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"THE ANALYTICAL CHEMISTRY OF PHOSPHORUS AND SILICON WITH PARTICULAR REFERENCE TO ATOMIC ABSORPTION SPECTROSCOPY"

-by-

A. M. Smith, B.Sc., A.R.C.S.

Department of Chemistry
Imperial College
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ABSTRACT

The hot, reducing nitrous oxide-acetylene flame has been applied to atomic absorption spectroscopy. Molybdenum in aqueous solution and steel sample solutions has been determined in such a flame.

This has led to the indirect, sequential analyses of microgram amounts of both phosphorus and silicon by formation and extraction of their heteropolymolybdates into organic solvents followed by analysis of the molybdenum content by atomic absorption spectroscopy.

Niobium and titanium have also been determined in a similar manner and the stoichiometry of their ternary heteropoly acids has been investigated.

The selectivity of certain organic solvents in extracting phosphomolybdic acid has led to the titrimetric determination of microgram amounts of phosphate being re-examined.

Microgram amounts of orthophosphate have also been determined by an indirect complexometric procedure.

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The work described in this thesis is entirely original except where due reference is made. No part of this work has been submitted previously for any other degree. The work was performed in the Analytical Chemistry Department of Imperial College between October 1965 and August 1968.

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DEDICATION

As a small compensation for the many sacrifices which they have made throughout my college days and for their unfailing encouragement and enthusiasm, I would like to dedicate this thesis to my parents.

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CHAPTER 1

INTRODUCTION

The determination of phosphorus and silicon is extremely important in industry, agriculture and medicine, and consequently a voluminous literature has accumulated in the analytical chemistry of these elements. In this introduction no attempt has been made to review every available method for the determination of phosphorus and silicon. The more popular modern methods have so many minor variations that it would be difficult to review and corrolate all the different conditions which have been employed by various authors within these procedures. There are, however, several main categories under which the methods of analyses may be divided, and a brief outline and discussion of these will be given.

1.1 Gravimetric Methods for the Determination of Phosphorus and Silicon

1.1a Phosphorus

Naturally, the matrix in which the phosphorus is situated will control the method which is to be used for its dissolution and estimation. Throughout these studies it is assumed that phosphorus can be obtained in the orthophosphate state.

There are several procedures for the gravimetric determination of phosphorus as orthophosphate. The most extensively used procedures are those in which the orthophosphate is precipitated as ammonium phosphomolybdate (1,2), magnesium ammonium phosphate or magnesium pyrophosphate (3,4). The first weighing form is often preferred, and even when the phosphorus is finally weighed as magnesium pyrophosphate, the ammonium phosphomolybdate is often precipitated first in order to effect a preliminary separation. The preference for this method lies in the large number of ions which interfere in the direct quantitative estimation of phosphate as magnesium ammonium phosphate as the precipitation is conducted in an alkaline medium.

The ammonium phosphomolybdate method was first suggested by Sonnenschein (5). He realized that his method had many potential sources of error, and this has been amply confirmed by the vast literature which has accumulated for this one procedure alone. The difficulties which arise are largely due to uncertainties in the composition of the precipitate. Stockdale (6) has made a study of this feature. The use of the dried (7, 8, 9) or ignited precipitates (10) has however been recommended. The method is not recommended when very accurate results or rapidity are required.

The use of the cations of organic bases, rather than the ammonium ion, to yield insoluble salts of phosphomolybdic

acid appears to have been first applied to the determination of phosphorus by Pouget and Chouchak (11). These workers considered strychnine the most suitable base. Embden (12) utilized the reaction for a gravimetric procedure which was later modified by Antoniani and Jona (13). Duval (14) made a thermogravimetric study of strychnine phosphomolybdate, and found the composition different from that given by other workers. Thus owing to uncertainty concerning its composition, and the poisonous nature of strychnine, this weighing form has now lost popularity.

Quinine has been used by Street (15). In this method the phosphorus content was determined by centrifuging the precipitate in a thin graduated tube and measuring its volume compared to those of standards. A similar method has been used with the ammonium salt (16, 17, 18).

Pyridine was the first of the simpler bases to be employed as a precipitant for phosphomolybdic acid (19) but later work by Wilson (20) showed that pyridine phosphomolybdate was not sufficiently insoluble for use even in macro work.

The use of oxine as a precipitate has been studied by many workers but the degree of hydration of the precipitate has been the subject of much controversy (14, 21, 22, 23, 24, 25). In a later study Gottschalk (26) reported that the anhydrous compound is found only after drying at 160°C for two hours. The precipitation with oxine has however been utilized

when a titrimetric finish is required.

In 1951 Wilson (20) recommended quinoline as a precipitant for phosphomolybdic acid. This method, however, has a limited range as a gravimetric procedure, as although the reaction is stoichiometric the precipitate cannot be obtained in a completely pure state if large amounts of phosphorus are present. However, further work by Perrin (27) and Lench (28) enabled a reliable gravimetric procedure to be utilized. Microgram amounts of phosphorus in organic compounds have been determined by Belcher et al. (29) using quinoline.

MacDonald and Rivero (30) studied organic bases as precipitants for phosphomolybdate and found α - picoline (2 - methyl pyridine) superior to quinoline. It is somewhat more sensitive to phosphate and is much less sensitive to silicate and arsenate. Radio-isotope tracer techniques were used by Heslop and Pearson (31), and they found that under the conditions for precipitation of phosphate as its heteropoly quinolium salt, arsenic was quantitatively precipitated as quinoline arsenomolybdate. This confirmed the findings of Meyer and Koch (32) and Lench (28). However phosphate can be precipitated as lutidinium phosphomolybdate using 2-4, 2-5, or 2-6, lutidine molybdate. Although these reagents are less efficient than quinoline they can be used under conditions which leave arsenate in solution.

1.1b Silicon

Again the primary concern is the dissolution of the silica sample, and the method employed for the determination of the silicon will depend to a large extent on the other elements present. In general, silica samples must be fused with a suitable flux before being brought into solution. Hildebrand et al. (33) give an excellent discussion of the individual requirements for sample dissolution. It is worth noting, however, that sodium carbonate or a mixture of equal parts of sodium carbonate and sodium borate are almost universal fluxes for silicate minerals.

The gravimetric procedure is the most satisfactory general method for the estimation of silica except when it is present only in very small quantities. This method entails dissolution of the fused melt in acid and evaporation to dryness, usually on a steam bath. The residue is then treated with concentrated acid, and after dilution with water the polymerized silicic acid is filtered off. The filtrate is then evaporated to dryness again and further dehydrated in an oven at 105 - 110°C. This residue is then treated as before. Silicic acid cannot be completely dehydrated by a single evaporation and heating, nor by several such treatments unless an intermediate filtration of silica is made (34). The residue is then gently heated in a platinum crucible until the filters are thoroughly charred and then at the full heat of a Meker burner for at least thirty minutes.

The silica is weighed. For most practical purposes this residue is accepted as silica, but for more accurate work it is subjected to the usual hydrofluoric acid evaporation, the loss in weight representing silica, SiO_2.

Various acids have been used to effect the initial dehydration, and a discussion of the factors involved is given by Lundell and Hoffman (35) and Lenher and Truog (36).

Organic bases have been used to precipitate silicomolybdate but have not achieved the widespread utility of the analog us methods for the determination of phosphate. Belcher and Goulden (37) have reviewed the methods available, but the majority employ a titrimetric or photometric finish. Gravimetric procedures have been proposed which employ oxine (38), pyridine and pyramidone (39) as precipitants for silicomolybdic acid. Cavallaro and Tanl. (40) recommend trimethylamine and triethylamine, and claim that the precipitates obtained were more easily filtered and washed than when pyridine was used. Duval (41, 42) made a comprehensive study of organic bases for this precipitation and chose hexamethylene tetramine as suitable for both the gravimetric and titrimetric determination of silicon. Wilson (43) recommended the use of quinoline, while Miller and Chalmers (44) examined a gravimetric finish. Armand and Berthoux (45) have made a further extensive examination of the quinoline silicomolybdate precipitation. Quinoline and pyridine derivatives have also been studied (44),

and 2,4-dimethyl quinoline was found the most suitable even though the resulting precipitate was hygroscopic. Majumdar and Banerjee (46) obtained stable, non-hygroscopic precipitates when 5,6 benzoquinaldine and 8-hydroxyquinaldine were employed.

MacDonald has reviewed the uses of organic bases as precipitants for the heteropolymolybdates of both phosphorus (47) and silicon (48), and more recently with Van der Voort attempted to find a selective organic base for silicate precipitation (49). Although this aim was not accomplished, a satisfactory method was developed for the separation and successive determination of phosphate and silicate. They also state that for the precipitation of silicomolybdate no organic base is preferable to quinoline.

1.2 Titrimetric Methods for the Determination of Phosphorus and Silicon

The determination of phosphate and silicate by titrimetric procedures show a remarkable similarity and as such will be discussed together. The majority of methods rely on the formation of a precipitate of a salt of the phosphate or silicate heteropolymolybdate anion, with subsequent dissolution and estimation or direct estimation of excess reactants.

The ammonium salt lends itself quite readily to a titrimetric finish. The salt is dissolved in an excess of

standard alkali and the excess is then back titrated with standard acid

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH \longrightarrow$$

$$NaNH_4HPO_4 + (NH_4)_2MoO_4 + 11Na_2MoO_4 + 11H_2O$$

For routine analysis the acid and alkali strengths are 0.324N to facilitate determination of phosphate content. 1 ml of sodium hydroxide solution of this strength is equivalent to 0.001g P_2O_5 (or 0.4365 mg P). The procedure has become a standard method for phosphate determination (1, 4, 50), although some authors state that experience is necessary for end point detection (51). The analogous silicon procedure suffers from the fact that the precipitate is not very insoluble.. This disadvantage was overcome in the original method to some extent by using an ammonium nitrate protective medium both during precipitation and to wash the precipitate (52).

Berg and Teitelbaum (53) introduced the use of 8-hydroxyquinoline as a precipitant. The 8-hydroxyquinoline (oxine) content of the insoluble salt was then determined by dissolving the precipitate in hydrochloric acid followed by bromination with a bromate-bromide solution. Various titrimetric finishes have been employed (53, 54, 55, 56), but generally an iodometric determination of excess bromate has been preferred (57).

Merz (58) used a similar method to precipitate oxine silicomolybdate by the addition of excess oxine and titration of this excess bromometrically. This method was later applied to the determination of the silicon content of organic compounds (59).

Wilson (20) in 1951 utilized quinoline to form the precipitate which was then treated in an analogous manner to the ammonium salt. This method has become widely used and may succeed the ammonium phosphomolybdate procedure as a standard method of analysis for phosphate. Fennellet al. (60) and Fernlund et al. (61) have successfully used the method, although the latter modified the system somewhat by incorporation of the molybdate and quinoline in a single reagent solution (62). Wilson (63) does not advocate this refinement because the mixed solution precipitates molybdic acid. Belcher and McDonald (64), however, found the use of a single reagent solution advantageous.

Mika (65) applied to use of pyridine (39, 66) to form the insoluble pyridinium silicomolybdate salt which was then dissolved in excess standard alkali and back titrated with standard acid to a phenol red end point.

Duval (42) chose hexamethylene tetramine as the base to precipitate silicomolybdic acid and developed a titrimetric finish. This involved hydrolysis of the hexamine to the aldehyde which was then treated with sodium bisulphite to

form the formaldehyde - bisulphite addition compound. This compound was then decomposed by alkali and titrated with iodine.

$$C_6H_{12}N_4 + 6H_2O \longrightarrow 6HCHO + 4NH_3$$

$$HCHO + NaHSO_3 \longrightarrow CH_2OH - SO_3Na$$

$$NaHSO_3 + I_2 + H_2O \longrightarrow NaHSO_4 + 2HI$$

Other methods of analysis which involve the estimation of the molybdenum content of the heteropoly precipitates will be discussed under Amplification Procedures (See Chapter 1.4)

1.3 Spectrophotometric Methods for the Determination of Phosphorus and Silicon

The spectrophotometric determination of both phosphate and silicate depends upon the formation of their respective heteropolymolybdates and measurement of either the yellow colour of the unreduced acid or of the reduced "heteropoly blue" form. Extensive use has been made of the reduction of the heteropoly species, while comparatively little attention has been paid to the measurement of the unreduced varieties. This is particularly true of methods involving measurement of the aqueous phase, probably due to the lack of selectivity and sensitivity - in terms of both molar absorptivity and instrument

response since measurement was made in regions of the visible spectrum near the ultra violet (ca. 250 - 350 m). Also it was not appreciated at first that two forms (α and β) of the heteropoly molybdates can exist in aqueous solution, and for a spectrophotometric method one form must be formed exclusively. Strickland (67) first postulated the existence of these two isomers - a stable α-form or an unstable β-form which reverts spontaneously to the α-form. Later, however, care was taken to ensure that only the more stable α-form was obtained (68, 69). The work of Chalmers (70) and Chalmers and Sinclair (71) on the stabilization of the various forms has now clarified the position and it appears that measurement of the stabilized β-form is advantageous because of its higher extinction coefficient.

Arsenic (72) and germanium (73) are known to form similar heteropoly molybdates to phosphorus and silicon and must be eliminated or accounted for if a spectrophotometric method for the determination of phosphate or silicate is to be employed. For the individual determination of either phosphate or silicate in an aqueous medium then each will interfere on the other. Various methods have been proposed for the elimination of silicate when spectrophotometrically determining phosphate (74 - 78), but the elimination of phosphate in the determination of silicate presents more serious problems. Silicate is frequently estimated by difference. As stated earlier, the sensitivities are very low and Bolz and Mellon (80) and

Brabson et al. (81) report that in aqueous solution the molar absorptivities are of the order of 1,000. Extraction methods have therefore been used as a means of concentration, and thus improve the available sensitivities and frequently result in greater selectivity. Wu (82) in 1920 first utilized an extraction technique for the determination of phosphate and since then numerous extractants have been employed (83-88). Keggin (89) and Leuck and Bolz (90) have reported that oxygen containing solvents are generally suitable for the extraction of heteropoly acids. Wadelin and Mellon (91) studied the solvent extraction of the various heteropoly acids and found 1-butyl acetate to be a selective solvent for the extraction of phosphomolybdic acid. They also studied n-butanol/ chloroform mixtures, and recommend a 20 per cent solution of n-butanol in chloroform as a more convenient extractant than 1-butyl acetate, as the phases separate more easily after the extraction. Also the chloroform medium would be less likely to extract coloured inorganic chloro complexes. Extraction with these solvents is selective, and owing to the intensification of colour which occurs (71) the molar absorptivity is raised to 24,400 1/mole cm (91). Other selective extractants for the heteropoly phosphate have been proposed (92-95), but in the author's experience only iso-butyl acetate (95) is entirely satisfactory. Selective extraction solvents for silicomolybdic acid only appear to be

used after the elimination of phosphate and as such are not included. It may be stated as a general rule that if an organic solvent extracts any of the heteropoly species, then phosphomolybdic acid will be among those extracted.

By far the most popular type of spectrophotometric method for determination of phosphate or silicate utilizes the measurement of the intensity of the heteropoly blue obtained when phosphomolybdic or silicomolybdic acid is reduced. This colour may be measured either directly in the aqueous phase or after extraction into oxygen-donor solvents. The literature abounds with various recommended reducing agents and conditions required for the reduction. Ascorbic acid, stannous chloride and 1-amino-2-naphthol-4-sulphonic acid are the more popular reductants. However, the individual methods require stringent adherence to the optimal experimental conditions. Careful time control is often required.

The reaction mechanism for the reduction and the composition of the reduced species is still the subject of controversy even though the work of Namiki (96) and later of Crouch and Malmstadt (97) goes some way to explain the nature of the processes involved.

When phosphate or silicate is to be determined by spectrophotometric measurement of the absorbance of "molybdenum blue", three choices are presented. Firstly

the heteropoly species may be formed and reduced in aqueous solution. Secondly the unreduced species may be extracted and reduced in the organic phase, or alternatively, the reduced forms may be extracted from aqueous solution into an organic solvent. (It is little wonder that the literature concerning the determination of phosphate and silicate via their heteropoly acids is so voluminous when one permutes the above three variations with the large number of reducing agents available). Again selectivity for the determination of the individual heteropoly acids will depend upon selective formation, reduction or extraction.

A well known observation concerning the effect of tartrate on the formation and reduction of phosphomolybdic and silicomolybdic acids has been explained by Chalmers and Sinclair (98). If tartrate is added to a molybdate solution before the addition of phosphate and silicate, then only the "phosphomolybdate blue" will be formed on reduction. When the tartrate is added after formation of phosphomolybdic and silicomolybdic acids, however, on reduction the silicomolybdate is the only heteropoly species reduced. They utilized this difference in the determination of phosphate and silicate in the presence of one another. Other molybdenum blue procedures have been published which could be used to determine mixtures of silicon and phosphorus (99-102). These rely on a

combination of acidity control and choice of reductant to effect selective reduction. The published conditions must be adhered to rigidly if reproducible results are to be obtained.

Extraction of the unreduced heteropoly acids into organic media has been summarized earlier, and authors have utilized the selectivity of butanol/chloroform and iso butyl acetate for extraction of phosphomolybdic acid prior to its reduction in the organic phase (103)(104). Naturally, other oxygen-donor solvents could be used to accomplish the extraction, but one must again look for selectivity. The reducing agents employed are similar to those used for aqueous phase reductions. The intensity of the blue colour is generally measured in the organic phase, but back extraction into an aqueous solution of the reductant has also been employed (105, 106).

The ability of different solvents to extract the reduced heteropoly acids has been studied by Paul (107), and he developed a method for the determination of phosphate and silicate in one aliquot of solution. Although the extraction of the reduced duodecamolybdates enhances the sensitivities somewhat, it is the author's opinion that the use of a reduction procedure yields increased sensitivity only at the expense of loss of reliability and precision. Increased sensitivity is available for the unreduced acids when spectrophotometers are

used which are capable of measurement in the U.V. where the heteropoly species exhibit their maximum absorbance.

Phosphorus, as orthophosphate, may also be determined colorimetrically by measurement of the absorbance of the yellow-orange ternary complex produced when solutions containing vanadate and molybdate are added to an acidic solution of orthophosphate. Here again the absorbance of the molybdo-vanadophosphoric acid may be measured in aqueous solution or after extraction into an organic solvent. This system has an advantage over the previous heteropolymolybdate methods in that the presence of nitric acid can be tolerated. This is beneficial in the determination of phosphorus in steels. Since Mission (108) first reported the method in 1908 its use has been widely reported even though there is considerable disagreement as to the optimum conditions and the order of addition of reagents (109-115). Several authors have carried out extensive studies of the heteropolyvanadate method, and Kitson and Mellon (110) recommended measurement of the yellow complex at 460 mμ to minimize the effect of certain interfering ions. Greater sensitivity, however, is obtained by measurement at 315 mμ where the absorption spectrum of the complex in aqueous solution shows its maximum (112). Gee and Dietz (116) developed a differential spectrophotometric method with absorbance measurement at 390 mμ to increase the sensitivity.

There is general agreement in the literature that the method is selective for phosphate in the presence of silicate (109, 110, 117, 118, 119) although large amounts of arsenate give low results. Arsenite, however, does not interfere (110). Comparative studies (120) have shown the method to be of equal accuracy to the gravimetric molybdophosphate method, while it has the advantage over some molybdenum blue procedures in that the colour is stable and the times between addition of reagents are not critical. The sensitivity of the colormetric determination of phosphate by this ternary system may be further increased by extraction of the complex acid and various organic solvents have been reported (121, 122). The reduced ternary heteropoly species has also been utilized but the system needs further development (123).

1.4 Amplification Procedures for the Determination of Phosphorus and Silicon

These procedures are based on the precipitation or extraction of duodecamolybdate species with their subsequent breakdown to release twelve molybdate ions for each ion of the central atom (P or Si) in the heteropoly complex.

A gravimetric method of this type involves the initial

precipitation of ammonium phosphomolybdate, its dissolution in ammonia and final precipitation of lead molybdate (124). It can be calculated that the final precipitate is nearly 150 times the weight of the original amount of phosphorus.

Titrimetric methods involve the reduction of the released molybdate ions to a lower valency state by means of a zinc, cadmium or silver reductor followed by titration with a suitable oxidant. Zinc and cadmium both reduced MoVI to MoIII, and although in this valency state molybdenum readily undergoes atmospheric oxidation, procedures have been proposed whereby the molybdenum is titrated back to the hexavalent state using standard permanganate solution (125, 126). The MoIII may also be collected in standard iron (III) solution and the iron (II) produced determined by titration with a standard oxidant solution(127). More recently reduction to molybdenum V has been preferred as in this valency the molybdenum is more stable to the atmosphere. Birnbaum and Walden (128) utilized this reduction followed by titration with standard ceric sulphate solution for the determination of phosphate. All these procedures involved the initial precipitation of the ammonium heteropoly molybdate but there is no reason why organic bases should not be used as precipitating agents. Indeed Babko used pyridine to precipitate pyridinium silicomolybdate and after dissolution and reduction on a cadmium column, titrated the molybdenum with standard permanganate.

He utilized this procedure for the analysis of silicates (129). However, unless precautions are taken for selective precipitation the other ions capable of forming heteropoly species will give positive interferences in all the above methods. Thus more recently selective extraction, especially of phosphomolybdic acid, has been employed (130, 131, 132, 133, 134). After extraction the twelve molybdate ions are easily released by retrograde extraction into alkali. The molybdate can be precipitated as 8-hydroxyquinoline molybdate, and after filtration the precipitate may be dissolved and titrated with standard potassium bromate solution (134). Alternatively the molybdenum content of the solution may be determined spectrophotometrically using thiocyanate (131, 132, 133) or by using the more sensitive 2-amino-4-chlorobenzenethiol (130, 135). Effective molar absorptivities of up to 359,000 can be obtained by these procedures.

1.5 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (A.A.S.) may simply be defined as the absorption of radiation by discrete atoms. The basic principles underlying A.A.S. were established by Kirchhoff (136) as long ago as 1860 using the atomic absorption lines in the Fraunhofer spectrum to deduce the presence of certain elements

in the solar atmosphere. The theory of A.A.S. was evolved in the early 1900's by physicists and astrophysicists. The work of these early researchers summarized in a treatise by Mitchell and Zemansky (137) was mainly performed at low pressures in enclosed vessels and was not directed towards analytical purposes, except for some astrophysical studies on the determination of the composition of the solar and stellar atmospheres.

Whereas emission methods of spectral analyses (using arc, spark and flame sources) soon became firmly established, atomic absorption methods were not developed until suitable sources became available. In 1953 Walsh (138), and later in 1955 (139) together with Alkemade and Milatz (140), demonstrated the use of A.A.S. as an analytical technique. Since then A.A.S. has become an effective method for chemical analyses and has been reviewed by Elwell and Gidley (141), Robinson (142) and several other authors (143, 144, 145).

In A.A.S. the concentration of an element in a sample is determined by measurement of the absorption of radiation in the atomic vapour produced from the sample after its introduction as a solution into a suitable flame. A hollow cathode lamp, whose cathode emits the line spectrum of the atoms of the element being determined, is employed. Absorption of the radiation, at one of the resonance lines from the lamp, by atoms of the same element in the sample in the flame, is then measured.

Consider a population of atoms at a given temperature in a uniform medium. A flame supplied with a given species from a pneumatic nebulizer is a fair approximation to this. The ratio of the number of atoms in the excited state to the number in the ground state is given by the equation

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} \exp - \left(\frac{E_1}{kT}\right)$$

where g_0 and g_1 = Statistical weights of the ground and excited states

N_0 = Number of atoms in the ground state

N_1 = Number of atoms in the excited state

k = Boltzmann Constant (e.v./^ok)

T = Absolute temperature (^ok)

E_1 = Energy of the excited state above the ground state (e.v.)

TABLE 1

RATIO OF NUMBER OF ATOMS IN THE EXCITED STATE

TO NUMBER IN THE GROUND STATE (139)

Resonance Line (Å)		T = 2000	3000	4000	5000°k
Cs	8521	4.4×10^{-4}	7.2×10^{-3}	3×10^{-2}	6.8×10^{-2}
Na	5890	9.8×10^{-6}	5.9×10^{-4}	4.4×10^{-3}	1.5×10^{-2}
Ca	4227	1.2×10^{-7}	3.7×10^{-5}	6.0×10^{-4}	3.3×10^{-3}
Zn	2139	7.3×10^{-15}	5.6×10^{-10}	1.5×10^{-7}	4.3×10^{-6}

It can be seen (Table 1) that the ratio of the number of atoms in the lowest excited state to the number of atoms in the ground state is small but increases exponentially with temperature and wavelength. Even at 3000°k only a small percentage of, e.g. Cs, atoms are in the excited state but it must be remembered that at this temperature appreciable ionization of the metal atoms will occur, thus seriously depleting the ground state population. This effect will be observed for all easily ionized atoms, and is usually overcome by adding an excess of an easily ionizable element (e.g. potassium) to the flame to suppress the ionization. However, it can be seen that only a negligible proportion of atoms will exist in the excited state in the flame. Also

interelement effects in the flame can easily arise to cause interference in the emission method of flame photometry. These include deactivation by collision, preferential excitation of other species and energy transfer processes in general. These effects do not however affect the absorption of radiation by the ground state population.

Consider a parallel beam of radiation, of intensity I_0 at frequency f, incident on an atomic vapour of thickness 1 cm. The intensity of the transmitted radiation I_f is given by the relationship

$$I_f = I_0 \exp - (K_f 1)$$

where K_f is the absorption coefficient at frequency f. The value of K_f varies with f, since the absorption line has a finite width, but it can be shown that the integrated absorption ($\int_0^\infty K_f df$) is given by the equation

$$\int_0^\infty K_f df = \frac{\pi e^2}{mc} N. s$$

where e = electronic charge

m = electronic mass

c = velocity of light

N = number of atoms/cm^3

s = oscillator strength (average number of electrons/ atom capable of being excited by incident radiation)

Thus for a transition from the ground state, the integrated absorption is proportional to the concentration of free atoms and is relatively independent of the temperature of the atomic vapour.

The problem arises, however, of how to measure the integrated absorption. At temperatures between 2000 and 3000°K the width of an absorption line is ca 2×10^{-2} Å and this mainly results from Doppler and collisional broadening as the natural absorption line width is ca 10^{-4} Å. The factors that establish the line width are

1 Natural broadening

This is due to the finite lifetime of the atom in the excited state but may generally be neglected in relation to the other factors.

2 Doppler broadening

This is caused by the absorbing atoms having different component velocities along the line of observation i.e. movement of the atoms relative to the observer.

3 Collisional broadening

Collisional broadening (also known as pressure or

Lorentz broadening) is due to perturbation of the absorbing atoms by foreign gas atoms. When broadening is due to perturbation by atoms of the same kind as those absorbing radiation, the effect is known as resonance broadening. This broadening is generally negligible in analytically used flames unless high concentrations of a given element are introduced into the flame.

4 Stark and Zeeman broadening

These effects are caused by external electric and magnetic fields respectively. Again these are negligible in flames, but are an important factor with hollow cathode sources used in A.A.S.

5 Hyperfine structure

Hyperfine structure is due to nuclear spin and/or the presence of several isotopes and results in the fact that each line consists of a number of separate hyperfine components each behaving as an independent line.

To measure the profile of an absorption line accurately would require a monochromator with a resolution of about 500000 which is well beyond the capabilities of most monochromators. By using a sharp-line source that emits lines with a much smaller half-width than the absorption line, the absorption coefficient at the centre of the line can be measured. This eliminates the

need for a high resolution instrument as the only requirement is the ability to separate a selected line from all other lines emitted by the source. Although the use of a sharp line source affords a satisfactory method of measuring peak absorption, it has the disadvantage of requiring a separate source for the study of each individual element.

The technique of A.A.S. for the determination of traces of inorganic ions in solution has reached a stage of development whereby some 60 elements can be determined with good sensitivity. At first sight, it may appear that all elements should be capable of being determined by A.A.S. but there are two important factors which restrict the range when an atomizer and flame are used to produce an atomic vapour. Firstly some elements form refractory compounds in the flame and are not appreciably dissociated into atomic form. Hence no atoms are available for absorption, although the use of hotter flames (e.g. oxy-acetylene and nitrous oxide-acetylene) has extended the range of detectable elements. Secondly the resonance lines of many elements lie in the far ultra-violet region of the spectrum, and any absorption which may occur is swamped by absorption in the flame gases and surrounding atmosphere.

Unfortunately two of the most important elements for which both the above problems apply are phosphorus and silicon. For phosphorus, even if an atomic population could be formed

efficiently, the principal resonance lines lie in vacuum ultra violet. Although use has been made of these lines (146, 147), conventional equipment is not available for A.A.S. measurement. For silicon, although a principal resonance line is available at 2516Å, it is difficult to form free atoms in the conventional flames. The hazardous, fuel rich, oxy-acetylene flame has been used with limited success and low sensitivity in conjunction with a total consumption burner (148). The recently developed nitrous oxide-acetylene flame (149) gives a better sensitivity for silicon (150) but is not entirely satisfactory.

CHAPTER 2

THE INDIRECT SEQUENTIAL DETERMINATION OF PHOSPHORUS AND SILICON BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

As stated previously, in Chapter 1.5, phosphorus and silicon are difficult to determine directly by A.A.S., but an amplification procedure, based on measurement of the molybdenum content of their respective heteropoly molybdates by A.A.S., appeared quite feasible. Earlier work in these laboratories (130) resulted in a satisfactory method for the determination of phosphorus by an amplification procedure with a solution spectrophotometry finish. In this method phosphorus is converted into phosphomolybdate and selectively extracted away from excess molybdate reagent into chloroform-butanol. After retrograde extraction into alkali, the twelve molybdate ions associated with each original phosphate ion are determined by their reaction with 2-amino-4-chlorobenzenethiol. This reagent forms a green extractable complex with molybdate in acid medium at pH2. Although the sensitivity of the reaction is not appreciably greater than that of the corresponding molybdenum-toluene-3,4-dithiol reaction, it is equally selective. The reagent is more easily

handled and more stable than toluene-3,4-dithiol. Indirect determination of phosphate via molybdenum by this procedure entails several separations, so that although the method is selective and very sensitive it becomes tedious and time consuming. This is particularly true when both phosphorus and silicon are determined sequentially. Attempts were made therefore to devise a more rapid procedure for determining phosphate and silicate in the same sample. It was required that the molybdenum be determined directly in the organic phases containing the phosphomolybdic or silicomolybdic acids. Atomic absorption spectroscopic determination of the molybdenum in a nitrous oxide-acetylene flame at 3132 Å was adopted. The optimum conditions for the determination of the molybdenum itself by A.A.S. were also studied and are reported later (See Chapter 6).

2.1 Apparatus

The equipment used in this work was the Unicam SP 900 A flame spectrophotometer with a Unicam molybdenum hollow cathode lamp. The instrument condit ons used throughout were:- slit width 0.06 mm; wavelength 3132 Å; lamp current 15 mA. The burner for A.A.S. measurements in air-acetylene flames was replaced by a brass burner of similar dimensions for the nitrous

oxide-acetylene flame. This burner is described in detail in Chapter 6 . The sample was aspirated directly with nitrous oxide at 15 p.s.i., and sufficient acetylene was pre-mixed with the nitrous oxide in the burner base to produce a flame with a red-feather of about 1-2 cm in height. The burner height was adjusted so that as much as possible of the radiation from the hollow cathode lamp passed through this red zone.

2.2 Extraction of Phosphomolybdic Acid

The extraction of phosphomolybdic acid from aqueous solution was conducted under similar conditions of hydrochloric acid concentration (0.96 M) and molybdate reagent concentration (0.024 M) to those used by Wadelin and Mellon (91). However it was found that the chloroform-butanol mixture (4 : 1, v:v) used by these workers to obtain selective extraction could not be nebulised directly into the nitrous oxide-acetylene flame as with this solvent the flame became dangerously luminous. Also, apart from high flame background and noise levels, a terrifying whistle was heard with the result that discretion became the better part of valour, and the use of A.A.S. in chloroform butanol was abandoned. Two choices were now presented:-

a) retrograde extraction of molybdate into an aqueous alkaline medium prior to nebulisation into the flame

or

b) use of another selective solvent for phosphomolybdic acid extraction which could be conveniently introduced into a fuel rich nitrous oxide-acetylene flame.

Both these avenues were explored but work on the former was discontinued when it was found that iso butyl acetate suggested by Paul (95) could be nebulised directly into the flame, without excessive luminosity, while directly replacing the chloroform-butanol mixture used in the procedure by Wadelin and Mellon. The latter method was also preferred as it leads to an increase in sensitivity due to the greater efficiency of nebulisation of organic solvents relative to aqueous solutions, while it also has the advantage of rapidity.

Repeated extractions were made to establish that quantitative recovery of as much as 50 μg of phosphorus as the phosphomolybdic acid could be achieved with 10 ml of iso butyl acetate from 25 ml of aqueous solution. Blank experiments with no phosphorus present, revealed that no appreciable amount of the molybdate reagent is extracted into iso butyl acetate. However, before aspiration into the flame, the organic phase was washed with 10 ml of 2M hydrochloric acid to remove any molybdate reagent which is mechanically transferred from the

aqueous phase because of incomplete separation of the solvent from the molybdate solution. This was similar to the precaution employed by Djurkin, Kirkbright and West (130).

When iso butyl acetate was sprayed into the nitrous oxide-acetylene flames a slight luminosity resulted. This was easily eliminated by decreasing the acetylene flow-rate into the flame. The molybdenum content of the phosphomolybdic acid in the iso butyl acetate phases was initially measured against a "procedure" blank containing no phosphorus but for later work all organic phases were measured against iso butyl acetate solvent blank.

2.3 The Extraction of Silicomolybdic Acid

The optimum conditions for the formation and extraction of silicomolybdic acid were initially studied in pure aqueous silicate solutions. The results confirmed the findings of previous workers (91). An overall hydrochloric acid concentration of 0.15 M when the total molybdate concentration was 0.24 M, was employed. Butanol was the organic solvent used for the extraction of the silicon heteropolymolybdate and the silicon content of this phase was determined by A.A.S. measurement of the associated molybdenum atoms. However a large blank was

obtained when a sample solution containing no added silicate was taken through the extraction procedure. This blank was thought to be due to the extraction of free molybdate reagent and thus the butanol phase was washed with acid to remove this molybdate preferentially without removing the silicomolybdic acid. The results of the effect of acidity of the wash solution on the molybdenum absorbance obtained for 16 µg of silicon extracted from 0.15 M hydrochloric acid is shown in Figure 1. A single washing with 0.15 M hydrochloric acid was found to be insufficient, and it was established (Figure 2) that three rapid washings with 10-ml aliquots of 0.15 M hydrochloric acid were required. Because of the miscibility of butanol with water, the butanol phase becomes depleted seriously during this washing procedure, and therefore the use of a 0.15 M hydrochloric acid wash solution which had been pre-saturated with butanol was adopted.

Even with all these refinements for the extraction of silicomolybdic acid into butanol and in the back-washing procedure, a significant blank for silicon was still obtained. This was caused by the silicon content of the reagents employed. Thus the reagents used were chosen for their low silicon content when specifications of these chemicals were available. Again, the distilled water used throughout these studies came from a glass still and it was thought that this might contribute quite

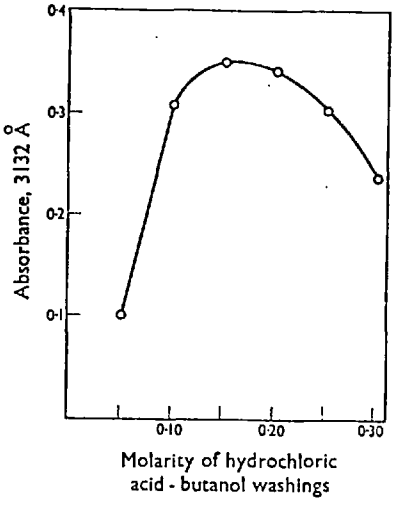


Figure 1 Effect of net absorbance for 16 µg of silicon of molarity of hydrochloric acid used to wash the butanol phase.

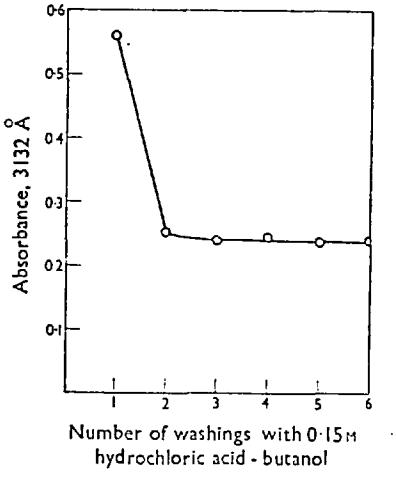


Figure 2 Effect of number of washings with 0.15 M hydrochloric acid on absorbance produced by 12 µg of silicon.

considerably to the silicon content of the blank. There was no significant difference in the blank value when various distilled and de-ionized water samples from the Chemistry Department were employed. (Analysis of tap water, however, revealed a substantially higher silicon content.) The blank from the "glass still" distilled water, however, was reproducible - representing about 10 μg of silicon - and the molybdenum absorbance arising from it could be subtracted from the absorbance produced by the standards taken through the procedure.

Having thus found the optimum conditions for the extraction of silicomolybdic acid from pure aqueous solution, it was necessary to study the effect of extraction of the phosphomolybdic acid from the solution prior to the extraction of silicon. The phosphomolybdic acid was formed and extracted at 0.96 M hydrochloric acid and it was necessary to lower this acidity to 0.15 M before extraction of silicomolybdic acid. This was accomplished using 4M ammonia solution and the optimum volume of this solution was established (Figure 3) by addition of the ammonia to the aqueous phase containing silicon before its extraction and after it had been taken through the preliminary phosphorus extraction procedure. Slightly less than the calculated amount of 4M ammonia solution was used to lower the acidity to 0.15M because a small amount of hydrochloric acid was lost during the separation of the phosphorus, probably by extraction into the iso butyl acetate phase.

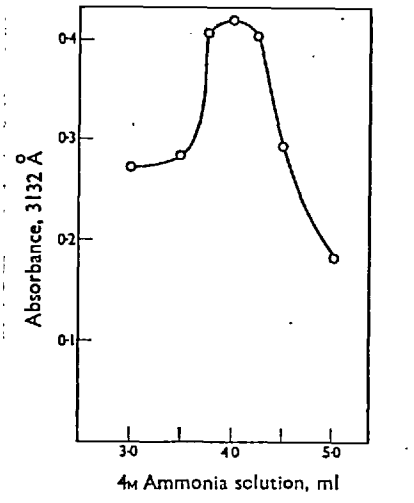


Figure 3 Effect on net absorbance for 20 μg of silicon of volume of ammonia solution used to adjust acidity before silicon extraction.

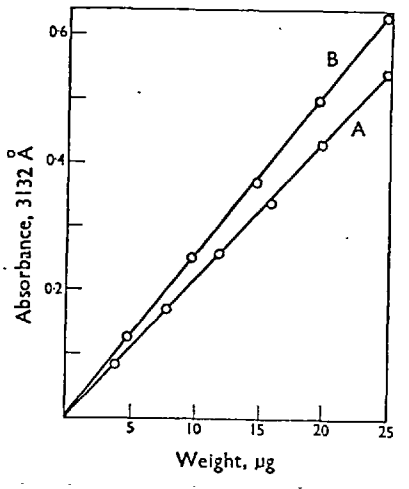


Figure 4 Calibration graphs for A, silicon in the presence of 200 μg of phosphorus; and B, phosphorus in the presence of 200 μg of silicon.

2.4 Reagents

Ammonium molybdate solution

Dissolve 10.69 g of AnalaR ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in distilled water and dilute to exactly 1 litre.

Standard phosphorus solution

Dissolve 0.1098 g of potassium dihydrogen orthophosphate, KH_2PO_4, (AnalaR grade) in distilled water and dilute to 1 litre.

1 ml of solution contains 25 μg of phosphorus.

Standard silicon solution

Fuse 0.3385 g of powdered sodium silicate with about 3 g of sodium hydroxide pellets (AnalaR grade) in a platinum crucible, and leach the melt with hot water. Allow the solution to cool, and dilute it to 1 litre in a calibrated flask. This solution was standardised gravimetrically by the hydrofluoric acid volatilisation procedure.

1 ml of solution contains 100 μg of silicon.

Store the alkaline stock solution in an opaque polythene bottle.

Solutions containing 40 μg per ml of silicon were prepared by neutralisation of this solution and dilution to volume as required, and these were also stored in polythene bottles.

Ammonia solution, analytical-reagent grade

Supplied by May and Baker, Proanalys.

Hydrochloric acid, analytical-reagent grade

Supplied by May and Baker, Proanalys.

The hydrochloric acid and ammonia solution used were chosen for their low silicon content (not more than 0.0001 per cent of SiO_2). All other reagents used were of analytical-reagent grade.

Wash liquid for butanol phase

This is dilute hydrochloric acid, 0.15 M, saturated with butanol, and is stored in polythene bottles.

2.5 Recommended Procedure

To a series of six 100-ml separating funnels add 10 ml of molybdate reagent, 10 ml of distilled water and sufficient concentrated hydrochloric acid to make the solution 0.96 M with respect to hydrochloric acid. Add 0, 0.2, 0.4, 0.6, 0.8 and 1.0-ml aliquots of the standard phosphorus solution and 0, 0.1, 0.2, 0.3, 0.4 and 0.6-ml aliquots of standard silicon solution to the funnels. Mix the solutions and allow them to stand

for 5 minutes. Add 10 ml of isobutyl acetate, shake the mixture for 1 minute, and allow the phases to separate. Transfer the lower aqueous phases (A) to a second series of 100-ml separating funnels for the subsequent silicon determination. Wash the isobutyl acetate phases by shaking the solution for about 30 seconds with 10 ml of 2 M hydrochloric acid. Discard the lower aqueous phases and aspirate the isobutyl acetate solutions into the nitrous oxide-acetylene flame for the determination of the molybdenum by atomic absorption at 3132 Å against a solvent blank of isobutyl acetate.

To the aqueous phases (A) containing the silicon, add 4 ml of 4 M ammonia solution and allow the mixture to stand for 15 minutes to ensure complete formation of the silicomolybdic acid. Introduce 10 ml of butanol into each funnel and shake them for 1 minute. Discard the lower aqueous phases, and wash the organic phase three times with 10 ml of the prepared butanol-wash solution. Spray the butanol phases directly into the nitrous oxide-acetylene flame and determine the molybdenum as before against a butanol solvent blank.

When more than 25 μg of silicon are present with 5 to 25 μg of phosphorus, the above procedure should be modified by using a larger volume (15 to 20 ml or more) of butanol to enable the silicon concentration in the organic phase to be kept within the range of the calibration curve.

When more than 25 μg of phosphorus are present with 2 to 20 μg of silicon, the procedure should be changed to enable this greater weight of phosphorus to be extracted quantitatively, and also to keep the concentration of phosphorus in the organic phase within the range of the calibration curve. This is easily accomplished by the use of a larger volume of isobutyl acetate. Thus for the determination of 20 μg of silicon and 200 μg of phosphorus, two extractions of the phosphomolybdic acid with 20 ml of isobutyl acetate should be made.

This procedure is less sensitive than when the molecular spectrophotometric finish to the determination is used. This is due entirely to the less sensitive determination of the molybdenum by the atomic-absorption method. The ease of operation and rapidity of the procedure, however, compensate for the loss of sensitivity, and the sensitivity can be increased, if necessary, by suitable adjustment of the phase volumes in the extraction procedure. The method loses nothing in selectivity by the atomic-absorption method; when foreign ions extractable into isobutyl acetate or butanol from dilute hydrochloric acid are present, a gain in selectivity is obtained as these may interfere with the molecular spectrophotometric determination in solution.

2.6 Results

When the recommended procedure is used, the calibration graph for the determination of phosphorus in the presence of up to 200 μg of silicon is linear over the range 2 to 25 μg of phosphorus. The absorbances corresponding to these concentrations of phosphorus in the original aqueous solution (0.083 to 1 p.p.m.) are 0.048 and 0.64. The calibration graph for the determination of silicon in the presence of up to 200 μg of phosphorus is linear over the range 2 to 25 μg of silicon. The absorbances corresponding to these concentrations of silicon in the original aqueous phase (0.08 to 1 p.p.m.) are 0.043 and 0.54 (Figure 4).

To measure the precision of the system a series of absorbance values was obtained from the replicate analysis of 25 ml of a solution containing 20 μg (0.8 p.p.m.) of phosphorus and 20 μg (0.8 p.p.m.) of silicon. The average absorbance for phosphorus was 0.510 and the standard deviation was 0.005 absorbance unit or 1.03 per cent. The average absorbance for silicon was 0.404 and the standard deviation was 0.01 absorbance unit or 2.45 per cent.

The effect of a selected group of elements on the absorbances produced in the determination of 10 μg of phosphorus or 12 μg of silicon by the recommended procedure has been investigated. An ion was considered not to interfere, for the purpose of this study, when less than 5 per cent. error in absorbance was produced for

the test solutions compared with the standards. The presence of a 100-fold excess by weight of the following ions produced no interference: Al, Au, Bi, Ca, Cd, Co(II), Cr(III), Cu, Fe(III), Ni, Pb, Mg, Mn, Se(IV), Te(IV), Ti(IV), Zn, fluoride, EDTA, NO_3^- and SO_4^{2-}. The effect of arsenic and germanium, which are known to form the central atoms of heteropoly acids in which molybdate is the co-ordinated group, was also examined. Neither of these elements (as arsenic(V) and germanium(IV)) interferes in the determination of phosphorus, because of the selectivity of the isobutyl acetate for extraction of the phosphomolybdic acid. Both arsenic(V) and germanium(IV), however, interfere in the silicon determination and yield high results. This is caused by the extraction of arsenomolybdic and germanomolybdic acids into the butanol with the silicomolybdic acid. The presence of a 100-fold excess by weight of antimony(V) and vanadium(V) causes no interference in the phosphorus or silicon determination. A 100-fold excess of tungsten(VI) causes no interference in the determination of silicon, but produces low results in the phosphorus determination. This is presumably caused by formation of some phosphotungstic acid that is not extracted into the isobutyl acetate. It was established, however, that a 10-fold excess of tungsten(VI) causes no interference in the determination of phosphorus. It seems, as reported elsewhere,(130), that it is possible to tolerate larger excesses of tungsten when Tiron (1,2-dihydroxybenzene-3,5-disulphonic acid) is used as masking agent.

A measure of the accuracy of the method was obtained by the determination of phosphorus and silicon sequentially in synthetic solutions treated as unknown samples. The results of these analyses are shown in Table 2.

TABLE 2

DETERMINATION OF PHOSPHORUS AND SILICON IN SYNTHETIC MIXTURES

Phosphorus present, p.p.m.	Silicon present, p.p.m.	Phosphorus found, p.p.m.	Silicon found, p.p.m.
1.0	0	1.02	0
0	0.80	0	0.80
0.10	0.24	0.10	0.23
0.34	0.32	0.32	0.30
0.64	0.50	0.57	0.49
0.88	0.62	0.88	0.61
0.10	0.80	0.10	0.81
0.20	0.80	0.20	0.78
1.00	0.16	1.01	0.17
1.00	0.32	0.98	0.32

CHAPTER 3

A SELECTIVE AMPLIFICATION - TITRATION PROCEDURE FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF PHOSPHATE

After the work described in Chapter 2 on the amplification determination of phosphate by A.A.S. of the associated molybdenum atoms in the heteropoly acid (151), it was decided to investigate an alternative titrimetric finish in order to obtain higher precision in the determination. The same selective extraction system was employed and the phosphomolybdic acid in the isobutyl acetate phase was back extracted into alkali. Experiments designed to measure the amount of standard alkali which was neutralized during this retrograde extraction failed to show any consistent results. This was probably due to the extraction of hydrochloric acid into the iso butyl acetate phase as had been previously observed (151).

It was therefore decided to investigate the feasibility of a titrimetric determination of the molybdenum after retrograde extraction and destruction of the phosphomolybdic acid. Molybdenum (VI) was reduced to molybdenum (V) by a silver reductor

column and the determination was then completed by direct visual or photometric titration of the molybdenum (V) with standard cerium (IV) sulphate solution from a 50-ml grade A burette using ferroin as indicator.

3.1 Apparatus

An E.E.L. photoelectric titrator and galvanometer (Evans Electroselenium Ltd., Halstead, Essex) was used.

Reductor column

Silver for the reductor column was prepared by the method of Kolthoff and Belcher (152). The column used was a laboratory 10-ml burette of internal diameter 1 cm.; a column length of 7 cm. was used. This column is smaller than that used by Birnbaum and Walden (128), so that a smaller total volume of eluate can be obtained. The column was maintained in 2 N hydrochloric acid at all times, and was equilibrated with hot (60° to 80°C) 2 N hydrochloric acid immediately before use. (128, 153).

3.2 Reagents

Standard orthophosphate solution

Dissolve 0.1098 g of analytical-reagent grade potassium

dihydrogen orthophosphate in distilled water and dilute to 1 litre.

1 ml of solution ≡ 25 μg of phosphorus.

Molybdate reagent solution

Dissolve 10.69 g of analytical-reagent grade ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in distilled water and dilute to 1 litre.

Cerium(IV) sulphate solution

Prepare by diluting British Drug Houses, Ltd. concentrated volumetric solution. Dilute the stock 0.05 M solution to 10^{-3} M with 2 N sulphuric acid as required.

1 ml of 10^{-3} M cerium(IV) solution ≡ 2.58 μg of phosphorus.

Ferroin indicator solution

Use a 5×10^{-3} M aqueous solution of ferroin, $Fe(C_{12}H_8N_2)_3SO_4$. Two drops of indicator solution were used for each titration.

Hydrochloric acid

Analytical-reagent grade.

Ammonia solution, sp.gr. 0.88

Analytical-reagent grade.

Isobutyl acetate

General-purpose reagent grade.

3.3 Recommended Procedure

The optimum conditions for the selective extraction of phosphomolybdic acid from excess of molybdate reagent into isobutyl acetate have already been described,(95,151) and were used here.

Transfer the sample solution (up to 5 ml), containing between 3 and 30 μg of phosphorus, into a 100-ml separating funnel containing 10 ml of molybdate stock solution and 10 ml of water. Add sufficient concentrated hydrochloric acid to make the solution 0.96 M with respect to hydrochloric acid. Allow the solution to stand for 5 minutes, add 10 ml of isobutyl acetate and shake the funnel for 1 minute. Allow the phases to separate, discard the aqueous phase, and wash the organic phase with 10 ml of 2 N hydrochloric acid. Shake the organic phase with 5 ml of 4 M ammonia solution, discard the isobutyl acetate and retain the alkaline solution containing the molybdenum(VI).

Transfer the molybdenum solution from the extraction funnel into a 50-ml beaker, add sufficient 6 N hydrochloric acid to neutralise the ammonia and make the solution 2 N with respect

to hydrochloric acid. Transfer the solution quantitatively into the top of the reductor column by using 2 N hydrochloric acid as wash liquid. Reduce the molybdenum(VI) to molybdenum(V) on this column by using the method described by Birnbaum and Walden (128), eluting the sample three times with 5-ml portions of hot 2 N hydrochloric acid and three times with 5-ml portions of cold hydrochloric acid. Collect the eluate (35 to 40 ml) in the titration cell, heat rapidly to boiling, cool the solution to near room temperature, and titrate the molybdenum(V) with standard 10^{-3} M cerium(IV) sulphate, with ferroin indicator and E.E.L. filter No. 603. Alternatively, after some experience, the end-point can be detected visually by the disappearance of the last trace of pink colour. The visual method was found to be entirely satisfactory.

3.4 Results and Discussion

Before the determination of phosphate was attempted via the selective solvent-extraction procedure, pure aqueous molybdenum(VI) solutions were reduced and titrated with cerium(IV) sulphate to ensure that quantitative reduction and recovery of molybdenum was obtained on the reductor column. The molybdenum concentrations were chosen in these experiments to correspond to those which would

be obtained after the amplification of the initial phosphorus content (3 to 30 μg) of samples. It was found that a significant blank [1.8 ml of 10^{-3} M cerium(IV)] was obtained in the absence of molybdenum in the reduction - titration procedure. At the ferroin indicator concentration used, the indicator blank accounts for about one third of this blank (0.65 ml) when the titration is carried out with 10^{-3} M cerium(IV) sulphate. The blank was initially thought to arise from other ions present in the reagents used, which were reduced on the reductor column (e.g. iron or copper) and subsequently oxidized by the cerium(IV) solution. However, the use of cation or anion exchangers failed to affect the blank titre. This led the author to believe that hydrogen peroxide was being formed on the column. Consequently, nitrogen was bubbled through the eluting acid prior to its passage down the column. This had no significant effect on the titre and as such the use of this refinement was discontinued. Again hydrogen peroxide in the eluate could not be detected by conventional means. It was found that the blank titre was eliminated if the eluate was momentarily boiled and then cooled before titration. This brief boiling would not normally be expected to destroy hydrogen peroxide efficiently, but its destruction is probably catalysed by traces of silver present in the solution. The indicator blank is reproducible and can safely be subtracted from the sample titration volume.

Other indicators examined (N-phenylanthranilic acid and diphenylamine-p-sulphonic acid) did not give an end point change as sharp as that obtained with ferroin.

Quantitative recovery and titration of 12 moles of molybdenum is obtained for each mole of phosphorus in the sample. As reported previously, the isobutyl acetate extraction separates phosphomolybdic acid efficiently from the excess of molybdate reagent. The procedure has selectivity equal to those previously reported, and no interference is caused by the presence of large excesses (100-fold by weight) of silicate, arsenate, antimony(V) and germanium(IV). (Table 3)

TABLE 3

Phosphorus taken (μg)	Theoretical titre (ml)	Titre obtained (ml)*	Foreign anions (weight excess)
10	3.87	3.85	Arsenate 100
15	5.81	5.80	Germanate 100
20	7.74	7.76	Antimonate 100
25	9.68	9.68	Silicate 100

* Mean of five determinations.

As shown in Table 4 phosphorus can be determined in the presence of several milligrams of each of a wide range of cations without interference.

TABLE 4

DETERMINATION OF PHOSPHORUS IN

SYNTHETIC MIXTURES TREATED AS UNKNOWNS

Phosphorus taken (µg)	Theoretical titre (ml)	Titre obtained (ml)	Phosphorus found (µg)	Foreign ions present, mg	
10.0	3.87	3.87	10.0	Selenium(IV) Tellurium(IV)	1.59 1.28
12.5	4.84	4.64	12.0	Barium Manganese Silicon	6.87 5.5 2.0
20.0	7.74	7.78	20.1	Aluminium Lead	1.0 2.07
20.0	7.74	7.88	20.3	Cobalt Nickel	2.95 2.95
5.0	1.94	2.05	5.3	Selenium(IV) Tellurium(IV)	1.59 1.28
25.0	9.68	9.68	25.0	Arsenic(V) Germanium(IV) Silicon Calcium	2.0 2.0 4.0 2.5
20.0	7.74	7.93	20.5	Iron(III) Zinc	3.0 6.5
25.0	9.68	9.94	25.7	Barium Manganese Silicon	6.87 5.5 2.0
25.0	9.68	10.06	26.0	Zinc Cadmium Copper	6.5 5.6 6.4

The precision of the reduction - titration procedure was established by repetitive analysis of a pure molybdenum(VI) solution. The standard deviation in the titration value for the determination of 929 μg of molybdenum (equivalent to 25 μg of phosphorus) was 0.05 ml, or 0.55 per cent. The precision of the whole procedure was established by the repetitive determination of 25 μg of phosphorus by the solvent-extraction, reduction and titration procedures. The standard deviation in the titration volume for the determination of 25 μg of phosphorus, repeated seven times, was 0.135 ml, or 1.3 per cent. A measure of the accuracy of the procedure was obtained by determining phosphorus in synthetic solutions containing foreign ions. The results of these analyses are shown in Table 4. The results obtained for the determination of phosphorus in microanalytical-reagent grade triphenylphosphine are shown in Table 5. Different sample weights (in the range 60 to 200 μg) were digested with a sulphuric acid-perchloric acid mixture, and the perchloric acid was removed by evaporation. The residual sulphuric acid smear was then treated directly by the recommended procedure. The determination of 10^{-6} -g amounts of phosphorus, by using an ordinary burette with titration volumes of several millilitres of a 10^{-3} M titrant and visual detection of the end-point, furnishes a good illustration of the analytical value of amplification reactions.

TABLE 5

DETERMINATION OF PHOSPHORUS IN TRIPHENYLPHOSPHINE SAMPLES

Phosphorus in sample (μg)	Phosphorus found, (μg)	Error, per cent.	Phosphorus in triphenylphosphine, (theory 11.81 per cent.)
12.11	12.12	+ 0.1	11.82
11.27	11.25	- 0.2	11.79
7.53	7.50	- 0.3	11.76
16.77	16.50	- 1.6	11.62
9.10	9.00	- 1.0	11.68
16.65	16.12	- 3.2	11.44
20.20	21.00	+ 3.9	12.27
21.63	21.25	- 1.7	11.76
10.76	10.56	- 2.0	11.59
11.72	11.87	+ 1.3	11.96

Although it was not established experimentally, there should be no reason why a similar method could not be devised for the titrimetric determination of silicate by modification of the amplification procedure previously described (151). There is no reason to suppose that the presence of silicate ions should interfere in any way with the functioning of the Birnbaum and Walden reductor column.

CHAPTER 4

THE INDIRECT AMPLIFICATION DETERMINATION OF NIOBIUM BY ATOMIC ABSORPTION SPECTROSCOPY

The ternary complex formed between niobium, phosphate and molybdate in acidic solution has been previously used as a spectrophotometric method for the determination of niobium (154, 155, 156). In these methods the molybdoniobophosphoric acid (MNPA) is reduced to "heteropoly blue", after the selective decomposition of the excess of binary molybdophosphoric acid (MPA), by increasing the acidity of the solution. The methods reported are not sensitive, and strict adherence to the time of addition of acid and reducing agent, as well as measurement of the heteropoly-blue absorbance, must be observed. Babko and Shkaravskii (157) have investigated the equilibria governing the formation of the molybdoniobophosphoric acid, and its composition in aqueous solution. They report the formation, in an acid medium, of a stable complex, in which the combining ratio of niobium - phosphorus - molybdenum is 1:1:11. The same authors also observed that, whereas molybdophosphoric acid is readily extracted into butyl acetate at pH 1, molybdoniobophosphoric acid is not extracted. Shkaravskii (158) has reported that tantalum does not form a ternary heteropoly

complex with molybdenum and phosphate.

Following the work reported in Chapter 2 it seemed that a sensitive determination of niobium with high selectivity might similarly result from formation and extraction of the molybdoniobophosphoric acid, and the determination by atomic-absorption spectroscopy of the eleven molybdenum atoms associated with each niobium atom in the heteropoly complex. In the procedure reported MNPA is formed in 0.5 M hydrochloric acid by addition of molybdate and phosphate to the sample solution, and the excess of phosphomolybdic acid is extracted into isobutyl acetate. The MNPA in the residual aqueous phase is then extracted into butanol; the organic phase is washed with 0.5 M hydrochloric acid and the molybdenum present determined by atomic absorption in a nitrous oxide-acetylene flame at 313.2 nm.

4.1 Apparatus

Techtron AA4 flame spectrophotometer, fitted with a 5-cm nitrous oxide-acetylene burner and molybdenum high intensity hollow-cathode lamp. The instrument settings used for the determination of molybdenum were: slit width, 100 μm; wavelength, 313.2 nm; nitrous oxide pressure, 15 p.s.i.; the acetylene flow-rate was adjusted to produce a flame with a "red-feather" of about 1 to 2 cm height.

The burner height was adjusted so that as much as possible of the light from the hollow-cathode lamp passed through this red zone.

4.2 Reagents

All reagents should be of analytical-reagent grade; it was found that reagents conforming to the AnalaR specifications were suitable.

Molybdate reagent solution

Dissolve 10.69 g of ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in distilled water and dilute to exactly 1 litre.

Phosphate reagent solution

Dissolve 0.1098 g of potassium dihydrogen orthophosphate, KH_2PO_4, in distilled water and dilute to exactly 1 litre; 1 ml of solution contains 25 μg of phosphorus.

Wash liquid for butanol phase

Saturate hydrochloric acid (0.5 M) with butanol, and store in polythene bottles.

Isobutyl acetate and butanol

General-purpose reagent grade.

Niobium

Spectrographically standardised niobium powder (Johnson and Matthey Ltd.).

4.3 Preparation of Niobium Stock Solutions

It was expected that silicon would seriously interfere on the determination of niobium in the method used, and consequently the niobium solutions should be rendered silicon-free. Thus niobium stock solutions were prepared by the following procedure:

Dissolve 0.1000 g of niobium powder in 10 ml of 40 per cent. hydrofluoric acid containing a few drops of concentrated nitric acid. Evaporate the solution almost to dryness in a platinum crucible. Dissolve the residue in 10 ml of warm 40 per cent. hydrofluoric acid. Transfer the solution to a polythene bottle and dilute to exactly 100 ml with distilled water. This solution contains 1 mg of niobium per ml. Transfer a 5-ml aliquot of this solution to a platinum crucible and evaporate to dryness. Dissolve the residue in 5 ml of 40 per cent. hydrofluoric acid,

add a few drops of concentrated sulphuric acid, and evaporate the solution until no further evolution of white fumes occurs. Cool, re-dissolve the residue, then repeat the evaporation with hydrofluoric and sulphuric acids. Make a final evaporation of the solution of the residue with 5 ml of 40 per cent. hydrofluoric acid without addition of sulphuric acid. Dissolve the residue in the minimum amount of hydrofluoric acid (about 2 ml) and dilute to exactly 100 ml with distilled water. The silicon-free niobium solution contains 50 μg per ml of niobium.

Pure silicate solutions, after the treatment, were examined for their silicon content and this proved negligible. The preparation of niobium solutions by this procedure was found to be far more successful than the bisulphate fusion of the pentoxide. This is due firstly to the elimination of silicon from the solutions, and secondly because the bisulphate melt is leached into a tartrate medium. Although on a qualitative scale tartrate could be tolerated, it was expected to affect the formation of both MPA and MNPA when a quantitative approach was employed.

4.4 Preparation of Sample Solutions

Samples whose niobium content is to be determined should be dissolved in a mixture of hydrofluoric and nitric acids and

treated further to remove silicon, as detailed in the instructions for the preparation of the niobium stock solution.

4.5 Formation and Extraction of MNPA

It is not possible to form MNPA in aqueous solution without the simultaneous formation of MPA. Consequently, throughout the studies undertaken to determine the optimal solution conditions for the formation and extraction of MNPA, the following general procedure was adopted to remove the MPA formed.

Both MPA and MNPA were allowed to form in acidic solution, and then the MPA was extracted into two 25-ml aliquots of isobutyl acetate before the extraction of MNPA into 10 ml of butanol. The molybdenum associated with the niobium in the MNPA was then determined by direct atomic-absorption spectroscopy in the washed butanol phase. Each solution was measured against a blank produced under identical conditions, but containing no niobium.

The effect on absorbance of variation in the acidity of an initial aqueous solution, which was 2.7×10^{-2} M in molybdate, 3.6×10^{-4} M in phosphate and contained 40 μg of niobium, is shown in Figure 5.

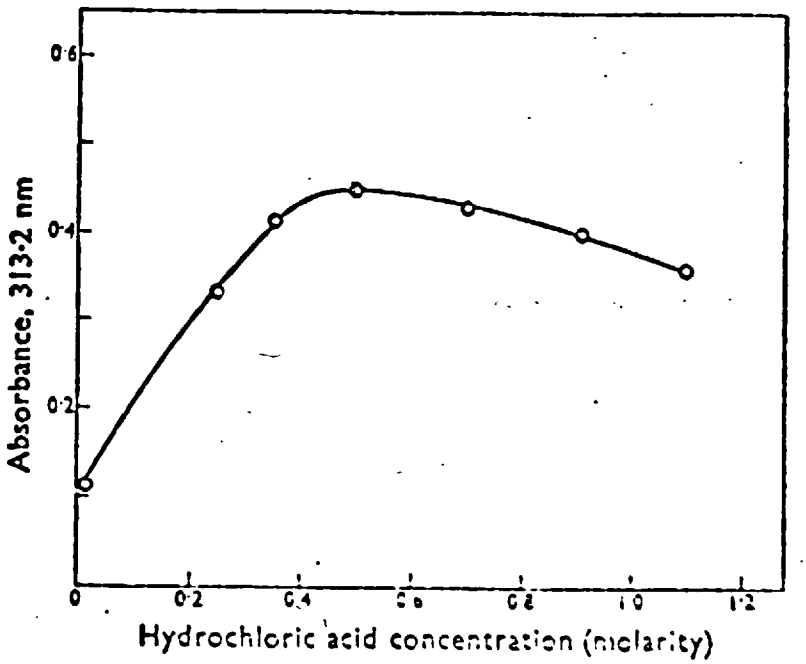


Figure 5. Effect on absorbance for 40 μg of niobium of molarity of hydrochloric acid during formation of molybdoniobophosphoric acid.

The effect on absorbance of variation of the phosphate concentration of the initial aqueous solution, which contained 30 μg of niobium and was 2.7×10^{-2} M in molybdate and had an over-all acidity of 0.5 M, is shown in curve A of Figure 6. The effect of varying the molybdate concentration of the initial 3.6×10^{-4} M aqueous phosphate solution at the same acidity, but containing 25 μg of niobium, is shown in curve B of Figure 6.

When an over-all hydrochloric acid concentration of 0.5 M was used, the molybdate and phosphate concentrations in the initial aqueous phase were standardised at 2.7×10^{-2} M and 3.6×10^{-4} M, respectively. Under these conditions it was shown, from determinations by atomic absorption of the molybdenum in the organic phase, that two extractions with 25-ml aliquots of isobutyl acetate quantitatively remove the excess of MPA from the aqueous phase. Radiotracer experiments with niobium-95 proved that no MNPA was extracted into isobutyl acetate under these conditions. After these isobutyl acetate extractions treatment with a single 10-ml aliquot of butanol was shown to extract the MNPA quantitatively. In the previous work on the determination of silicon by a similar amplification procedure, it was found that butanol extracts some of the excess of molybdate. Consequently, in all the present experiments, the butanol phase was washed with butanol saturated with dilute hydrochloric acid before determining its molybdenum content by atomic absorption. Curve C in Figure 6

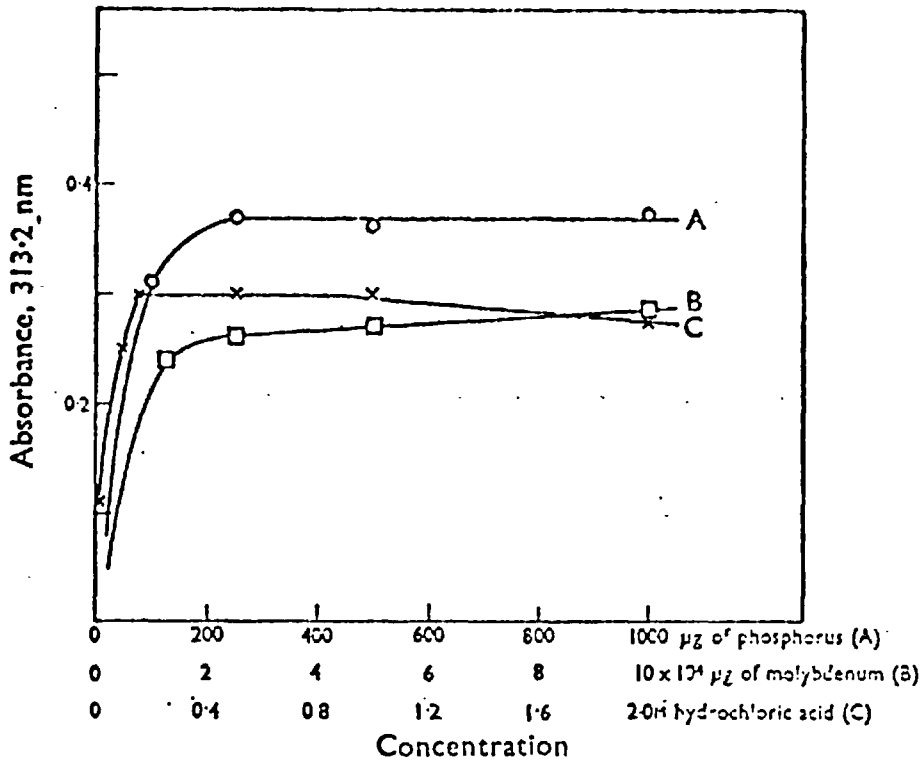


Figure 6. Curve A, effect seen on absorbance for 30 μg of niobium of variation in phosphate reagent concentration (solution 0.5 M in hydrochloric acid, 2.7×10^{-2} M in molybdate); curve B, effect seen on absorbance for 25 μg of niobium of variation in molybdate reagent concentration (solution 0.5 M in hydrochloric acid, 3.6×10^{-4} M in phosphate); curve C, effect seen on absorbance for 25 μg of niobium of variation in molarity of hydrochloric acid used to wash final butanol phase

shows the effect of washing the final butanol phase with various concentrations of hydrochloric acid. From the results obtained it was decided that three rapid washes with 10-ml aliquots of butanol-saturated 0.5 M hydrochloric acid were sufficient.

4.6 The Molybdenum to Niobium Combining Ratio in MNPA

Babko and Shkaravskii (157) observed that the composition of the MNPA in solution depends on the acidity at its formation, and report that the molybdenum-to-niobium ratio is 11:1 at pH 0 to 1.0, 11:2 at pH 1.5 to 3.5 and 11:3 at pH 4.5 to 5.5. Thus the best amplification ratio is obtained by forming the complex at pH 0 to 1.0.

An experiment was devised to establish whether the MNPA was formed and extracted stoicheiometrically as the 11:1 complex under the conditions used in our procedure. Different amounts of niobium were taken through the procedure, and the MNPA in the final butanol phase was decomposed and back-extracted into dilute ammonia solution and diluted to a known volume (25-ml) with distilled water. The molybdenum content of the aqueous solutions was determined by atomic-absorption spectroscopy in a nitrous oxide-acetylene flame. The solutions prepared for the calibration graph for molybdenum in aqueous solution were saturated with butanol and contained

dilute ammonia solution. The results of these determinations gave a reproducible molybdenum-to-niobium ratio of 11.4 ($\pm$ 0.2):1. After correction for the small amounts of molybdenum not removed in the hydrochloric acid washing procedure, which constitutes the blank in the recommended procedure for niobium, a reproducible molybdenum-to-niobium ratio of 11.0 ($\pm$ 0.2):1 was obtained. Thus, under the recommended conditions, it is the 11:1 MNPA that is formed and extracted quantitatively into butanol.

4.7 Preparation of Calibration Graph for Niobium

To each of a series of six 100-ml separating funnels, add 10 ml of the molybdate reagent solution, 0, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the niobium solution (containing 50 μg of niobium per millilitre), 10 ml of the phosphate reagent and sufficient 6 M hydrochloric acid and water to make the final solution 0.5 M with respect to hydrochloric acid. Mix the solutions, allow to stand for about 5 minutes, and proceed with each as follows. Extract the MPA into two 25-ml portions of isobutyl acetate by shaking each time for 1 minute and discarding the organic phase. Add 10 ml of butanol to the remaining aqueous phase and shake for 1 minute to extract the MNPA. Some free molybdate is extracted at this stage into the butanol, but it is

readily removed by rapid successive shakings with three 10-ml aliquots of butanol-saturated 0.5 M hydrochloric acid.

Spray the butanol phase directly into the nitrous oxide-acetylene flame and determine the molybdenum content by atomic-absorption spectroscopy. (Chapter 6).

4.8 Results

The calibration graph obtained when the recommended conditions are used is linear over the range 5 to 50 μg of niobium. After subtraction of the reagent blank the graph passes through the origin, and the absorbances corresponding to these concentrations in the aqueous solution (0.22 to 2.2 p.p.m.) are 0.06 and 0.63. The blank, which results from the small amount of molybdate reagent not removed from the butanol phase by the washing procedure, is reproducible and may be subtracted from the absorbance produced by the standards taken through the procedure. This blank gives rise to an absorbance for molybdenum in the flame of about 0.05 absorbance unit *versus* a butanol solvent blank.

To measure the precision of the system a series of absorbance values was obtained from the replicate analysis of 11 samples each with 23 ml of a solution containing 30 μg of niobium. These gave an average absorbance of 0.39 and the relative standard

deviation was 0.009 absorbance unit or 2.4 per cent.

The effect of twenty-eight other ions on the absorbance produced in the determination of 30 μg of niobium by the recommended procedure has been investigated. An ion was considered not to interfere when an error in the absorbance of less than twice the standard deviation of the determination of niobium alone (4.8 per cent) was produced. The addition of 1 ml of 10^{-1}M solutions of the following ions in the determination of 30 μg of niobium caused no interference: aluminium, silver, bismuth, beryllium, calcium, cadmium, cobalt(II), copper, iron(III), nickel, magnesium, manganese(II), antimony(V), zinc, sulphate, nitrate, fluoride and EDTA. In addition, the presence of 1 ml of 10^{-1} M solutions of the important refractory elements tantalum, tungsten and zirconium produced no interference when taken through the procedure (Table 6). The addition of 1 ml of 10^{-1} M solutions of any of the above twenty-one ions corresponds to a range of excesses by weight over niobium from 30-fold to 700-fold. Of the elements that also form heteropoly acids under similar conditions, arsenic and germanium can be removed by volatilisation of their chlorides, and silicon is eliminated by volatilisation of fluorosilicic acid during the sample preparation procedure. Titanium, however, has been reported to form a molybdotitanophosphoric acid (159) and, although the presence of large amounts causes serious interference, an equal amount of titanium (30 μg)

TABLE 6

Metal ions present (1 ml of 10^{-1} M solutions)	Niobium content (μg)	Absorbance
Ni ; Co	30	0.41
Hg (II) ; Pb	30	0.40
	30	0.41
Mg ; Cu	30	0.44
	30	0.43
Mn ; Zn	40	0.55
Fe (III) ; NH_4	40	0.54
	40	0.54
Bi (III) ; Be	40	0.56
	40	0.55
Ag ; Al	30	0.45
	30	0.45
Ca ; Cd	40	0.56
	40	0.57
Ta	30	0.45
Zr	30	0.44
W	30	0.43
	30	0.44

was found to be tolerable in the procedure. Attempts to eliminate the interference of titanium either by masking or extraction were unsuccessful. Vanadium(V) and chromium(VI) are tolerable up to 3-fold and 45-fold excesses by weight respectively (Table 7).

TABLE 7

EFFECT OF VANADATE AND CHROMATE ON THE NET ABSORBANCE PRODUCED BY 30 μg OF NIOBIUM

Metal present (weight excess)		Absorbance
V	1	0.37
V	2	0.38
V	3	0.38
V	5	0.41
V	8	0.43
V	10	0.48
		0.38
Cr	5	0.41
Cr	10	0.40
Cr	20	0.39
Cr	40	0.40
Cr	45	0.41
Cr	50	0.32
Cr	100	0.22
		0.40

A measure of the accuracy of the procedure was obtained by the determination of niobium in synthetic solutions containing other metals. The results of these analyses are shown in Table 8.

TABLE 8

DETERMINATION OF NIOBIUM IN PREPARED MIXTURES

Niobium added to initial aqueous solution μg per 25 ml	Other ions present, μg	Niobium found, μg
18	Zr (3680)	18
30	Cr(IV) (1350)	30
30	W(VI) (1840)	30.5
30	Co (2945) : Ni (2935)	29.5
30	Cu (3175) : Zn (3270)	30
6	---	6
50	---	49
10	Fe(III) (2800)	10.3
5	---	5
9	Ta (300)	8.9
40	Zr (736)	40.2
30	Ta (600)	30
21	Ta (30,000)	24*
21	W(VI) (1840)	21

* Results high because of traces of niobium in the tantalum used.

The method reported for the indirect determination of niobium by atomic-absorption spectroscopy is much more sensitive than the direct method for niobium in the nitrous oxide-acetylene flame (1 per cent absorption is given by 24 p.p.m. of niobium by the direct method, whereas by this method 1 per cent absorption results with an initial aqueous niobium solution of 0.015 p.p.m.). Because of the selectivity with which molybdoniobophosphoric acid can be formed and extracted, the selectivity of the procedure compared with the direct method is good. Extraction of MNPA into butanol achieves a separation of the niobium from other major element components of samples. In the direct method, the presence of large amounts of other elements frequently suppresses the niobium absorbance because of the formation of oxide in the flame, so that solvent extraction may be required. Thus the use of a solvent-extraction procedure in this indirect method does not constitute a disadvantage compared with the direct atomic-absorption method. The method reported is precise and, after the dissolution of the sample, almost as rapid as the direct procedure.

CHAPTER 5

THE INDIRECT COMPLEXOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF ORTHOPHOSPHATE

Several methods are available for the indirect titrimetric determination of orthophosphate with EDTA solution which utilize the precipitation of an insoluble metal phosphate. These methods usually entail either the collection of the precipitate and determination of the metal content after its dissolution (160, 161), or determination of the excess metal ion content of the filtrate after filtration (162, 163, 164). The methods are usually most satisfactory for the determination of semi-micro or macro amounts of phosphate (164, 165).

It was decided to investigate the possibility of determining microgram amounts of orthophosphate by precipitation of thorium orthophosphate with excess thorium nitrate solution and then back titrating this excess with EDTA solution.

Although the insolubility of thorium orthophosphate in acidic medium has been employed for the separation of thorium from other metals (166), it does not appear to have been utilized as the basis of a method for the indirect determination of phosphate. Thorium was chosen as a suitable precipitant firstly because its phosphate is insoluble in weakly acid medium, whereas many of its

other salts are soluble, and secondly because it may be titrated satisfactorily with EDTA solution in acid medium using xylenol orange as indicator (167, 168).

It was found on a qualitative scale that when an excess of thorium nitrate solution was added to a neutral or slightly acid solution of orthophosphate, a white gelatinous precipitate was obtained, the bulk of which naturally corresponded to the amount of orthophosphate initially present. Thus when microgram amounts of orthophosphate were employed, no precipitate could be detected visually. However when xylenol orange indicator solution was added to this solution, the excess of throium could easily be titrated with EDTA solution. The value of the titre so obtained was found to be significantly less than that obtained when no phosphate was present and as such the possibility of determining phosphate by this means and without filtration of the solution was studied.

5.1 Apparatus

An arrangement similar to that described by Belcher et al. (169) for small scale titration with syringe burettes of 0.50 ml capacity was employed throughout. Laboratory 10-ml beakers or sample bottles were used as titration flasks.

5.2 Reagents

Stock orthophosphate solution

Dissolve 0.4392 g of analytical reagent grade potassium dihydrogen orthophosphate in distilled water and dilute to one litre.

1 ml of stock solution ≡ 100 μg of phosphorus.

EDTA solution

Prepare a 10^{-2} M solution of analytical reagent grade disodium EDTA in distilled water.

Thorium stock solution

Dissolve 2.535 g of analytical reagent grade thorium nitrate, $Th(NO_3)_4.6H_2O$, in distilled water and dilute to one litre. Standardize with EDTA solution using xylenol orange indicator at pH 3.

1 ml of stock solution ≡ 1,000 μg of thorium. (The strengths of the thorium and EDTA solutions were chosen as such to eliminate the need of recharging the syringe burette during titrations.)

Indicator solution

0.1 per cent aqueous solution of Xylenol Orange. This was preferred to an alcoholic solution in order to prevent any possible solubility effects.

Acetic acid

10 per cent aqueous acetic acid solution.

5.3 Recommended Procedure

Transfer the sample solution (containing 10 - 50 μg of phosphorus as orthophosphate in a volume not greater than about 4 ml.) to the titration flask. Add 1 ml. of the stock thorium solution from a pipette and dilute to about 5 ml. with water if necessary. Stir the solution magnetically and add 4 drops (ca 0.2 ml.) of 10 per cent acetic acid followed by 4 drops (ca 0.2 ml.) of 0.1 per cent xylenol orange indicator solution. Titrate the solution with EDTA (10^{-2} M) from the syringe burette until the appearance of a red precipitate. Add more indicator (1 drop) and titrate further to the lemon yellow end point.

5.4 Results

When the solution containing phosphate and an excess of thorium was titrated with EDTA solution at ca pH 3, a red precipitate was obtained just before the end point. The supernatant solution still showed the characteristic red-purple colour of the soluble thorium-xylenol orange complex, however, provided that sufficient indicator was present. Thus owing to depletion of the indicator concentration in the solution by its adsorption on the thorium

phosphate aggregate in this way, an additional drop (ca 0.05 ml.) of indicator solution was required after the appearance of the precipitate and before the end point. The supernatant solution was then further titrated to the yellow end point, with the precipitate being allowed to settle between additions of titrant. The use of filter pulp, cotton wool and various organic liquids (eg nitrobenzene) as precipitate collectors was examined but were found to be of no substantial benefit.

5.5 Effect of Buffer and Indicator Concentrations

To a series of titration flasks containing phosphate and thorium solution which had been diluted to approximately 5 ml. with water, were added 0 - 10 drops (0 - 0.5 ml.) of 10 per cent acetic acid and 3 drops (0.15 ml.) of the indicator solution. The solution was then titrated with 10^{-2} M EDTA solution, an extra drop of indicator being added after formation of the precipitate. Consistent results were obtained for the addition of 3 - 6 drops of the acid while above and below this amount the end point was sluggish and tended to revert to the original colour. Narrow range indicator paper was used to measure the pH of solutions containing between three and six drops of acid both before and after titration and this did not vary substantially from 3 (ie within the range 2.8 - 3.2). As such, 4 drops of 10 per cent

acetic acid (0.20 ml.) for a solution volume of approximately 5 ml. was chosen as optimal.

Similarly, varying amounts of 0.1 per cent aqueous xylenol orange indicator solution (1 - 10 drops; 0.05 - 0.5 ml.) were added to a series of solutions containing phosphate and throium in a volume of ca 5 ml. and at pH 3. These solutions were then titrated as described previously. The bulk of the precipitate obtained was proportional to the amount of indicator initially present but was also found to vary with the phosphate content of the solution. When a large volume (6 - 10 drops) of indicator was employed the end point was diffuse and difficult to observe, while small volumes (1 and 2 drops) of indicator produced a barely visible precipitate especially when smaller amounts of phosphate were determined. The range 3 - 5 drops (0.15 - 0.25 ml.) was found to produce good end points and gave consistent results for all the phosphate concentrations examined. Although 4 drops of indicator solution was chosen as optimum for an unknown phosphate concentration, it was found preferable to have the indicator strength inversely proportional to the phosphate concentration when "known" amounts of phosphate were being determined.

Also, provided the sample solution to be titrated was maintained at ca pH 3, the theoretical titre was obtained for solution volumes which varied between 3 and 10 ml. Repetitive titrations on various phosphate sample solutions showed that under

the recommended conditions the reaction

$$3Th^{4+} + 4PO_4^{3-} \longrightarrow Th_3(PO_4)_4$$

proceeds quantitatively, as the excess thorium available for titration was equivalent to the amount theoretically expected.

5.6 Effect of Diverse Ions

A study of the effects of the common anions was made and the presence of a 100-fold weight excess of the following caused no interference on the determination of 10 to 50 μg of phosphorus:- chloride, bromide, iodide, nitrate, sulphate, perchlorate and silicate. Interference due to precipitate was caused by the presence of a 100-fold excess of fluoride, molybdate, selenite and tellurite. Arsenate and borate were also found to interfere at this level by destroying the thorium-xylenol orange colour prior to titration, while vanadate interfered with the observation of the end point. Cations were not studied as their behaviour is predictable. Heavy metal ions titratable with EDTA must be removed from the sample by preliminary cation exchange treatment. The results of the analyses of synthetic orthophosphate sample solutions in the presence of other common anions is shown in Table 9.

TABLE 9

DETERMINATION OF PHOSPHORUS IN SYNTHETIC ORTHOPHOSPHATE SOLUTIONS

Phosphorus taken, μg.	Theoretical titre, ml.	Titre obtained, ml.	Phosphorus found*, μg.	Foreign ions Present (weight excess of each)	
10.0	0.4068	0.4066	10.10	SO_4	100
				Cl	100
12.5	0.4008	0.4010	12.40	NO_3	100
				Br	100
15.0	0.3948	0.3940	15.30	I	100
				SO_4	100
20.0	0.3827	0.3824	20.10	ClO_4	100
				SO_4	150
				SiO_3	100
				Cl	100
25.0	0.3706	0.3706	25.00	Cl	500
				SO_4	250
				NO_3	200
				Br	100
				Cl	200
				ClO_4	200
40.0	0.3343	0.3350	39.7	Br	100
				I	100
				Cl	100
				Br	100
50.0	0.3101	0.3098	50.1	Cl	250
				SO_4	100
				NO_3	100
				ClO_4	100
				SiO_3	100
				Br	100
				I	100
				Cl	100

* Average of a minimum of 10 determinations.

CHAPTER 6

THE DETERMINATION OF MOLYBDENUM IN ALLOY STEELS BY ATOMIC-ABSORPTION SPECTROSCOPY IN A NITROUS OXIDE-ACETYLENE FLAME

Molybdenum is an element which forms a relatively refractory oxide, and as such its determination by atomic absorption spectroscopy is not very sensitive in conventional flames. Before any appreciable absorption by atomic species can be observed it is necessary to provide reducing conditions within a hot flame. For an air-acetylene flame this requires that the flame be luminous or fuel rich. David (170) and later Mostyn and Cunningham (171) have described the determination of molybdenum in steels using such a flame. It is possible, however, to obtain a population of ground state atoms suitable for A.A.S. by the use of a non-luminous nitrous oxide-acetylene flame (149) which provides both reducing conditions and is sufficiently hot to promote the dissociation of most salts. The possibility of utilizing this flame for the determination of molybdenum both in pure solutions and steel samples was examined.

6.1 Experimental

The equipment used in this work was the Unicam SP 900 A flame spectrophotometer with a Unicam molybdenum hollow-cathode lamp. The instrument conditions used throughout were: slit width, 0.02 mm; wavelength, 3132 Å; lamp current, 15 mA. The burner supplied with the SP 900 A for atomic-absorption measurements in air-acetylene was replaced by a brass burner of similar dimensions for the nitrous oxide-acetylene flame (cf. Fig. 7). The burner head-plate used, however, had a slit 2 inches long and 0.015 inch wide, and was cooled by an attached water-cooled plate clamped to the side of the burner. This system requires that a larger acetylene jet (0.052 inch in diameter) be used at the base of the burner than when an air-acetylene burner and flame are used. Aspiration via the SP 900 A atomiser was by nitrous oxide (pressure 15 lb per sq. inch) and the acetylene pressure used was just sufficient to produce the maximum height of red "feather" in the flame without luminosity. The burner height was adjusted so that as much as possible of the converging light beam from the hollow-cathode lamp passed through the red "feather" above the primary reaction zone. The strongest absorbance for molybdenum is always obtained in this band, which is highly characteristic of the nitrous oxide-acetylene flame. The flame was first ignited on an air-acetylene mixture, and the air was then gradually replaced

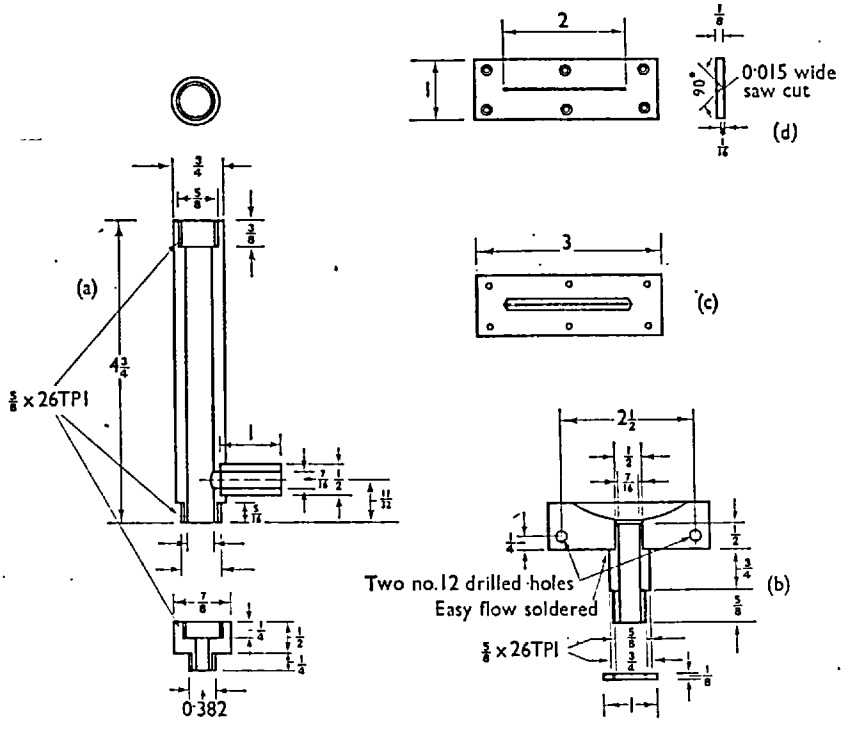


Fig. 7. Diagram showing burner parts with dimensions; all measurements are in inches. (*a*) Burner pre-mixing chamber, side view; (*b*) burner head, side view; (*c*) under surface of burner-head plate; (*d*) upper surface of burner-head plate

by nitrous oxide (via two rotameters and a T-piece arrangement) until the air was completely shut off. Although with experience this method of obtaining a nitrous oxide-acetylene flame became a standard routine, it should be noted that great care should be taken when "bleeding in" nitrous oxide into the air-acetylene flame. It was also found advantageous to aspirate distilled water when undertaking the change-over. This ensures that the water trap pressure control is kept at a constant head and minimizes the chances of "flash-back". Under no circumstances could an organic or combustible solvent be aspirated with the available burner! To turn off the flame the process is completely reversed whereby the nitrous oxide is gradually replaced by air until the nitrous oxide is completely shut off, again aspirating distilled water. (It should be mentioned that although these procedures may appear somewhat hazardous, the modern nitrous oxide-acetylene burners and control systems enable the flame to be ignited either directly or by a rapid change from air to nitrous oxide. Although the author and his colleagues had several minor "flash-backs" in the pioneering experiments, no such misfortunes have occurred since the introduction of commercial nitrous oxide-acetylene A.A.S. equipment).

A calibration graph was prepared for molybdenum in the range 20 to 200 p.p.m. in an aqueous solution. These concentrations of molybdenum gave absorbance values from 0.06 to 0.39 and a 2 p.p.m. molybdenum solution gave 1 per cent. absorption at 313.2 n.m.

However, when the molybdenum solutions contained a similar amount of iron and acid to that expected to be present in the steel samples, it was found that the absorbance values were severely depressed. Thus the effect of iron on the absorbance of a solution which contained 200 p.p.m. of molybdenum was studied. The results of this investigation are shown in Figure 8. The presence of the acids required for dissolution of the steel samples was found to be negligible. It can be seen from Figure 8 that provided the solution aspirated was about 1 per cent. with respect to iron (111), the ratio of excess of iron to molybdenum was not critical and a rectilinear calibration graph for molybdenum was obtained.

Determination of the atomizer efficiency for a pure aqueous 200 p.p.m. molybdenum solution and for a similar solution which contained 1 per cent. of iron and was 2 M with respect to hydrochloric acid revealed only slightly lower efficiency of sample transfer to the flame for the solution containing iron. The suppression of the molybdenum signal therefore results from the presence of the iron itself in the flame. It was therefore decided that if 1-g samples of low alloy steels were to be taken, their molybdenum content would have to be obtained by comparison with a calibration graph, prepared from standards containing similar amounts of iron (1 g per 100 ml.).

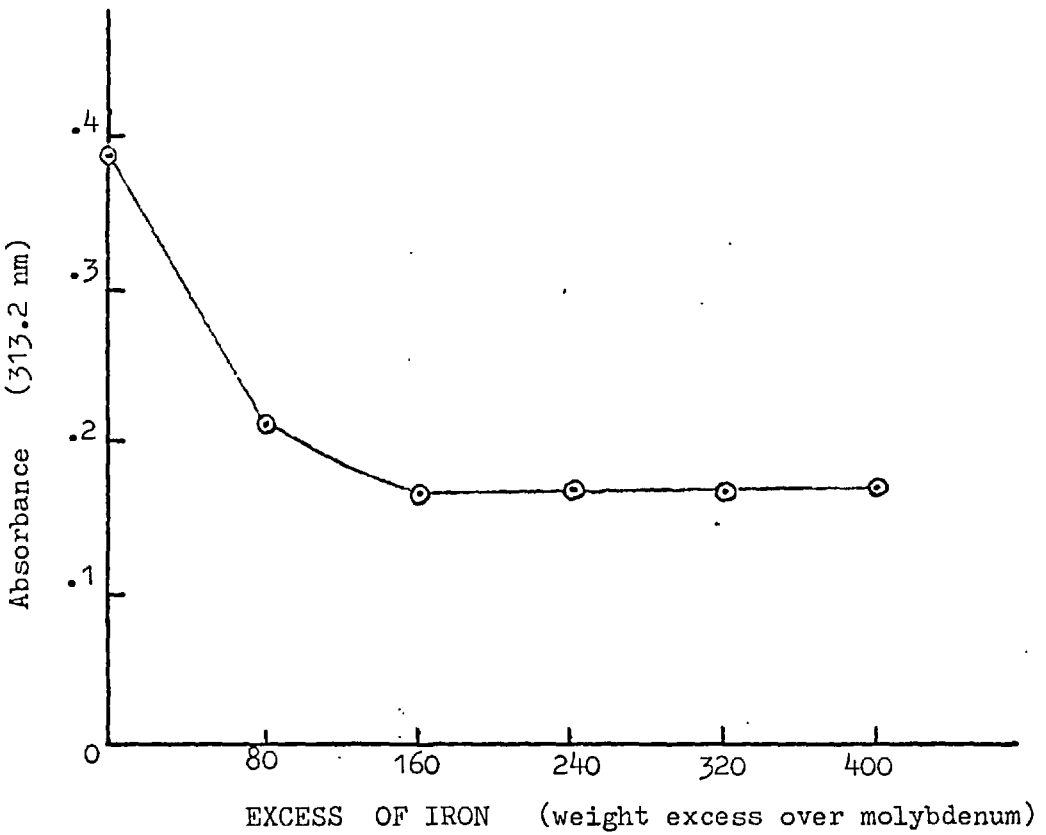


Fig. 8 Effect of iron on the absorbance of a 200 ppm molybdenum solution.

6.2 Reagents

Molybdenum (VI) solution, 0.1 M

Dissolve 17.66 g of analytical-reagent grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 1 litre of distilled water in a calibrated flask.

Iron (III) chloride solution

Weigh 48.46 g of analytical-reagent grade iron (III) chloride, $FeCl_3.6H_2O$, and dissolve in 100 ml of distilled water.

1 ml of solution = 0.1 g of iron (III).

6.3 Preparation of Calibration Graph

Transfer accurately 0.5, 1.0, 2.0, 3.0 and 4.0 ml of 0.1 M molybdenum solution to a series of 100-ml calibrated flasks. Add 10 ml of the standard iron solution, 20 ml of concentrated hydrochloric acid and 2 ml of nitric acid to each, and dilute to 100 ml with distilled water. Measure the absorbance of the solutions at 3132 Å in the nitrous oxide-acetylene flame. The calibration graph is linear, passes through the origin and produces absorbance values between 0.08 and 0.49 for 50 and 400 p.p.m. of molybdenum (3.3 p.p.m. of molybdenum produce 1 per cent absorption).

6.4 Preparation of Samples

Weigh accurately about 1.0 g of the steel sample into a 100-ml beaker. Add 20 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid, and warm to aid dissolution. After effervescence has ceased, boil the solution. Cool, dilute to 50 ml with distilled water, and transfer to a 100-ml calibrated flask. For low alloy steels, dilute to 100 ml with distilled water. For high alloy steels, add the calculated volume of iron (III) chloride solution to make the total weight of iron present about 1 g, and then dilute to 100 ml with distilled water. Spray the solutions into the nitrous oxide-acetylene flame using the instrumental conditions described above, and measure the absorbance of the 3132 Å molybdenum line for each sample. By interpolation, determine the molybdenum content of each from the calibration graph.

6.5 Results

The recommended procedure works well for the rapid determination of molybdenum in low alloy steels, as shown in Table 10. When applied to high alloy steels, however, the incorporation of 1 g of iron into the standard solutions used to prepare the calibration graph results in over-compensation, as the steel samples taken contain only 60 to 80 per cent. of iron.

TABLE 10

DETERMINATION OF MOLYBDENUM IN ALLOY STEELS

Sample number	Certificate analysis, molybdenum, per cent.	Molybdenum found, per cent.	Other major constituents, per cent.			
Low alloy steel -						
B.C.S. 252/1	1.05	1.06, 1.04	Nickel	2.23	-	
B.C.S. 253/1	0.67	0.66, 0.67	Nickel	1.00	Chromium	0.99
B.C.S. 251/1	1.57	1.53, 1.56	Nickel	1.24	Manganese	1.5
B.C.S. 255/1	0.30	0.30, 0.31	Nickel	4.98	-	
B.C.S. 256/1	0.53	0.53, 0.52	Chromium	2.3	Manganese	1.02
B.C.S. 258/1	0.83	0.83, 0.84	Chromium	1.29	-	

The procedure adopted for these samples was, therefore, modified, and additional iron in the form of standard iron (III) chloride solution was added to the 1-g steel samples after dissolution to make the total weight of iron present about 1 g. This procedure enables the correct results to be obtained for this type of steel. The results for these analyses are also shown in Table 11.

It is also possible, when only high alloy steels are to be analysed, to construct a calibration graph from standard solutions containing the same weight of iron (0.6 to 0.8 g) as that present in the high alloy steel samples. This would allow a more sensitive means of determining molybdenum in high alloy steels, but would necessitate the use of two calibration graphs. The method proposed here sacrifices some sensitivity for these high alloy steels, but is applicable to all types of steel with only one calibration graph.

After sample dissolution and dilution, two steel samples and two standard check solutions may be aspirated and measured in 10 minutes. The method is, therefore, easy to operate, and is rapid and precise in practice. No chemical manipulation or pretreatment of the steel sample is required other than its dissolution in acid. A method could be devised to analyse steels of lower molybdenum content with some sacrifice of rapidity and simplicity by the introduction of a concentration stage involving extraction of the molybdenum from the iron into an organic solvent, either

TABLE 11

DETERMINATION OF MOLYBDENUM IN ALLOY STEELS

Sample number	Certificate analysis, molybdenum, per cent.	Molybdenum found, per cent.	Other major constituents, per cent.					
Alloy -								
B.C.S. 219/2	0.43	0.46, 0.42	Nickel	2.54	Chromium	0.8	-	
B.C.S. 220/1*	5.20	5.15, 5.30	Chromium	5.13	Tungsten	6.8	Vanadium	2
B.C.S. 241/1*	0.52	0.52, 0.53	Chromium	5.03	Tungsten	19.6	Cobalt	5.6
B.C.S. 246	2.89	2.89, 2.86, 2.98	Chromium	18.8	Nickel	12	Niobium	0.8
B.C.S. 336	2.42	2.50, 2.42, 2.40	Chromium	17.6	Nickel	9.5	Manganese	0.8
62/16/2 XB stainless	1.10	1.17, 1.10	Chromium	13.6	Nickel	10.2	Manganese	1.4
62/16/3 XC stainless	2.25	2.28, 2.24	Chromium	15.46	Nickel	10.13	Manganese	1.37

* 2 ml of 40 per cent. hydrofluoric acid was added to both sample and standards to retain tungsten in solution.

as molybdenum 8-hydroxyquinolinate or molybdenum(V) thiocyanate. It should then be possible to determine as little as 0.01 per cent. of molybdenum in mild and carbon steel by atomic-absorption spectroscopy. This possibility has not been examined as most interest appears to lie in steels with molybdenum contents greater than 0.2 per cent.

6.6 Discussion and Comparison of Methods

David (170), and Mostyn and Cunningham (171), both used fuel-rich luminous air-acetylene flames for determining molybdenum. The sensitivities they report benefit from both scale-expansion of the signal attentuation and from the use of relatively long absorbance path lengths. The molybdenum absorbance also varies markedly with the composition of the air-acetylene mixture, and the sensitivities quoted are those obtained with the recommended flow-rates. These are not expressed in litres per minute of air and acetylene, and are thus difficult to compare. The sensitivity is higher in the richer flames, but the noise-to-signal ratio becomes rather great. Mostyn and Cunningham sacrifice considerable sensitivity by using the 3798 Å resonance line of molybdenum to reduce null meter noise.

Several other resonance lines, in addition to the 3132 Å line, were examined by the author and were found to give either

inadequate sensitivity or high noise levels. The author's results for the 3798 Å resonance line with the nitrous oxide-acetylene flame agree well with those of David for luminous air-acetylene, i.e., about half the sensitivity is obtained compared with that available at 3132 Å. The sensitivity, expressed as p.p.m. required to produce 1 per cent absorption per unit path length, is therefore, greater when using a non-luminous nitrous oxide-acetylene flame than both of those previously quoted and is also better than that obtainable with the author's instrumentation when using a luminous air-acetylene flame, (c.f. Table 12). The sensitivity found for the air-acetylene flame agrees quite well with the manufacturer's quoted sensitivity (2 p.p.m.).

It is physically more pleasant to work with the nitrous-oxide acetylene flame because it radiates less heat into the monochromator than the luminous air-acetylene flame, and the noise levels are considerably less than those obtained with air-acetylene. In addition, the absorbance resulting from a given amount of molybdenum is not as dependent on the flame composition as it is with air-acetylene.

The procedure recommended here for determining molybdenum in alloy steels requires considerably less sample pre-treatment than those used by David and by Mostyn and Cunningham. David points out that the addition of aluminium chloride to both sample and standard solutions will suppress all major interferences with

TABLE 12

COMPARISON OF SENSITIVITIES FOR ATOMIC-ABSORPTION SPECTROSCOPY OF MOLYBDENUM

	Flame and instrumental conditions	Molybdenum, sensitivity for 1 per cent. absorption, p.p.m. At recommended conditions	At unit path length
David	A.D., scale-expansion, luminous air-acetylene, 10-cm path length, 3132Å	3.3*	33*
Mostyn and Cunningham	A.C., scale expansion, luminous air-acetylene, 10-cm path length, 3798Å	1.3†	13†
Proposed method	A.C., no scale-expansion, 3132 Å		
	(a) luminous air-acetylene, 7-cm path length	2.3	16
	(b) nitrous oxide - acetylene, 5-cm path length	2.0	10

* Corrected for scale-expansion by David's own results.

† Uncorrected for scale-expansion (no results available).

molybdenum absorption and give a result for any sample solution to about 10 per cent. accuracy. He also suggests, to obtain more accurate results, that the major element composition be taken into account and the standards prepared accordingly, and that aluminium chloride should be added as before. The author's results for the analysis of steels of different minor element compositions reveal that the addition of aluminium chloride is not necessary to suppress interference or to obtain accurate results if the major element is incorporated in the standards used to prepare the calibration graphs. Mostyn and Cunningham, however, found that addition of aluminium chloride and nitric acid to all solutions was not always effective in controlling interferences. They recommended the use of ammonium chloride as an interference suppressor in the determination of molybdenum in iron(III) alloys, and did not add iron to the standard solutions.

It is probable that these conflicting reports arise from the fact that the fuel-rich, air-acetylene flame acts as a rather inefficient medium for the production of molybdenum atoms.

The author's recommended procedure reveals that the nitrous oxide-acetylene flame is more efficient at producing molybdenum atoms capable of absorbing radiation. Mostyn and Cunningham also used the method of standard additions for their analyses whereas in the method proposed the only pre-treatment of samples arises with higher alloy steels when an addition of iron(III) chloride is made to compensate for matrix composition.

CHAPTER 7

CONCLUSIONS

The work described in this thesis has shown how elements, which previously were either impossible to determine satisfactorily by atomic absorption spectroscopy or could only be determined with limited sensitivity, can be successfully analysed by formation, extraction and measurement of their heteropolymolybdates. The determination of the molybdenum content of these heteropoly species by A.A.S. has been found to be of substantially greater sensitivity by measurement in a nitrous oxide-acetylene flame than that which could be obtained in the existing conventional flames. Although measurement of the molybdenum atoms in this manner loses on overall sensitivity to other methods (e.g. molecular absorption spectrophotometry and spectrofluorimetry), the rapidity of the proposed methods more than compensates for this disadvantage. Probably the main disadvantage of the author's procedures is the lack of selectivity in the extraction of the ternary heteropolymolybdates. The extraction of the binary phosphomolybdate is, however, very selective and a titrimetric method for determining microgram amounts of phosphate has been re-examined. The heteropoly molybdates of the other elements studied (Si and Nb) are both extracted

into a non selective solvent and as such, elements capable of forming heteropoly species must be eliminated. The butanol solvent employed, however, has been found to be the most satisfactory for direct aspiration into the flame, and confers good sensitivities on the A.A.S. finish to the determination. If selective solvents for the binary silicomolybdate could be found, their ability to be sprayed directly into the flame would be a valuable asset, as this would eliminate the need of retrograde extraction into an ammoniacal medium.

It is stated in the literature (172) that at least 35 elements are capable of functioning as the hetero atom in heteropolymolybdate anions. However the ratio of molybdenum to element in the heteropoly species varies. Thus elements such as phosphorus, arsenic, silicon, germanium, etc. form anions of the general formula

$$\left[X^{n+} \quad Mo_{12} \quad O_{40} \right]^{(8-n)^-}$$

giving an amplification factor of twelve, whilst the elements tellurinum, iodine, cobalt, aluminium, chromium, iron and rhenium yield anions of the general formula

$$\left[X^{n+} \quad Mo_{6} \quad O_{24} \right]^{(12-n)^-}$$

where the amplification factor obtained by measuring the associated molybdenum atoms is six. Analogous heteropolytungstates exist,

but since the sensitivity of measurement of tungsten by A.A.S. is some thirteen times less than that obtainable for molybdenum even in a nitrous oxide-acetylene flame with sophisticated instrumentation (5.4 p.p.m. of W at 2551 Å and 0.4 p.p.m. of Mo at 3132 Å produce 1 per cent absorption respectively), the use of these complexes does not seem favourable for amplification of the heteroatom.

All these preceding heteropoly species have been of the binary type, but there also exists the ternary heteropoly molybdates, of which the phosphovanadomolybdate is probably the best known. This complex is generally used as a method of increasing the sensitivity in the determination of phosphate by molecular absorption spectrophotometry, but with the use of suitable solvents could easily be used to determine vanadium by indirect A.A.S. It is also rather fortunate that other ternary complexes contain elements which are difficult to determine with good sensitivity by direct A.A.S. and these lend themselves quite readily to an indirect analysis. Thus in Chapter 4, niobium can easily be determined by the indirect measurement of the associated molybdenum. Other elements which combine in a similar manner are hafnium, cerium, thorium, zirconium and titanium. All these have very low sensitivities by direct A.A.S. (sensitivities for 1 per cent absorption using the Techtron A.A.4 spectrophotometer: - Hf 14 p.p.m. at 3073 Å; Ce 250 p.p.m. at 5200 Å; Th 150 p.p.m. at 3719 Å; Zr 15 p.p.m. at 3601 Å; Ti 3.5 p.p.m. at 3643 Å.)

We have therefore conducted qualitative studies with their heteropolymolybdates. Hafnium was not studied. Thorium, zirconium and titanium formed the ternary complexes with phosphate and molybdate quite readily, while all experiments to produce the cerium analogue resulted in the precipitation of cerium molybdate. Investigation of the cerium complex was abandoned and studies were directed towards the other three elements. The general procedure was similar to that described for niobium, in that both the binary phosphomolybdate (MPA) and ternary complexes (MXPA) were formed in acid medium and the MPA then selectively extracted into either isobutyl acetate or a 4:1 mixture of chloroform-butanol. The MXPA species were then extracted into butanol and the molybdenum determined by A.A.S. The individual metal solutions used initially were all rendered silicon free in the manner described earlier (Chapter 4). All three ternary complexes were formed and extracted into butanol and therefore there is a very real possibility of indirect amplification of these elements. Further work has been undertaken on the titanophosphomolybdate with a view to development of an amplification method for titanium.

7.1 A Study of the Titanium - molybdate - phosphate System

This system was studied in a similar manner to that employed for the niobium analogue. The reagents used throughout were the

same except for the introduction of a 4:1, v:v chloroform-butanol mixture in place of iso butyl acetate. Also a 5 per cent solution of analytical reagent grade potassium aluminium sulphate in the molybdate reagent was prepared. This was prestripped of any silicate by making the solution 0.15 M in hydrochloric acid and extracting with butanol. The aqueous phase was stored in polythene and prepared fresh weekly. The titanium stock and sample solutions were rendered silicon free as described for niobium in Chapter 4.

Following the work on the determination of niobium, in which titanium interfered seriously, it was hoped that titanium would be able to directly replace niobium under the conditions employed. However at this acidity, 0.5 M in hydrochloric acid, low results were obtained and this was attributed to the incomplete formation or destruction of the molybdotitanophosphate complex (MTPA). Also since fluoride is known to destroy the ternary complexes, and as the silicon free residue of TiO_2 requires more hydrofluoric acid for dissolution before dilution as a standard solution, it was thought that the presence of the excess fluoride ions could result in this loss of sensitivity. Attempts were therefore made to mask the fluoride by the addition of borax, beryllium sulphate or potash alum. These salts were initially added as solids to solutions containing phosphate and molybdate, at an overall hydrochloric acid molarity of 0.5 M,

before the addition of titanium. The resulting solutions were then taken through the procedure recommended for niobium. The addition of 0.5 gm of potash alum was found to give the greatest overall sensitivity and the lowest blank. This blank, however, was still quite high (ca 0.20 absorbance units) owing to silicate in the potash alum, but was easily reduced to a consistent and acceptable value (0.04 absorbance units) by using the silicon prestripping method described earlier in this chapter. Half a gram of alum was found sufficient to give complete masking for the various fluoride concentrations which would normally be encountered. (Figure 9).

Iso butyl acetate, which had previously been used as an extractant for phosphomolybdic acid, was now replaced by the chloroform-butanol mixture. This was done to facilitate the transfer of the organic solvent. The chloroform-butanol was found to be equally selective for the extraction of MPA from MTPA, but complete extraction required three 25 ml aliquots.

7.2 Apparatus and Reagents

As well as the Techtron AA4 flame spectrophotometer (Chapter 4), an EEL 140 flame spectrophotometer was employed during these studies. This was fitted with a 5 cm nitrous oxide-acetylene burner and a molybdenum hollow cathode lamp.

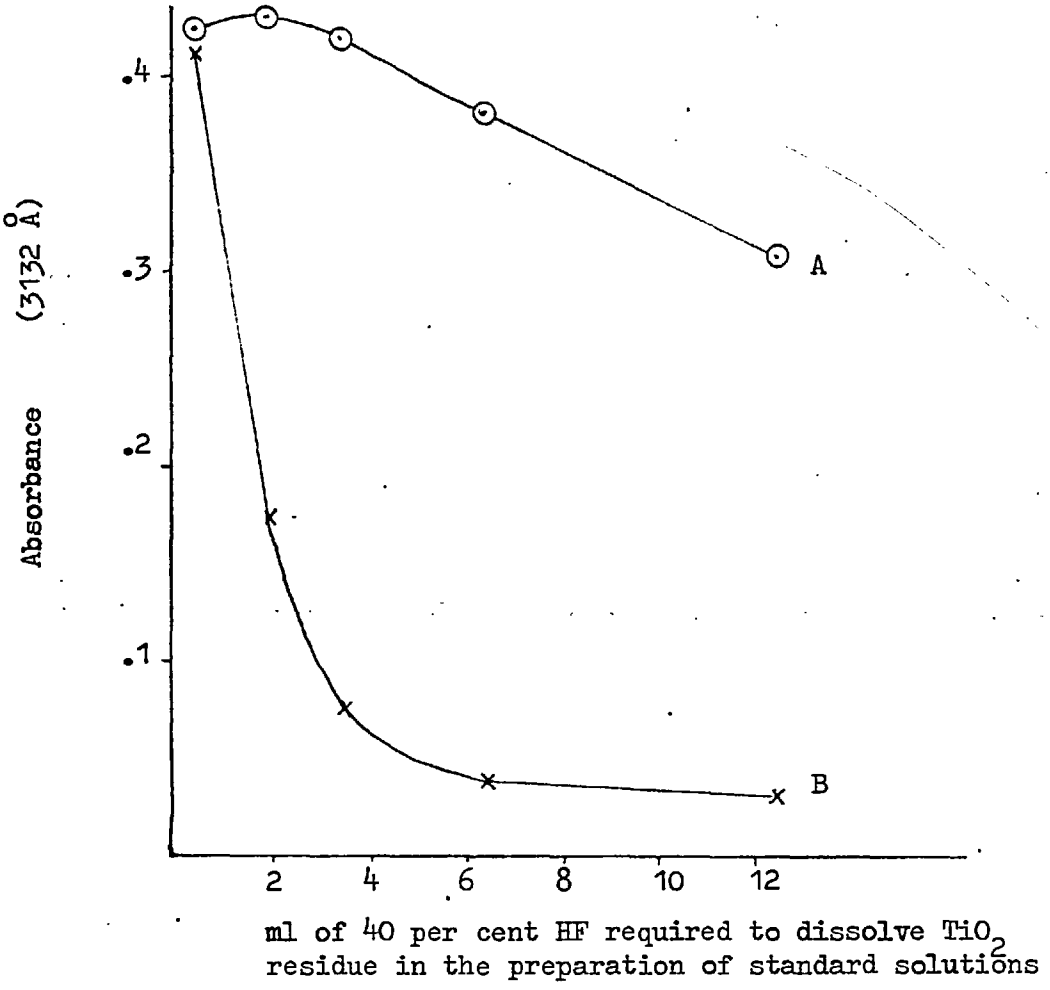


Figure 9. The effect seen on absorbance for 40 μg of titanium on variation of hydrofluoric acid required in preparation of standards. Curve A with 0.5 gm of potash alum and Curve B without alum in the molybdate reagent.

The instrument settings were: - slit width, 400 μm; wavelength, 3132 Å; nitrous oxide pressure, 10 p.s.i; the acetylene flow rate and light path through the flame were adjusted as described for the AA4 spectrophotometer. Although the EEL 140 instrument was used to investigate the variation in sensitivity with acid concentration, reagent concentration etc., throughout these studies, it lacked the sensitivity which could be obtained on the Techtron AA4 machine and as such was not used for precision or calibration measurements.

The reagents used were similar to those employed in the determination of niobium except for the refinements mentioned earlier. Silicon free titanium solutions were prepared by the hydrofluoric acid volatilisation as described for niobium and contained 50 μg of titanium per ml.

7.3 Recommended Procedure

To a series of six 100-ml separating funnels add successively 10 ml of the mixed prestripped molybdate-alum solution, 10 ml of the phosphate solution, sufficient 6 M hydrochloric acid to make the acidity 0.5 M and 0, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the 50 p.p.m. titanium solution. Mix the solutions and allow to stand for about 5 minutes. Extract the MPA in three 25 ml aliquots of 4:1 chloroform-butanol by shaking each time for 1 minute

and discarding the lower organic phase. Add 10 ml of butanol and extract the MTPA by shaking for 1 minute. Discard the aqueous phase and remove any free molybdate extracted into the butanol at this stage by rapid successive shakings with three 10-ml aliquots of butanol-saturated 0.5 M hydrochloric acid. Spray the washed butanol phase directly into the nitrous oxide-acetylene flame and determine the molybdenum content by atomic absorption spectroscopy at 3132 Å, (Chapter 6).

7.4 Formation and Extraction of MTPA

Both MPA and MTPA were allowed to form in acidic solution and the MPA extracted into chloroform-butanol. It was shown that three 25 ml aliquots were sufficient to quantitatively remove the MPA without extracting the MTPA. This was proved by separating the organic layers, washing with 2N hydrochloric acid to remove any free molybdate mechanically transferred across the phase boundary, and then back-extracting the MPA into 4N ammonia solution. The molybdenum content of these alkaline solutions was measured by A.A.S. The non-extraction of titanium was shown by measurement of the aqueous phases before and after extraction using the technique of thermal emission in a sheathed nitrous oxide-acetylene flame (173).

After extraction of MPA the remaining MTPA was extracted into butanol. 10 ml proved sufficient for all the titanium

concentrations examined. Again, as had been noticed when studying silicon and niobium by a similar amplification procedure, the butanol was found to extract free molybdate reagent and as such this was removed by rapid successive shakings with three 10-ml aliquots of butanol-saturated 0.1 M hydrochloric acid. The molybdenum content of these butanol phases was measured by A.A.S. in the nitrous oxide-acetylene flame.

The effect on the final molybdenum absorbance at 313.2 nm on variation in the acidity of the initial aqueous solution which was 3.6×10^{-4} M in phosphate, 2.7×10^{-2} M in molybdate containing 5 per cent potassium aluminium sulphate and contained 50 μg of titanium is shown in Figure 10.

The effects on absorption of varying the initial phosphate and molybdate concentrations of solutions which were 0.5 M in hydrochloric acid and contained 50 μg of titanium are shown in Figure 11.

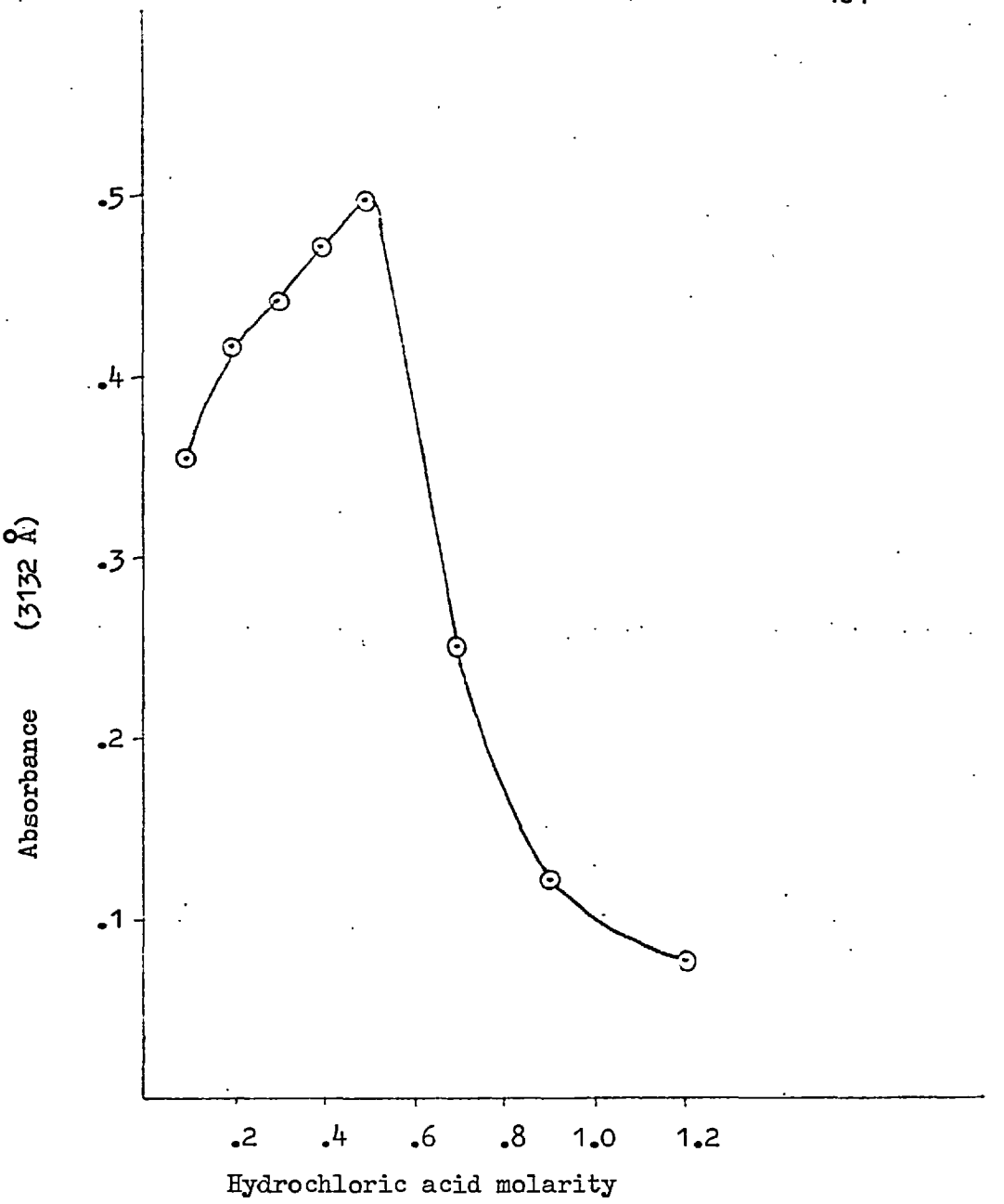


Figure 10. Effect on absorbance for 50 μg of titanium of molarity of hydrochloric acid during formation of molybdotitanophosphoric acid

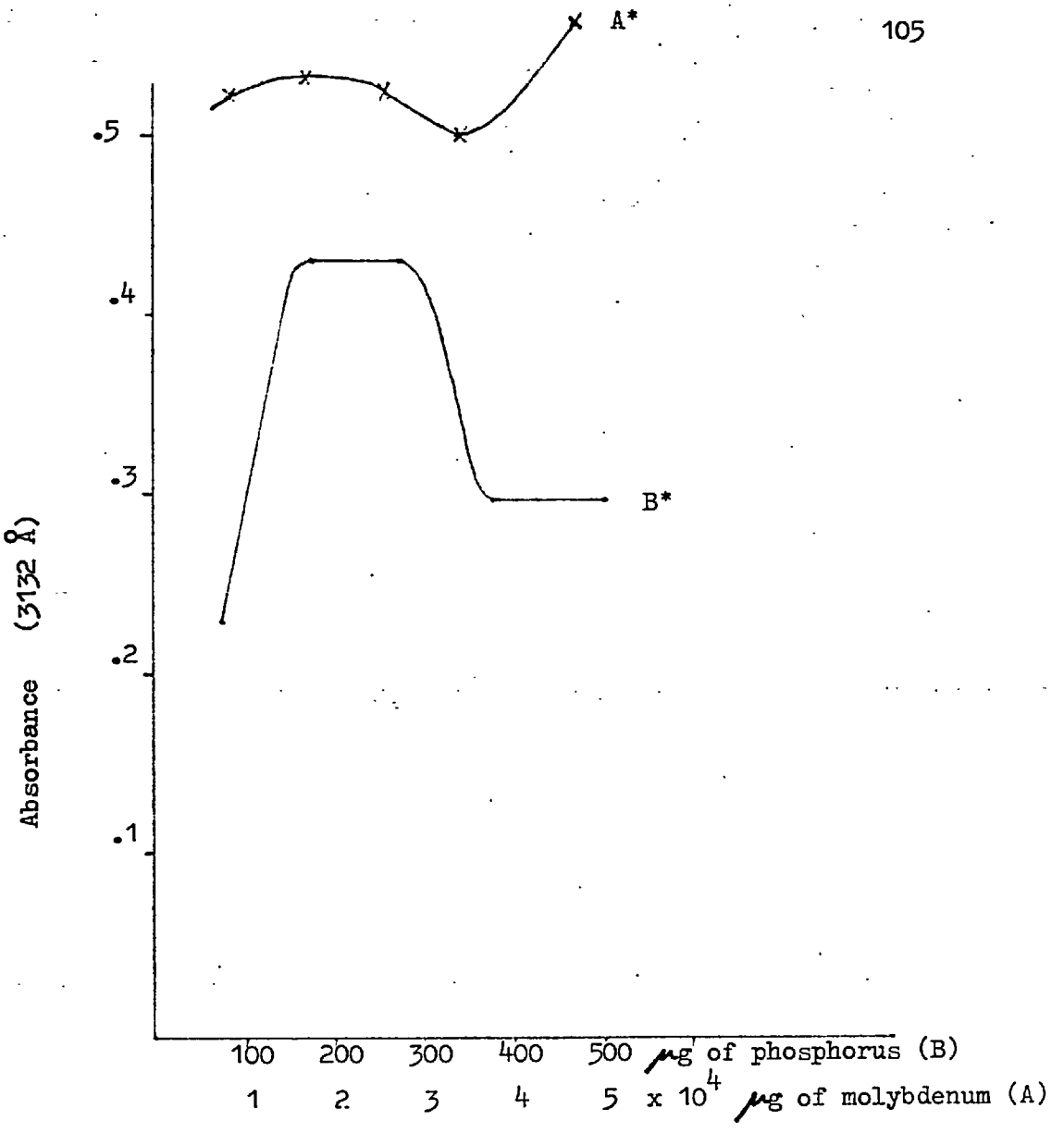


Figure 11. Curve A, effect seen on absorbance for 50 µg of titanium of variation in molybdate reagent concentration (solution 0.5 M in hydrochloric acid, 3.6×10^{-4} M in phosphate and containing 0.5 gm of alum.) Curve B, effect seen on absorbance for 50 µg of titanium of variation in phosphate concentration (solution 0.5 M in hydrochloric acid, 2.7×10^{-2} M in molybdate and containing 0.5 gm of alum)

* Discrepancy in results is due to the use of different spectrophotometers (See text).

7.5 Molybdenum to Titanium Combining Ratio in MTPA

Although it has been reported that the ratio of molybdenum to titanium in MTPA is 12:1 (159), it is probable that this ratio changes with acidity of formation in a similar manner to the niobium analogue. Thus for MNPA, Babko and Sharavskii have reported ratios of molybdenum to niobium of 11:1 at pH 0 to 1.0; 11:2 at pH 1.5 to 3.5 and 11:3 at pH 4.5 to 5.5 (157).

An experiment was devised to establish the stoichiometry of the MTPA complex formed and extracted under the recommended conditions. Varying amounts of titanium were taken through the procedure and the MTPA in the final butanol phase was decomposed by retrograde extraction into 1:1 ammonia solution. The molybdenum content of these ammoniacal phases was determined by A.A.S. in a nitrous oxide-acetylene flame and the results interpreted from a calibration graph for molybdenum in aqueous solutions which were saturated with butanol and contained similar amounts of ammonia. The results of these determinations gave a reproducible molybdenum to titanium ratio of 5.7 ($\pm$ 0.5):1. After correction for the small amounts of molybdenum not removed in the hydrochloric acid washing procedure, which constitutes the blank in the recommended procedure for titanium, a reproducible molybdenum to titanium ratio of 5.5 ($\pm$ 0.5):1 was obtained. Thus under the recommended conditions, the 5.5:1 or 11:2 MTPA appears to be

formed and extracted quantitatively into butanol. It was hoped that this ratio could be checked by thermal emission of the titanium in the final ammoniacal phase, but although titanium standards were prepared and measured the back extract solutions did not give any titanium signal even when they were made acidic with the aim of dissolving any $Ti(OH)_x$ which may have been precipitated in the alkaline solutions.

7.6 Calibration Graph and Optimum Concentration Range

The calibration graph obtained when the recommended conditions and the Techron AA4 spectrophotometer are used is linear over the range 7 to 70 μg of titanium. After subtraction of the blank, the graph passes through the origin and the absorbances corresponding to these concentrations in the initial aqueous solution (0.30 to 3.0 p.p.m.) are 0.07 and 0.68. The blank value is reproducible and may safely be subtracted from the absorbance produced by the standards taken through the procedure. This blank gives rise to an absorbance for molybdenum in the flame of about 0.04 units versus a butanol solvent blank.

7.7 Results

A measure of the precision of the method was obtained by

the replicate analyses of eleven samples each with 22 ml of solution containing 40 μg of titanium (1.8 p.p.m.). These gave an average absorbance of 0.38 and the relative standard deviation was 0.011 absorbance unit or 2.9 per cent.

The effect of twenty eight other ions on the absorbance produced in the determination of standard amounts of titanium by the recommended procedure was studied. An ion was considered not to interfere when an error in the absorbance of less than twice the standard deviation for titanium alone was produced. The addition of between 100 and 1000-fold excesses by weight of the following ions produced no interference on the determination of standard amounts of titanium: - magnesium, calcium, barium, strontium, chromium(III), manganese (II), iron(III), cobalt(II), nickel, copper, zinc, lead, selenium, beryllium, bismuth, tellurium, borate, sulphate, nitrate and chloride. Of the elements that also form heteropoly acids under similar conditions, arsenic and germanium can be removed by volatilisation of their chlorides and silicon is eliminated by volatilisation during the sample preparation procedure. However, the refractory elements tantalum, tungsten and niobium produce a serious positive interference even when present in equal amounts to titanium. Zirconium can be tolerated to the 20-fold weight excess level, above which a positive interference is produced.

A measure of the accuracy of the system was obtained by

performing chemical analyses for titanium in prepared solutions treated as unknown samples. These results are shown in Table 13.

TABLE 13

Titanium added (µg)	Other ions Present (µg)	Titanium found (µg)
30	Zr; 736	30.5
7	-	7
50	Co; 3540	50
50	Ni; 7860	49.5
18	Fe(III); 2850	18
25	Zn; 6640	25.5
25	-	25
10	Cu; 1590	10
30	Mn(II); 7450	30.5
21	Cr(III); 2700	21
70	-	69.5
50	Se; 7820	50.5
50	Te; 8560	49
40	Sr; 10000	39

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