl alcohol above pH 1. These observations are of particular importance in the application of TPA to the determination of phosphate. The enhanced stability of poly Y species in n-amyl alcohol should facilitate its characterization.

III. E. SUGGESTIONS FOR FURTHER WORK

1. In the application of the TPA method to water samples, only the determination of total soluble phosphorus was attempted. No attempt to determine separately orthophosphate, condensed inorganic phosphates and organically-bound phosphorus in the same sample was made. In the TPA method, the acidity of the aqueous solution is lower than that required for the molybdenum-blue and molybdovanadophosphate methods and a lesser degree of hydrolysis of condensed phosphates is expected. (The higher temperature required, 60-100°C, might more than offset this potential advantage.) In any event, the use of the TPA method for the separate determinations should be examined.

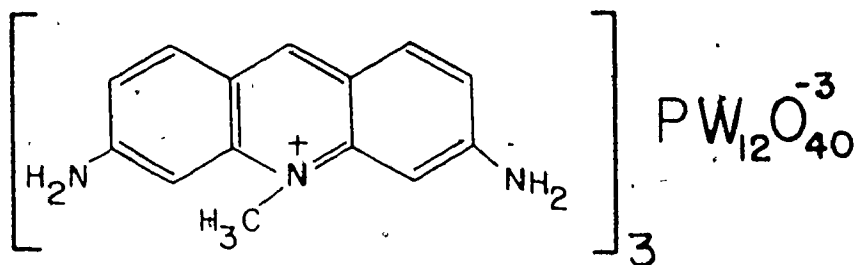
2. Automation of the TPA method should be explored, particularly, since several laboratories are faced with the task of processing large

numbers of samples (e.g., water and clinical samples) daily. The fact that the TPA method requires heating the aqueous solution to 60-100°C and an extraction step encumbers its automation; however, there are already examples of automated analytical procedures that involve heating of a solution [e.g., blood-glucose⁽²⁶⁶⁾] and extraction.⁽²⁶⁷⁾

3. The elucidation of the mechanism of formation of TPA would be interesting, although difficult. Some qualitative work has already been described in the present study but more definitive work is required. A kinetic study of the initial reaction rate along the lines reported by Malmstadt et al.⁽²⁵⁵⁾ in their work with the 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) system should be attempted. A successful study of this kind could lead to a reaction-rate method for the determination of phosphate.

4. In the course of the present study, it was found that TPA can be formed by reaction of phosphate in acid solution with freshly-precipitated white tungstic oxide. This reaction could be the basis of an even simpler (and faster) method for the determination of phosphate, and should be investigated for this purpose.

5. The 12-heteropoly anions are known to form complexes with nitrogen- or oxygen- containing organic cations (e.g., alkaloids, dyes such as brilliant green, malachite green, etc.). It would be of interest to study some of these complexes of TPA, with possible application to the determination of phosphate. Particular mention should be made of the fluorescent acriflavonium-TPA complex⁽²⁶⁸⁾ below.



Preliminary studies have shown that it is a 3:1 complex in solution. Additional studies are needed to determine whether the complex can serve as the basis of a very sensitive fluorimetric method for phosphate.

6. The formation of 'tungsten blues' in solution upon reduction of TPA has already been reported. (269) Hitherto, few attempts have been made to elucidate the formation, properties and structural features of the tungsten blues, let alone their potential application to the determination of phosphate. In view of the instability of the 'molybdenum blues', it would be particularly interesting to study the stability of the corresponding 'tungsten blues'.

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