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Atomic-absorption Spectroscopy as a Tool for the Determination of Inorganic Anions and Organic Compounds

A Review

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INTRODUCTION

Atomic-absorption spectroscopy (AAS), which has developed rapidly in recent years, is mainly characterised by high speed, sensitivity and selectivity in the determination of most metallic elements. In order to extend the range of application of AAS to other elements, such as F, Cl, Br, I, O, S, N, P and C, much attention has been paid to the development of direct and indirect methods of analysis.[1–8] Considerable attention has also been devoted to the application of indirect methods permitting the determination of organic compounds.[3,4,9,10] The reader interested in this field is strongly advised to examine the *Annual Reports on Analytical Atomic Spectroscopy* (published annually by the Royal Society of Chemistry since 1971), and Fundamental Reviews from *Analytical Chemistry* (published biennially on AAS since 1970). An up-to-date bibliography can be found in the 6-monthly bibliography published in *Atomic Absorption Newsletter* (at present Atomic Spectroscopy).

The direct methods available for the determination of the elements listed above by AAS are few and of low sensitivity ($>5\ \mu g\ ml^{-1}$ per 1% absorption[3,4]), so that they cannot be readily determined at trace levels in solution. This is due to the fact that they exhibit their main resonance lines in the vacuum ultraviolet region (below 190 nm) and, therefore, they cannot be directly determined with a conventional instrument covering the spectral range from 190 to 850 nm. Further, there are great difficulties in making absorption measurements in the vacuum ultraviolet region, owing mainly to absorption by air, absorption by the flame itself, lack of an appropriate source and lack of transparency in the optical components. On the other hand, when higher wavelengths (secondary or non-resonance lines) are used, the sensitivity is poor. Therefore, indirect methods are employed more by necessity than by choice.

No systematic study of the determination of organic compounds by AAS appears to have been undertaken. Of the methods reported, some are very selective and rely on the formation of a particular complex and its subsequent extraction, whereas others utilise a more general reaction that can be applied to the determination of a range of compounds. On the other hand, a few direct methods have been proposed for the determination of organic compounds.

A critical survey of AAS methods described for the determination of anions and organic compounds in various materials from 1965 up to early 1982 is presented here.

The atomic-absorption methods used for the determination of anions and organic compounds may be broadly classified into two main groups, indirect and direct. The methods are readily seen as direct if the atomic absorption of the analyte is related to its concentration. In contrast, indirect methods are based on the chemical reaction between the analyte and one or several species, one of which is a metal easily measurable by AAS, and a relationship is established between the metal atomic absorption and the concentration of the analyte. Obviously, the applicability of these methods depends on the extent to which the selectivity for the determination of the analyte can be retained via the chemical reaction used before the final absorbance measurement. Difficulties can also arise from non-stoicheiometric reactions. On the other hand, indirect methods are rarely used for routine analysis because most of them are difficult to automate.

Taking into account the chemical reaction involved in each procedure, indirect methods are further divided into methods based on the formation of compounds in solution and in the atomisation cell and of volatile compounds. The direct methods are classified as flame and flameless. In this review, the methods considered are discussed critically on these bases.

1. INDIRECT METHODS

The application of these methods to the determination of non-metallic elements and organic compounds involves carrying out a suitable chemical reaction. This reaction is essential for the performance of the procedure, as problems arising from the atomic-absorption determination are easily circumvented. Therefore, the choice of one or several suitable reagents (one of which is a metallic element) to react with the analyte is very important. In these methods, the atomic signal of a metal (consumed or unconsumed in the reaction) is directly or inversely related to the concentration of the analyte.

These methods are divided into methods of formation of compounds in solution, formation of compounds in the atomisation cell and formation of volatile compounds.

1.1. Methods Based on the Formation of Compounds in Solution

These are classified into methods based on a reaction of precipitation with a metal ion, formation of metal complexes, formation of heteropolyacid compounds and redox reactions.

1.1.1. Reaction of Precipitation

These methods are usually based on the reaction of an anion (inorganic or organic species) with a solution of a cation of appropriate concentration, to yield an insoluble compound. This compound should have a very low solubility. In these methods, the maximum molar concentration of the anion in the samples must be exceeded by the molar concentration of the cation, in order to obtain complete precipitation. The mixture is then filtered, centrifuged or decanted and the unconsumed metal or the metal incorporated in the precipitate is determined by AAS. In general, these methods are specific only if the medium in which the anion is precipitated does not contain other anionic species that might also be precipitated. Interferences from cations in the anion-containing solution can be easily avoided by using a cation exchanger.

These methods are divided into two groups: determination of either the metal excess or the metal incorporated into the precipitate. In both instances, the atomic-absorption signal of the metal is adequately related to the concentration of the analyte precipitated. A general scheme of the procedures employed for the determination of inorganic anions is illustrated in Fig. 1.

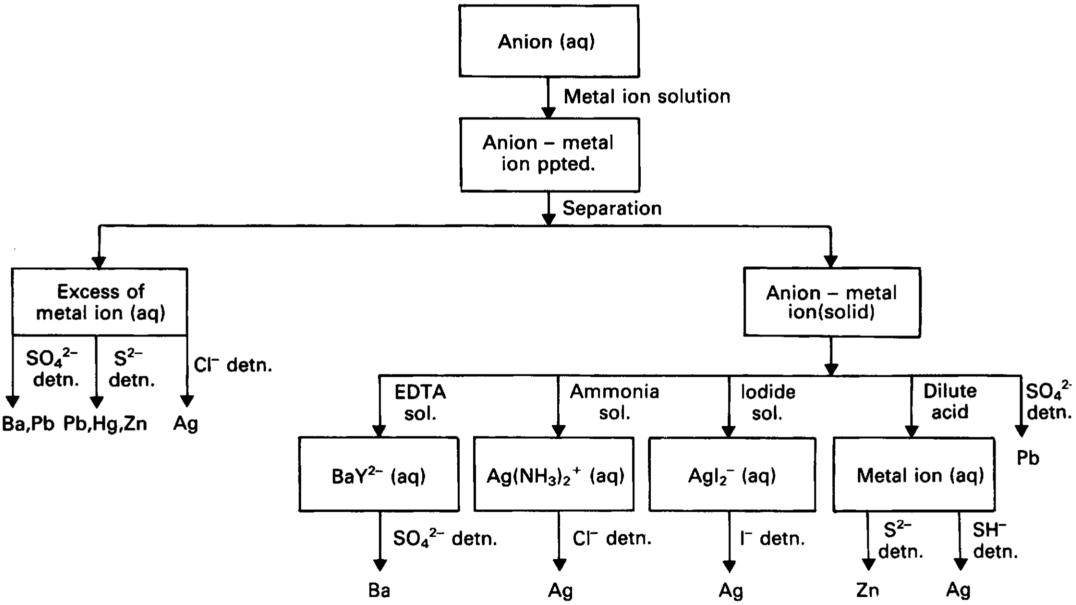

Fig. 1. General outline of procedures for the indirect determination of inorganic anions by means of their precipitation.

1.1.1.1. *Determination of the metal excess*

The determination by AAS of the unreacted metal ion used as the precipitation reagent, in the supernatant solution, is the basis of this method, which is more often employed than the alternative methods based on the determination of the precipitated metal after dissolution of the precipitate, as less manipulation is required. The standard solutions needed for the construction of calibration graphs are generally prepared from the anion standard solutions treated in the same way as the unknown samples. This procedure is more time consuming than the direct use of the metal standard solutions, but it avoids errors due to the nature of the precipitation reaction and also some operational errors.

In this indirect method, the procedures described have been systematised according to the anion involved in the reaction of precipitation.

1.1.1.1.*a*. *Precipitation as sulphate: determination of sulphur.* Sulphate ions are usually precipitated by a definite amount of barium chloride solution in a strongly acidic medium. The excess of barium remaining in solution is then measured by flame AAS at the 553.5-nm resonance line, after several hours of digestion of the precipitate to ensure quantitative precipitation. It has been pointed out[1] that this indirect method allows the determination of 5–60 μg ml^{-1} of SO_4^{2-} using a barium ion solution of concentration equal to or lower than 100 μg ml^{-1} of Ba(II). When barium standard solutions are used for the construction of calibration graphs, the sulphate recovery ranged between 98.0 and 100.5%.[11] A number of determinations of sulphur in different samples are summarised in Table I.

TABLE I

DETERMINATION OF SULPHUR BY PRECIPITATION AS BARIUM OR LEAD SULPHATE AND MEASUREMENT BY FLAME AAS OF THE EXCESS OF METAL IN SOLUTION AT THE 553.6-nm (Ba) OR 283.3-nm (Pb) RESONANCE LINES

Sample	Precipitation medium	Separation of excess of metal	Metal measured; flame	Comments	Reference
Soil extracts*	†	Filter	Ba; air - C_2H_2	Recovery is 96.5–103.8%	11
Potable water*	pH 2.2 buffer‡	Filter	Ba; air - C_2H_2		12
Plants	HNO_3 - $HClO_4$ - HCl	Filter	Ba; air - C_2H_2	Triple slot burner is used. Recovery is 94.9–102.2%	13
Natural water	0.02 N HCl	Decant	Ba; N_2O - C_2H_2	$BaSO_4$ allowed to stand for 18 h. Relative standard deviations ranged from 22–1% for 13–508 μg ml^{-1} of SO_4^{2-}	14
Polluted water	†	Centrifuge	Ba; air - C_2H_2	Method compares favourably with both turbidimetric and gravimetric methods	15
Textile extracts	0.002 N HCl	Filter or decant	Ba; air - C_2H_2	$BaSO_4$ allowed to stand for at least 12 h	16
NH_4HCO_3	†	Filter	Ba; air - C_2H_2	40 g of sample decomposed with boiling water. Recovery 95.8–98.8%	17
Biological materials	0.1 M HNO_3	Centrifuge	Ba; N_2O - C_2H_2	S is oxidised by concentrated nitric acid at 250 °C	18
Fuel oils	—	Centrifuge	Ba; N_2O - C_2H_2	S is oxidised to sulphate by 30% H_2O_2 after application of Schöniger's oxygen flask method	19
Surface waters, soils, plants	40% ethanol	Centrifuge	Pb; air - coal gas	$PbSO_4$ allowed to stand for at least 12 h. Either the 217.0- or the 283.3-nm Pb lines are used. Recovery 95–100%	20
Water	25% ethanol	Centrifuge	Pb; air - C_2H_2	SO_2 oxidised to sulphate by 3% H_2O_2	21
Sulphides, sulphospinels	0.05 M HCl	Filter	Ba; air - C_2H_2	Method applied to small size samples of *ca.* 10 mg. Standard deviation is 1.47%	22
Brines	†	Filter	Ba; air - C_2H_2	Burner must be cleaned often and Ba originally present in brine must be taken into account	23

* The approximate concentration of sulphate is calculated by measuring the conductivity of a sample solution.
† At the pH of the solution.
‡ Chloroacetic acid - Na_2CO_3 buffer solution.

The influence of foreign ions on the determination of sulphates via the barium - AAS procedure has been examined by several workers. In general, to overcome ionisation interferences, an alkali metal is added to both standards and samples.[12,14,17,18] Varley and Chin[11] have shown that Na, K and Mg in soil extracts cause no measurable interference at any level on 50 μg ml^{-1} of SO_4^{2-}; neither was there any interference from either Mn or Fe(II) at concentrations of 100 μg ml^{-1}. Ca and P do not interfere at 30 and 10 μg ml^{-1}, respectively, but if they are present at higher concentrations, it has been recommended by several workers that both samples and standard solutions should be matched with a lanthanum solution. Montiel[12] has reported that in the air - acetylene flame, errors due to the presence of alkali or alkaline earth metals on the atomic absorption of barium are corrected by the addition of Ca^{2+} ions to the standards and by the presence of sodium in the buffered precipitation medium. Moreover, high concentrations of calcium enhance the atomic signal of barium owing to spectral interference of the CaOH band.[13,14] It has been pointed out that either background correction or the dinitrogen oxide - acetylene flame may be used to minimise the CaOH interference.[14] Bataglia[14] has indicated that to overcome interference from aluminium and perchloric acid, the addition of strontium in the first instance and matching both samples and standards for perchloric acid in the second are necessary. It has been pointed out by Ametani[22] that Fe(II), Cu(II), Cr(III) and Cd(II) do not significantly affect the barium atomic signal when sulphur is determined in minerals such as $CuCr_2S_3Cl$ and $CdCr_2S_4$. However, for samples containing titanium, both unknown and standard solutions should be matched for titanium concentration.[22] Column-packed alumina has been employed for the prior separation of sulphates from other ions in brines, in order to avoid interferences in the atomic absorption of barium.[23]

The precipitation of sulphate as $PbSO_4$ in water - ethanol media has also been proposed (Table I). Sulphur may be determined at concentrations as low as 1 μg ml^{-1} of SO_4^{2-} or 2 μg ml^{-1} of SO_2 when $PbSO_4$ is precipitated from 40%[20] or 25%[21] *V*/*V* ethanolic solution, respectively. The effect of different ions on the lead atomic signal in the air - acetylene flame was studied by Rose and Boltz[21] with 5 μg ml^{-1} of SO_2 present. Cl^-, NO_2^-, NO_3^-, ClO_4^-, Na, K, NH_4^+, Ca and Mg do not interfere at levels up to 500 μg ml^{-1}, or acetate, EDTA, Ba or Al at levels of 250, 20, 10 or 10 μg ml^{-1}, respectively. Iron(III) and phosphate should be absent. To overcome interference from phosphate, Little *et al.*[20] added aluminium solution, so that up to 10 μg ml^{-1} of P in the final solution can be tolerated by this procedure.

The determination of sulphate in fresh water involving precipitation as $BaSO_4$ in acidic medium, precipitation of the excess of Ba^{2+} ions with chromate in ammonia medium followed by determination of the unconsumed chromium by AAS has been described.[24]

1.1.1.1.*b*. *Precipitation as sulphide*: *determination of sulphur.* Yoshida and Takahashi[25] determined micro and submicro amounts of sulphides in lake and river waters by addition of Hg(II) (3–60 μg of Hg for 0–9.5 μg of S^{2-}) to a 100-ml sample in sulphuric acid medium, addition of tin(II) chloride solution, warming in a water-bath at 40 °C and determination of the reduced free mercury in an absorption cell by electrothermal AAS. The method allows sulphide ion to be determined at levels down to 0.2 μg l^{-1} with a relative standard deviation of less than 2%. Cl^-, Br^- and F^- can be tolerated at levels up to 10 mg in the determination of 0.23–0.31 μg of S^{2-}, but 1–2 μg of I^-, SCN^- or $S_2O_3^{2-}$ can not. Interferences from cations that form stable metal sulphides have also been reported[26] when sulphur is distilled as H_2S and determined by measuring the signal due to excess of zinc after precipitation with Zn(II) in ammonia medium. The recovery of zinc was about 83% from sodium sulphide standards. The method is simple and relatively free from interferences.

The precipitation as PbS has also been used for the microdetermination of sulphur in organic compounds (5–10 mg of thiols, sulphides, disulphides and thiocarbonyls) with an average recovery of 99%.[27]

1.1.1.1.*c*. *Precipitation as chloride*: *determination of chlorine.* Chlorides are precipitated with a solution of silver nitrate and the unconsumed silver is determined by AAS at the 328.1-nm resonance line. Pinta[1] has shown that for the analysis of a solution containing between 5 and 100 μg ml^{-1} of Cl^- the addition of 300 μg ml^{-1} of Ag(I) solution is necessary. Bromide and iodide interfere seriously. Another source of error in this indirect method is the decomposition of AgCl by ultraviolet radiation. However, the results obtained compare favourably with those obtained by both titrimetric[28–32] and gravimetric[33] methods. Analytical applications of the precipitation as silver(I) chloride are summarised in Table II.

An interesting method for the determination of micro amounts of chlorides has been described by Tofuku and Hirand.[37] The method is based on the addition of increasing known amounts of silver nitrate solution to aqueous ethanolic solutions of chlorides and the determination of the supernatant silver in an air - acetylene flame at 328.1 nm. Extrapolation of the graph of absorbance *versus* silver content gives the end-point at which chlorides in the samples have been precipitated by the added silver. The recovery for 2–10 μg of Cl^- ranged from 80 to 100%. An analogous method of end-point determination using a short-path burner head and a mercury hollow-cathode lamp to produce radiation at the 338.3-nm secondary resonance line of Ag has also been reported.[38] The method has been applied to samples with Cl contents from 1.2 to 236 μg ml^{-1} in distilled, surface, ground, treated and waste waters (recovery 92–108%).

TABLE II

DETERMINATION OF CHLORINE BY PRECIPITATION AS SILVER CHLORIDE AND MEASUREMENT BY FLAME AAS OF THE REMAINING AMOUNT OF METAL IN SOLUTION AT THE 328.1-nm RESONANCE LINE

Sample	Separation of excess of metal	Comments	Reference
NH_4HCO_3	Filter	40 g of sample decomposed in boiling water. Recovery 95.2–100.5%	17
Plant material	Filter	Results compare favourably with those obtained by Mohr's titrimetric method. Detection limit 0.01% of Cl^- in bulk plant	28
Cr chalcogenide spinels	Filter	Indirect method more satisfactory than gravimetric method	33
Plant liquors	Filter	Precision is better than that achieved by titrimetric methods. Recovery 99.9–100.1%	29
Serum	Centrifuge	Indirect method, checked by a standard mercurimetric method, indicates maximum difference of 1.08% in chloride concentration	30
Red wines	Filter	Indirect method simpler, more rapid and precise than the Volhard's titrimetric method adopted by OIV (Office Internationale de la Vigne et du Vin). Recovery 99–101.8%	34
Vinegar	Filter	As above	31
Poly(vinyl chloride)	Centrifuge	Chlorine released in Schöniger's oxygen flask combustion reduced to chloride by 30% H_2O_2. Recovery 98–100.4%. Indirect method compares favourably with X-ray fluorescence and Schöniger's analyses	35
Amine salts	Centrifuge	Indirect method compares favourable in accuracy and precision with mercurimetric and Fajan's titrimetric procedures. Recovery 98.6–103.7%	32
Cr plating solution	Centrifuge	Total chlorine determined after reduction of chlorate with sulphite. Recovery 99–104%	36
NaOH	Filter	Acetone (28% *V*/*V*) added. Relative standard deviation 0.12% for 0.02% NaCl	39
Semiconductor crystals	Filter	AgCl coprecipitated with $BaSO_4$. Relative error $\leqslant$10% for 0.002–0.2% Cl content	40

1.1.1.1.*d*. *Other types of precipitation*: *determination of organic compounds*. Several methods for the determination of organic compounds by means of precipitation reactions have been proposed. Table III summarises the species determined and the characteristics of the gravimetric and spectrophotometric procedures employed.

1.1.1.2. *Determination of the metal precipitated*

These indirect methods involve the formation of an insoluble compound and its further separation. In most instances the precipitate is dissolved and the metal determined by AAS. An advantage of these methods with respect to the above methods is that the amount of cation added is not so critical. However, greater manipulation is required. The procedures described have been systematised into five groups according to the method of dissolution employed to dissolve the precipitate.

1.1.1.2.*a*. *Dissolution with EDTA solution*: *determination of sulphur*. This method has been applied to the determination of sulphates by precipitation with barium ion solution. The $BaSO_4$ is dissolved with EDTA solution in alkaline media and determined at the 553.8-nm resonance line of barium in an air - acetylene flame. Calibration graphs may be obtained from barium chloride standard solutions, containing 1500 μg ml^{-1} of Na to overcome ionisation effects. Under these conditions, the recoveries of sulphur in soil extracts ranged between 98.7 and 100.4% (Arrayan, Temuco and Corte Alto soils) and 79.2 and 101.9% (Puerto Octay soil).[48] Wollin[49] uses sulphate standard solutions treated as the samples for the calibration graphs. Under these conditions, the recovery of sulphur in sulphamide, thiourea, ammonium sulphate and Azure A ranged from 99.5 to 101.1%.

The determination of total sulphur in organic[49,50] and inorganic[49] materials by precipitation as $BaSO_4$ in the presence of La(III) solution (to avoid interference from phosphate) has been reported. However, addition of lanthanum has been claimed to be unnecessary, as precipitation in hydrochloric acid medium will rule out any barium phosphate precipitation.[48] On the other hand, the determination of readily soluble sulphate and total sulphur in soil[51] and inorganic sulphate in urine[52] has been carried out in the absence of lanthanum solution with recoveries of sulphur of 97–103 and 98%, respectively.

TABLE III

DETERMINATION OF ORGANIC COMPOUNDS VIA PRECIPITATION AND MEASUREMENT BY FLAME AAS OF THE EXCESS OF METAL

Compound	Matrix	Quantitative relationship	Measured metal	Comments	Reference
Oxalic acid..	Urine	CaC_2O_4	Ca	Method can be employed as a routine micro-method	41, 42
Phenylacetylene	Water	$AgC{\equiv}CPh$	Ag		43
CHI_3, theobromine, Na salicylate, mercaptobenzothiazole, K ethyl xanthate, organic acids	—	Insoluble Ag compounds	Ag	Method could also be adapted to the determination of alkylated barbiturates and mercaptans	44
NN'-Diphenylguanidine (DFG)	—	$(DFG)_2CdI_4$	Cd	$Zn(SCN)_4^{2-}$ or $CdBr_4^{2-}$ can be also used. Method may be compared to back-titration of excess of metal with EDTA	45
Sulphonamides	Tablets, suspensions, injections	Insoluble Ag compounds	Ag	Indirect method is selective, simple and precise and can favourably compare with USP XIX procedure	46
Non-ionic surfactants ..	Water	Adsorbed surfactant on Ba molybdophosphate	Mo	An empirical factor must be determined for each batch and multi-component system owing to non-stoicheiometric nature of precipitate	47

1.1.1.2.*b*. *Dissolution with ammonia solution*: *determination of chlorine.* The precipitation of chlorides with silver solution, dissolution of the precipitate in ammonia solution and determination of the silver in the resulting solution is the basis of the method. Both air - acetylene[53,54] and air - hydrogen[55] flames have been employed. Calibration graphs are constructed from standard silver solutions in ammonia. Bromide and iodide interfere in the chloride determination.[53] This method has been applied satisfactorily to the determination of chlorine (0.2–100 μg ml^{-1}) in selenium (via distillation as hydrogen chloride)[53] and to the determination of chloride in ZnO and PbO (Cl content 0.02–3%)[54] and in titanium metal,[55] with prior dissolution of the sample in acidic medium.

Smith and Nessen[32] have indicated that this method, when applied to the determination of chlorides in eleven quaternary amine chlorides, gives low recoveries for Cl^- (93.5–98.2%). It is therefore less convenient than those methods based on the determination of the unreacted silver. However, this effect may possibly arise from inadequate protection of the AgCl precipitate from direct ultraviolet light.

An interesting determination of trace amounts of Cl^- in semiconductor crystals has been developed by Gladysheva *et al.*[40] The procedure requires the coprecipitation of AgCl and $BaSO_4$ followed by dissolution of the AgCl in ammonia. Relative errors are reported to be $\leqslant$10% for 0.002–0.2% of chlorine.

1.1.1.2.*c*. *Dissolution with iodide solution*: *determination of iodine.* Iodine in organic compounds (implying previous conversion into iodide by redox reactions) has been determined, via dissolution of AgI with iodide solution, by flame AAS. The method has good sensitivity for Ag (0.1 μg ml^{-1}) and consequently for iodide.[56] Chloride and bromide interfere seriously.

1.1.1.2.*d*. *Dissolution with mineral acids*: *determinations of sulphur and ammonia.* Ray *et al.*[26] proposed another indirect method for the determination of sulphides in flooded acid sulphate soils (0.29 mg of S^{2-} per gram of sample) by means of ZnS precipitation in ammoniacal medium and dissolution of the precipitate in hydrochloric acid. The method is practically free from interferences, as sulphide is distilled as hydrogen sulphide.

The precipitation with silver ions has been successfully applied to the analysis of mercaptans.[57,58] The silver precipitate is filtered off and digested with nitric acid. A single calibration graph prepared from silver nitrate is utilised. Pure thiol standards are not required. The method is relatively free from interferences, but substances that reduce silver ions to metal or form insoluble silver salts may interfere.

Danchick *et al.*[59] have shown that the coprecipitation of ammonium molybdophosphate with a known amount of thallium molybdophosphate followed by dissolution of the precipitate provides the basis for an indirect atomic-absorption method for the determination of ammonia. The dissolved molybdate is determined at 313.2 nm in an air - acetylene flame. The method shows poor selectivity, heavy metals being precipitated as molybdophosphates.

1.1.1.2.*e*. *Direct atomisation of the precipitate: determination of sulphate.* Siemer *et al.*[60] described the determination of sulphates in natural waters (32–2640 μg ml^{-1} of SO_4^{2-}) by precipitation with lead(II) nitrate in 50–75% *V/V* ethanol - water using a modified Woodriff furnace for direct lead determination at the 405.7-nm non-resonance line. They showed that barium cannot be satisfactorily employed even at temperatures as high as 2400 °C. Large amounts of calcium and chloride do not interfere, but phosphate, chromate, iodide and arsenate cause serious interferences.

1.1.2. Metal Complexes

In these methods, the analyte reacts with either one or two reagents, giving rise to the formation of a charged or neutral metal complex or an ion-association complex. The metal is then determined by AAS after filtration or liquid - liquid solvent extraction. The ion-association or metal complex formed should be very stable. Generally, calibration graphs are constructed from standard anion solutions prepared in the same way as the unknown samples. Common interferences arise from other anionic species that might also be complexed. An obvious interference is due to the presence of the metal used for the indirect determination in the anion-containing solution. In these instances, the atomic absorption of the metal in the unreacted sample has to be determined.

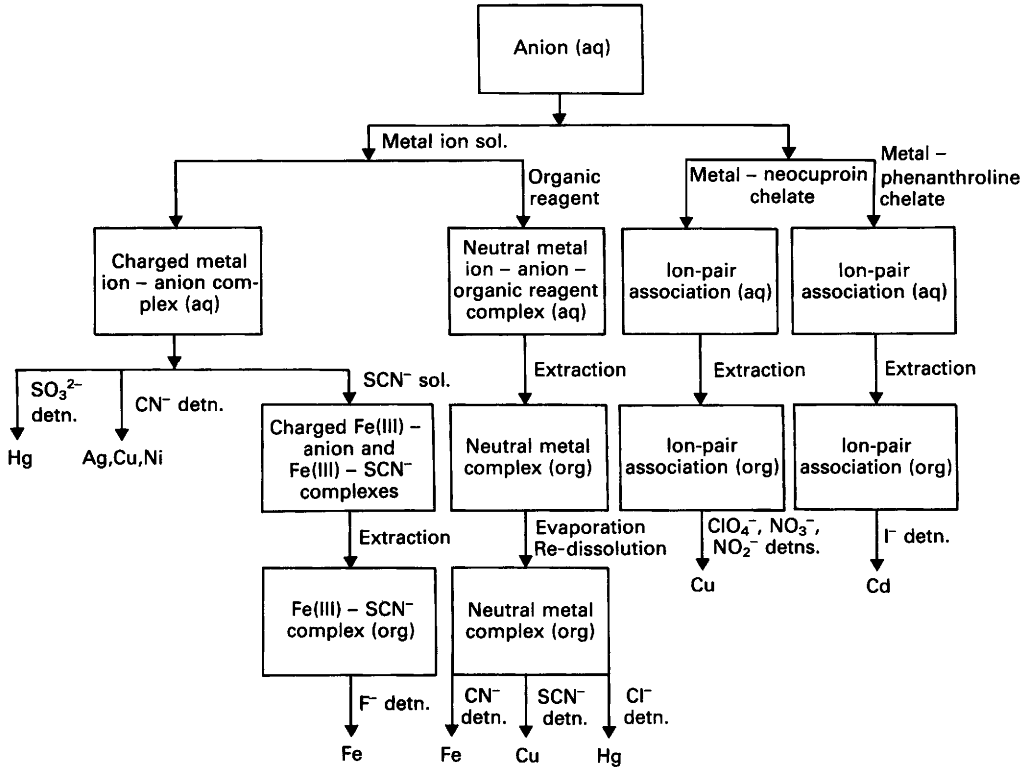

Fig. 2. General outline of procedures for the indirect determination of inorganic anions via the formation of metal complexes.

These methods are classified into two groups: those based on the formation of a metal complex with an analyte as ligand and those based on the formation of an ion-association complex with an analyte as counter ion. An outline of procedures for the analysis of inorganic anions is given in Fig. 2.

1.1.2.1. *Analyte as ligand*

These methods make use of stoicheiometrically formed complexes of metals that can be isolated, determined by AAS and quantitatively related to the complexed anion. Interferences arise from the presence of metals that can form more stable complexes with the anion to be analysed or from species forming more stable complexes with the cation employed for the atomic-absorption measurements. In both instances, separations are required. The reported procedures have been organised according to the charge of the compounds formed.

1.1.2.1.*a*. *Charged metal complexes: determinations of cyanide, sulphite, pyrophosphate, fluoride and organic compounds.* These procedures are rapid and simple. They are based on the reaction of an anion-containing solution with a metal (in solution or in the solid state), a metal oxide or a metal salt in their solid states. The complexed metal is then normally determined in aqueous solution by either electrothermal[61] or flame[62–78] AAS.

Cyanides have been determined indirectly by measuring the atomic signal of Ag,[61,62] Cu[63,64] or Ni[65] in the complexes $Ag(CN)_2^-$, $Cu(CN)_3^-$ or $Ni(CN)_4^{2-}$, respectively (Table IV). The most sensitive procedure has been described by Jungreis and Ain.[61] The method uses silver wool placed on a membrane filter in a closed system. The sample solution (0–100 μg l^{-1} of CN^-) is injected from a 35-ml syringe. Silver is determined in the effluent by injecting a 100-μl volume of the sample into the graphite furnace. Cl^-, Br^-, I^-, F^-, SCN^-, SO_4^{2-} and NO_3^- do not interfere, but $S_2O_3^{2-}$ does.

TABLE IV

SENSITIVITIES OF INDIRECT AAS DETERMINATION OF ANIONS BY FORMATION OF CHARGED METAL COMPLEXES

Anion	Sample	Substance used for complex formation	Sensitivity/μg ml^{-1} anion per 1% absorption	Reference
CN^- ..	.. Water	Ag wool*	0–0.1†	61
CN^- ..	.. Water	Ag pieces	0.5	62
CN^- ..	.. Water	Cu(I) cyanide	1–10†	63
CN^- ..	.. Sewage effluents	Basic Cu carbonate	0.5	64
CN^- ..	.. Biological materials	$NiCl_2$ solution‡	1	65
SO_3^{2-} ..	.. Water	HgO suspension	13§	66
$P_2O_7^{4-}$	.. Water	Copper sulphate solution¶	0.87–8.7†	79
F^- ..	.. Organic compounds	Fe(III) - SCN^-‖	0.5–6†	80

* HGA 2100 graphite furnace was used.
† Range of determination in micrograms per millilitre.
‡ Excess of Ni(II) is eliminated by precipitation with Na sulphide.
§ Detection limit defined as the concentration (in micrograms per millilitre) that produces an absorption signal equivalent to twice the standard deviation in the noise fluctuation of the background signal.
¶ Copper(II) ions are extracted by a 10% (*V*/*V*) liquid ion exchanger into IBMK or ethyl acetate.
‖ Excess of Fe(III) is extracted as thiocyanate into IBMK.

Jungreis and Anavi[66] proposed a method for the determination of sulphite that appears to be useful in air-pollution analysis. The procedure is based on the reaction of sulphite (119–833 μg) with red HgO (about 120 mg) at pH 11 to yield $Hg(SO_3)_2^{2-}$. The atomic signal of the complexed Hg is measured at 253.7 nm in an air - acetylene flame. The method is affected by I^-, $S_2O_3^{2-}$ and SCN^-, but SO_4^{2-}, NO_2^- and CN^- do not interfere. A very sensitive method for the determination of SO_3^{2-} (or SO_2) based on the disproportionation reaction

$$Hg_2^{2+} + 2SO_3^{2-} \rightarrow Hg + Hg(SO_3)_2^{2-}$$

has been developed by Marshall and Midgley.[81] The procedure monitors the Hg released at 40 °C in the above reaction using the cold vapour atomic-absorption technique. This method can determine sulphite at levels up to 5 ng. The selectivity is good, as some anions may be tolerated at high foreign ion to sulphite ratio: CO_3^{2-}, 10000:1; SO_4^{2-} and NO_2^-, 1000:1; F^- and HPO_2^-, 100:1; Cl^-, 10:1; and S^{2-} (5:1); NH_4^+ did not interfere at a ratio of 3000:1.

West and Lorica[82] showed that iodide could be extracted as a cadmium complex with tributyl phosphate in isobutyl methyl ketone (IBMK) and utilised in AAS.

The only atomic-absorption spectrophotometric method reported for the determination of pyrophosphate ions in the presence of other condensed phosphates is based on its inhibitory effect on the extraction of copper(II) by Amberlite LA-1 [*N*-dodecyl(trialkylmethyl)amine] into isobutyl methyl ketone or ethyl acetate.[79] The extracted copper is monitored at the 324.7-nm line. The method is simple, rapid and selective. Tetrameta- and trimetaphosphates, phosphates, sulphates, chlorides and acetates do not interfere.

Some species may be determined by their masking action in the solvent extraction of a metal complex. This effect has been used by Kidani and Ito[80] for the determination of fluoride by means of extracting the Fe(III) - SCN^- complex into isobutyl methyl ketone. The decrease in the Fe atomic absorption in the organic layer is quantitatively related to the concentration of fluoride (0.5–6 μg ml^{-1} of F^-). Interferences occur owing to metals forming fluoride complexes more stable than that of Fe(III), but anions other than cyanide do not interfere. Also, EDTA may be determined by its masking effect on the extraction of a Cu(II) - quinolin-8-ol complex into isobutyl methyl ketone at pH 6.5.[6] In these methods it is evident that the test substance must form a more stable compound with the metal than the extracting agent.

These methods might be also applied to the determination of organic compounds, provided that they act as ligands. A summary of indirect procedures for the determination of organic

TABLE V

DETERMINATION OF ORGANIC COMPOUNDS BY FORMATION OF METAL CHARGED COMPLEXES AND MEASUREMENT BY FLAME AAS OF THE COMPLEXED METAL

Compound	Sample	Measured metal	Quantitative relationship	Comments	Reference
Histidine	Effluent of liquid - liquid chromatography	Cu	Cu complex	1 μg of histidine can be detected	67
EDTA	Streptomycin	Ni	Ni - EDTA and release of complexed Ni by pH adjustment	Detection limit near 4 μg of EDTA per g of compound. Phosphates do not interfere	68
EDTA, NTA	Effluent of liquid - liquid chromatography	Cu	Cu complexes	Detection limit 5×10^{-7} mmol of EDTA or NTA	69
α-Amino nitrogen	Plasma	Cu	Solubilisation of copper phosphate and filtration	Plasma deprotenised with Cl_3C-COOH, filtered and neutralised with alkali	70
EDTA, NTA	Effluent of high-speed liquid chromatography	Cu	Cu complexes	Detection limits are 10.7 and 23.6 ng of Cu for NTA and EDTA, respectively	71
EDTA	Water and waste water	Cu	Solubilisation of copper at pH 10 and filtration	Lower limit of analysis for EDTA is 1×10^{-6} M	72
Phenols (21 compounds) ..	Water	Co	Co complex extraction into IBMK	Recovery 94.5–104.5%. Cu(II), Fe(III) and $PhNH_2$ interfere	73
Biuret	Fertilisers and urea	Cu	In strongly alkaline solution, Cu forms a biuret complex; $Cu(OH)_2$ is filtered off	Although a stoicheiometric relationship does not exist, a linear relation between Cu and biuret may be obtained	74, 75
Amino acids	—	Cu	Schiff bases with salicylaldehyde are formed, complexed with Cu and Schiff base - Cu - bathophenanthroline complex is extracted into IBMK	Range of determination: 1.5–15.0 μg ml^{-1} of glycine	76
Noscapine	Drugs	Cr	Add Reinecke's salt and extract into chloroform	—	77
Alcohols	—	Cr	Add CrI_3 and pyridine to alcohol in benzene solution	Methanol added to benzene solution before nebulisation	78

compounds by formation of charged complexes is given in Table V. Of the procedures described, some use a selective reaction,[67–69,71,72,74,75,77] while others use a general reaction that may be applied to the determination of a range of compounds.[70,73,76,78]

1.1.2.1.*b*. *Neutral metal complexes: determinations of cyanide, thiocyanate, sulphide, halides and organic compounds.* These methods involve the formation of an uncharged metal complex, which is frequently separated by solvent extraction, and the complexed metal in the organic solution is then determined by AAS. These procedures have a greater sensitivity than the procedures described previously. However, the sensitivity can also be enhanced by the choice of a favourable $V_{aq}:V_{org}$ ratio.

Danchick and Boltz[83] proposed an accurate and highly selective method for the indirect determination of cyanides (sensitivity 0.06 μg ml^{-1} of CN$^-$). The method is based on the extraction into chloroform of the dicyanobis(1,10-phenanthroline) iron(II) complex, evaporation of the organic solvent, re-dissolution in ethanol and atomic absorption of the associated iron at the 248.3-nm resonance line. The formation of a highly insoluble silver cyanide precipitate is the basis of a second method for the determination of cyanides, described by the same workers.[83] The silver cyanide is quantitatively precipitated and the silver excess in solution is determined at 328.1 nm, after centrifugation. This method has a higher simplicity and sensitivity (0.03 μg ml^{-1} of CN$^-$) than the method based on the ferroin reagent.

A selective method for determining thiocyanate has also been described by Danchick and Boltz.[84] They proposed two procedures based on the quantitative formation of the dithiocyanatodipyridine - copper(II) complex and its selective extraction into chloroform. In one procedure, the organic layer is sprayed into an air - acetylene flame and the Cu atomic signal at 324.7 nm is measured (sensitivity 0.2 μg ml^{-1} of SCN$^-$). Toxic combustion products may be formed. In the other method, the organic phase is evaporated almost to dryness, diluted with ethyl acetate and the Cu atomic absorption measured (324.7 nm; air - acetylene). In this procedure the sensitivity is greater (0.05 μg ml^{-1} of SCN$^-$) and the method seems less hazardous. There are few interferences in the determination of SCN$^-$.

Christian and Feldman[6] used the masking effect of sulphide (up to 3×10^{-4} mmol) on the extraction of 3.1×10^{-4} mmol of copper as a copper - quinolin-8-ol complex, to propose an indirect procedure for determining S^{2-}, based on the direct atomisation of the organic phase.

Belcher *et al.*[85] determined chlorides at very low levels by extracting phenylmercury(II) chloride into chloroform, evaporation and re-dissolution in ethyl acetate. The Hg concentration is measured at 253.65 nm using an air - acetylene flame. As little as 0.015 μg ml^{-1} of Cl$^-$ can be determined in 250 ml of sample. Alternatively, but less convenient, the phenylmercury(II) chloride may be extracted into isopropyl acetate and this solution is sprayed into the flame. Both methods have some advantages with respect to other AAS procedures for determining chloride: they are more sensitivive and less affected by the presence of other ions. However, bromide and iodide are listed as interferents as they react quantitatively with the reagent to form the corresponding phenylmercury(II) halides, which are then extracted together with the chloride complex. This, of course, offers the possibility of a total halide determination followed by stepwise elimination of iodide and bromide by known chemical reactions to give the individual halide content of a sample. Chuchalina *et al.*[86] developed a method for the indirect determination of trace amounts of Cl$^-$, Br$^-$ or I$^-$ based on the addition of an excess of Hg(II) ions to the halide solution, percolation through a column packed with a KU-2X8 cation exchanger and atomic absorption of the Hg in the effluent. The detection limits are 2.1×10^{-10}, 4.8×10^{-10} and 7.6×10^{-10} g of Cl$^-$, Br$^-$ and I$^-$, respectively.

The method has also been applied, with excellent results, to the determination of many organic compounds (Table VI). The metal associated with the organic compound is frequently determined by AAS, after filtration[88–90,92,94,96] or solvent extraction,[6,91,93,97,98,100–102] and a relationship is obtained between the metal absorption and the amount of organic substance.

1.1.2.2. *Ion-association complexes*

The basis of this method is the enhancement of the solvent extraction of a charged metal complex by formation of an ion pair with the analyte. The quantitative reaction is normally

TABLE VI

DETERMINATION OF ORGANIC COMPOUNDS BY FORMATION OF NEUTRAL METAL COMPLEXES AND MEASUREMENT BY FLAME AAS OF THE COMPLEXED METAL

Compound	Matrix	Measured metal	Quantitative relationship	Characteristics of method	Reference
Thiol groups	Proteins	Hg	Protein - S - Hg *p*-hydroxybenzoate complex is formed. Excess of unreacted reagent is separated by gel filtration (Sephadex G-25)	1–5 μg of Hg can be determined in a 100-cm absorption cell. Recovery 96.0–100.9%. Detection limit: 0.1 μg ml^{-1} of Hg. Mg, Ca, Fe(II), Mn(II), Ni, Cu, Zn and Cd do not interfere	87
Esters	—	Fe	Hydroxamic acid formed is complexed with Fe(III) and filtered off. The Fe(III) complex determined in filtrate	Recovery for nine esters was 92.4–105%	88
Acid anhydrides	—	Fe	Hydroxamic acid formed is complexed with Fe(III) and filtered off. Iron(III) complex determined in filtrate	Recovery 97.5–102.8%. Acetone, HOAc, PhNH$_2$, PhNO$_2$, PhOH, K$^+$, Mg^{2+}, Ca^{2+}, EtOAc do not interfere. Cu(II) and Al(III) interfere	89
Biacetyl	—	Ni	Ni - dimethylglyoxime complex formed is filtered and dissolved in HNO$_3$	5–200 μg ml^{-1} of biacetyl can be determined	90
Ketones and aldehydes of low relative molecular mass	—	Cu	Cu - thiosemicarbazone complex is formed, extracted into benzene and diluted with ethanol	Recovery 96.7–101.1%. Co(II), Ni, Ag and Zn in a 10-fold excess interfere	91
Primary amines	Water	Cu	Schiff's bases are formed, complexed with Cu, filtered off and excess of Cu determined in filtrate, or precipitate dissolved in nitric acid and analysed for Cu	1 mg of amine can be determined. Secondary and tertiary amines in a 30-fold mass excess do not interfere, but Zn, Mg and Ca do	92
Secondary amines	Water	Cu	Cu - dithiocarbamate is formed and extracted into IBMK	1.1–6.6 μg ml^{-1} of Et$_2$NH.HCl can be determined. Recovery 93.3–103.2%. Lead(II), Fe(III), Mg(II), MeNH$_2$.HCl, Me$_3$N.HCl, Ph$_2$NH.HCl and aniline sulphate do not interfere	93
Aliphatic secondary amines	—	Ni	Ni - dithiocarbamate is formed, filtered and dissolved in HNO$_3$ - HCl	0.6–8.5 μg of Ni per mole of amine can be determined. Recovery 98.7–100.7%	94
Histidine, methionine		Cu	Schiff's bases formed are complexed with copper	3–30 μg ml^{-1} of compound can be determined	95
CS$_2$	Air	Cu	CS$_2$ trapped in KOH and H$_2$S removed with Cd. Copper - xanthate is formed, filtered and dissolved	Sensitivity 0.009 g m^{-3} of CS$_2$	96
CS$_2$	Air	Cu	Cu - dithiocarbamate formed and extracted into isoamyl acetate	Detection limit 7 μg of CS$_2$ per 10 ml of solution	97
CS$_2$	Air	Cu	Cu - dithiocarbamate formed and extracted into toluene	5–50 μg of CS$_2$ can be determined. Sensitivity 0.29 μg ml^{-1} of CS$_2$	98
CS$_2$	CCl$_4$, C$_6$H$_6$	Cu	Cu - dithiocarbamate solution evaporated to dryness and dissolved in HNO$_3$	Determination limit 2.52 × 10^{-5} mg of CS$_2$	99
Anthranilic acid	Water	Co	Co(II) - anthranilic acid - bathophenanthroline formed and extracted into IBMK	3–22 μg ml^{-1} of compound determined with 99.5% recovery	100
Na diethyldithiocarbamate (DDC)	Human serum and urine	Cu	Cu chelate formed and extracted into CCl$_4$	Down to 5 μg l^{-1} of DDC can be determined	101

TABLE VI—continued

Compound	Matrix	Measured metal	Quantitative relationship	Characteristics of the method	Reference
Ammonium tetramethylene-dithiocarbamate (APDC) ..	Water	Cu or Co	Cu (or Co) chelate formed and extracted into IBMK	Concentration of 10^{-5} M APDC can be determined	6
Quinolin-8-ol	—	Cu	Cu - quinolin-8-ol formed and extracted into IBMK or ethyl acetate	Concentration of 2×10^{-5} M quinolin-8-ol can be determined	6
Non-ionic surfactants ..	Sea water	Co	Co - thiocyanate - surfactant adduct is formed and extracted into benzene	Procedure better than that given in Ref. 47 as no empirical factor is required. Precision better than 10%	102
Free fatty acids	Blood serum	Co	Cobalt complex formed	177–585 µmol l^{-1} can be determined. Method less tedious than gas chromatography	103
Soap	Vegetable oil	Na	Na oleate formed	—	104

related to the formation of a metal - organic reagent positive complex with an anion. The atomic absorption of the complexed metal is usually measured in an air - acetylene flame and related quantitatively to the associated analyte. The selectivity of these methods depends essentially on both the extracted complex compound and the conditions under which extraction is carried out. They are divided into inorganic anions and organic compounds, according to the chemical nature of the analyte.

1.1.2.2.*a*. *Inorganic anions*: *determinations of perchlorate, nitrate and iodide.* Two organic reagents have been employed for the formation of ion-association pairs: 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (neocuproine).

The only method for the atomic-absorption determination of ClO_4^- has been described by Collinson and Boltz.[105] The method is based on the extraction of $[(\text{neocuproine})_2Cu(I)]ClO_4$ into ethyl acetate and measurement of Cu atomic signal at 324.7 nm in an air - acetylene flame. Between 0.5 and 5 µg ml^{-1} of ClO_4^- can be determined; 15 µg ml^{-1} of Ac^-, Cl^-, SO_4^{2-}, PO_4^{3-}, K and Fe(II) may be tolerated in the determination of 3 µg ml^{-1} of ClO_4^-.

A somewhat analogous method for determining nitrates (0.4–4 µg ml^{-1}) has been proposed,[106] but it includes extracting the ion pair into isobutyl methyl ketone.[106] The method is relatively free from interferences as indicated by several workers.[106–108] This indirect method has been applied to the determination of nitrates, nitrites (by oxidation with cerium sulphate) and nitro-groups (by oxidation with permanganate) in inorganic and organic compounds[108] and nitrates in plants.[109]

Iodide (0.5–5 µg ml^{-1}) can be extracted as $(\text{phen})_3Cd^{II}I_2$ into nitrobenzene and the atomic absorption of the chelated cadmium is measured at 228.8 nm in an air - acetylene flame.[110,111] PO_4^{3-}, SO_4^{2-}, CN^-, Cl^-, BrO_3^-, F^- and BO_2^- do not interfere, but IO_4^-, ClO_4^-, ClO_3^-, NO_3^-, NO_2^- and Br^- do. Yamamoto *et al.*[112] have described a less sensitive analogous method for iodide, based on the $(\text{phen})_3Fe(II)$ chelate. The calibration graph is linear from 10.1 to 40.4 µg ml^{-1} of I^-. The same foreign ions interfere in both procedures.

1.1.2.2.*b*. *Organic compounds.* Indirect atomic absorption methods have been developed for the determination of organic compounds via the formation and extraction of ion pairs. A special characteristic of these procedures is that they may be applied to organic compounds having a negative[113–118] or positive[119–126] charge. A summary of the analytical applications and characteristics of the procedures is shown in Table VII.

1.1.3. Heteropolyacid Compounds: Determination of Phosphate

These methods are based on widely known reactions of some anions with molybdate and other ions in solution, yielding heteropolyacids of definite chemical composition, which are usually extracted into an organic solvent. The metal is normally determined by AAS either in the organic layer or in aqueous solution, after suitable back-extraction. This method shows good sensitivity, because, according to the heteropoly-compound formed, 12,[127–149] 11[150] or 10[151] Mo atoms are associated to every P atom. However, Parsons *et al.*[152] claim that 15 atoms of Mo are extracted for each atom of P, although no evidence for the anomaly is given. A general scheme of methods for determining phosphates is given in Fig. 3.

TABLE VII

CHARACTERISTICS OF PROCEDURES FOR DETERMINATION OF ORGANIC COMPOUNDS BY FORMATION OF ION-ASSOCIATION COMPLEXES AND MEASUREMENT BY FLAME AAS OF THE COMPLEXED METAL

Compound	Sample	Measured metal (nm)	Quantitative relationship	Comments	Reference
Pentachlorophenol (PPh)	Water	Fe(248.3)	Fe(II) - (phen)$_3$ - (PPh)$_2$ formed and extracted into nitrobenzene	Up to 3 × 10^{-4} M PPh has been studied	113
Salicylic acid (SA)	Water	Fe(248.3)	Fe(II) - (phen)$_3$ - (SA)$_2$ formed and extracted into nitrobenzene		114
2-Hydroxynaphthoic acid (HNA)	Water	Ni(232)	Ni(II) - (phen)$_2$ - (HNA)$_2$ formed and extracted into nitrobenzene	From 8 × 10^{-5} to 4 × 10^{-4} M HNA can be determined. Naphth-2-ol does not interfere	115
Phthalic acid (PhA)	Water	Cu(324.7)	Cu(I) - (neocuproine)$_2$ - (PhA) formed and extracted into IBMK	From 4 × 10^{-6} to 4 × 10^{-5} M PhA can be determined. Both isomers of PhA do not interfere at the same concentration level of PhA	116, 117
Benzylpenicillium (BP)		Cd(228.8)	Cd(II) - (phen)$_2$ - (BP)$_2$ formed and extracted	18.6–111.6 µg ml^{-1} of BP can be determined. Starch, lactose, dextrin and Na saccharin do not interfere	118
Catechol (C)	Water	Cu(324.7)	CuC$_2$ is formed and extracted with trioctylmethylammonium chloride into CHCl$_3$ at pH 10	11.0–176.2 µg ml^{-1} of catechol can be determined	119
Anionic detergents (AD)	Fresh water	Cu(324.7)	Cu(I) - (phen)$_2$ - (AD) is formed and extracted into IBMK	Na dioctylsulphosuccinate can be determined in the range 3 µg l^{-1} to 2.5 µg ml^{-1}. Na stearate, MnO$_4^-$, Co, Ni, Fe(III), EtOH, ClO$_4^-$, IO$_4^-$, SCN$^-$, Cr$_2$O$_7^{2-}$ and dithiocarbamates at about 5 µg l^{-1} do not interfere. Precision is 5% for 25 µg of Na dioctylsulphosuccinate per litre	120, 121
Linear alkylbenzene sulphonate (LAS)	Water	Cu(342.7)	Cu(I) - (thiourea)$_2$ - (LAS) is formed	Calibration graph is linear in the range 0.001–20 µg ml^{-1} of LAS. Coefficient of variation is 2.4% for 0.1 µg ml^{-1} of LAS	122
Quaternary amines	—	Cu(342.7)	Amine is complexed with excess of dioctylsulphosuccinate (DDS); unreacted DDS is complexed with Cu(I) - (phen)$_2$ and extracted into IBMK	Method requires a 1–4 µM solution of the ammonium complex	123
Aliphatic amines (AA)	—	Co(240.7)	Co(II) - (SCN)$_4$ - (AA)$_2$ is formed, extracted into benzene and diluted with methanol	50–650 µg of AA per 5 ml can be determined	124
n-Butylscopolammonium bromide and tannate	Blood, urine and faeces	Co(240.7)	Co(II) - (SCN)$_4$ - (amine)$_2$ is formed and extracted into CHCl$_3$. Extract is evaporated and dissolved in IBMK	0.3–1.5 mg of compound can be determined	125
Hyoscine-*N*-butyl bromide (H)	Pharmaceutical preparations	Co(240.7)	Co(II) - (SCN)$_4$ - (H)$_2$ is formed and extracted into 1,2-dichloroethane	Linear relationship obtained in the range of 5 × 10^{-5} to ~7 × 10^{-4} M. No interferences from excipients	126

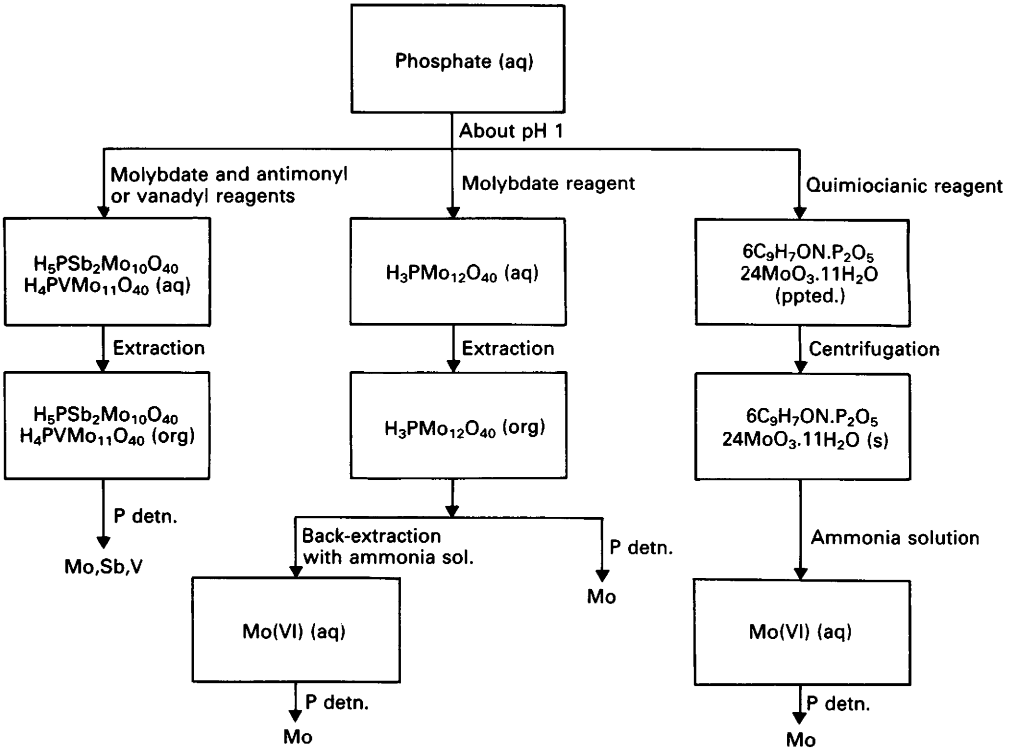

Fig. 3. General outline of procedures for the indirect determination of orthophosphates by heteropolyacid compounds.

1.1.3.1. *Binary heteropolyacids*

Phosphate has been widely determined using the formation of molybdophosphoric acid ($H_3PMo_{12}O_{40}$) when a molybdate solution is added to a phosphate-containing solution in a strong acid medium. After several minutes, the molybdophosphoric acid is usually extracted into an organic solvent, which is then washed repeatedly with citrate solution,[127–129,152] with dilute acid,[136,140,142–148] or with water[131] to remove the excess of molybdate transferred to the organic phase. The phosphorus content is related quantitatively to the atomic-absorption measurements of Mo at 313.2 nm, by either flame or electrothermal techniques. Usually the specificity of these methods is greatly dependent on both the extraction conditions and the extractant employed. Extensive use of molybdophosphoric acid analytically has been made (Table VIII).

These procedures are classified into methods based on single extractions, extraction-decomposition and precipitation of the heteropolyacid, according to the separation procedure used for the isolation of the molybdenum associated with the phosphorus.

1.1.3.1.*a*. *Single extraction*. These methods involve the determination of Mo by AAS in the organic phase. Three different types of organic solvents have been used: alcohols,[127–129] ketones[130,132,134,152] and esters.[133,135–141] In general, oxygenated solvents are the best extractants for heteropolyacids. Calibration graphs are usually constructed from phosphate standard solutions prepared in the same way as samples.

Zaugg and Knox[127–129] have examined the extraction of molybdophosphoric acid in several alcohols, butan-1-ol, isobutanol, hexan-2-ol, heptan-1-ol and octan-2-ol. They found the last to be the best, because it extracts less free molybdate. The method is sensitive using an air-acetylene flame (detection limit 0.015 $\mu g\ ml^{-1}$ of P), but it is subject to interferences, mainly from As and Si.

TABLE VIII

DETERMINATION OF PHOSPHORUS BY EXTRACTION OF MOLYBDOPHOSPHORIC ACID FOLLOWED BY ATOMIC ABSORPTION OF MOLYBDENUM AT 313.2 nm

Sample	Optimum pH	Solvent used*	Range of determination/ μg ml^{-1} of analyte	Atomisation technique	Comments	Reference
Plasma ..	1.7–2.1	IBMK	5–200 (P)	Air - C_2H_2	390.3-nm line is also used. Standard addition method (SAM) is employed for Mo measurement	152
Biological materials; fresh and sea water	1.0–1.1	Octan-2-ol	Up to 6 (PO_4^{3-})	Air - C_2H_2	Other lines used were 379.8, 386.4 and 390.3 nm. Sensitivity is 0.04 μg ml^{-1} of PO_4^{3-} at 379.8 nm	127, 128
Milk and blood serum	1.25 ml $HClO_4$	IBMK	100–200 (P) †	Air - C_2H_2	Recovery 97.9–106.0%. SAM is used	130
Hystamine diphosphate, pyridoxal phosphate, triphenyl-phosphorus ..	5 ml $HClO_4$	IBMK	Up to 2.5 (P)	Air - C_2H_2	Sample digested with H_2SO_4 - HNO_3 prior to determination	131
Bottom sediments ..	Acid medium	Benzophenone		Air - C_2H_2	Extract is cooled and dissolved in IBMK	132
Urine	1 M HCl	IBAc	0.5–2.5 (P)	Air - C_2H_2	Minimum determinable concentration is 0.1 μg ml^{-1} of P	133
Wines	1–2	IBMK	10–70 (Mo)	Air - C_2H_2	Excess of Mo is determined	134
Fe, steel ..	6 N HNO_3	IBAc	0.05–1.0 (P)		HF is added to avoid interferences from Nb, Ta, Ti, V, W and Zr	135
Synthetic mixtures ..	0.96 M HCl	IBAc	0.083–1.0 (P)	N_2O - C_2H_2	Recovery 89.1–102%. Method is adequate for sequential determination of P and Si	136
Synthetic mixtures ..	0.7	IBAc	Up to 1.0 (P)	N_2O - C_2H_2	Sensitivity 0.01 μg ml^{-1}. Recovery 85.7–110%. Method is adequate for sequential determination of P and Si	137
Fe, steel ..	Acid medium	BAc	Up to 0.35 (PO_4^{3-})	N_2O - C_2H_2	Precision is 3.56 or 1.55% for 0.011 or 0.052% P, respectively	138
Al alloy ..	1	BAc	0.01–1.0 (P)	N_2O - C_2H_2	Sensitivity 0.02 μg ml^{-1}. Recovery 83.3–133.6%	140
Silicon structures ..	0.7 N HNO_3	EtAc	0.006 (P)‡	N_2O - C_2H_2	Si is previously removed with HF. Results obtained agree with those obtained by neutron-activation analysis	141
Pure water ..	0.02 ml 7 N H_2SO_4	BAc	1–4 p.p.b. (Mo)	HGA 70 graphite furnace	10 pg of P in 0.4-ml samples of ultra-pure water determined with errors below $\pm$30%. Back-extracted with 4 N NH_3	142
Steel, cast iron ..	5 ml HNO_3 (1 + 2)	IBAc	0.01–0.1 (P)	Air - C_2H_2	Organic layer is evaporated and molybdophosphate dissolved in dilute nitric acid. Recovery 88–111%	143
Synthetic mixtures ..	2 M HCl	DE	0.1–1.2 (P)	Air - C_2H_2	Recovery 92–110%. Back-extracted with ammonia buffer	144
Rock	1	DE - pentan-1-ol (5:1)	1–10 (Mo)	N_2O - C_2H_2	10 separate determinations on same sample gave results ranging from 0.11 to 0.49% P_2O_5. Back-extracted with ammonia buffer	145
Blood and bovine serum	0.67 M HCl	DE - pentan-2-ol (5:1)		Electro-thermal	Back-extracted with ammonia buffer. Procedure has a relative standard deviation greater than spectrophotometric method	148

* IBMK, isobutyl methyl ketone; IBAc, isobutyl acetate; BAc, butyl acetate; EtAc, ethyl acetate; DE, diethyl ether.

† Given in micrograms of P.

‡ Sensitivity in micrograms per millilitre of phosphorus.

Isobutyl methyl ketone has been used as an extracting agent,[130–132,152] mainly for high phosphate concentrations. Few data on interference effects have been reported. The standard additions method has been employed to overcome matrix effects.[130,152]

The most suitable methods for the indirect determination of phosphate make use of the extraction of molybdophosphoric acid into esters, such as isobutyl acetate[133,135–137] and butyl acetate.[138–140]

Kirkbright *et al.*[136] have worked out a rapid and simple method for the indirect sequential determination of P and Si by the AAS of Mo heteropolyacids. The determination of P (sensitivity 0.007 μg ml^{-1} of P) is almost specific because of the selectivity of isobutyl acetate in the extraction of molybdophosphoric acid. The presence of a 100-fold mass excess of the following ions produces no interferences on 10 μg of P: Al, Au, Bi, Ca, Cd, Co(II), Cr(III), Fe(III), Ni, Pb, Mg, Mn, Se(IV), Te(IV), Ti(IV), Zn, F$^-$, EDTA, NO_3^-, SO_4^{2-}, As(V), Ge(IV), Sb(V) and V(V). A 10-fold mass excess of W(VI) causes no interference in the P determination. No appreciable amounts of free molybdate are extracted into isobutyl acetate.

Another important scheme has been devised for the sequential determination of P, As and Si by using the heteropoly chemistry of Mo.[137] Molybdophosphoric acid is also extracted into isobutyl acetate (sensitivity 0.01 μg ml^{-1} of P). The method is rapid, simple, accurate and practically free from interferences from several foreign ions. With the exception of Ti and Zr, which lead to a low recovery of P, none of the other 40 ions tested interfered at a foreign ion to P ratio of 80. The non-interfering effect of W(VI) and the interfering effect of Ti(IV) on the P determination is in disagreement with the observations made by Kirkbright *et al.*[136] This difference could probably be explained as being related to the different experimental conditions under which the molybdophosphoric acid is extracted.

Butyl acetate has proved also to be an excellent extractant for molybdophosphoric acid in the determination of phosphate.[138–141] Bernal *et al.*[140] compared butyl acetate with other organic solvents, such as isobutyl methyl ketone, acetophenone, diethyl ether, butan-1-ol, amyl alcohol and isoamyl alcohol. They found butyl acetate to be the best, because of its specific selectivity and as it gives virtually a 100% extraction in a single step. Twenty-four ionic species have been shown not to interfere up to a foreign ion to P ratio of 10000:1. Si(IV), W(VI) and Ge(IV) do not interfere up to a ratio of 8000:1 and Ge(IV) up to 6000:1.

1.1.3.1.*b*. *Extraction - decomposition.* The principle of these methods involves the extraction of the molybdophosphoric acid into esters,[142,143] ethers[144] or into mixtures of ethers and alcohols,[145,148] followed by its re-extraction with ammonia solution[142,144,145,148] or, alternatively, by evaporation of the organic layer and dissolution of the solid residue in nitric acid.[143] The Mo liberated into the aqueous solution is then determined by flame[143–145] or electrothermal[142,148] AAS. An advantage of these decomposition procedures is that the standard solutions needed for the construction of calibration graphs may be prepared directly from aqueous molybdate solutions. Furthermore, the atomic-absorption determinations of organic solutions are subject to a number of drawbacks. In spite of the fact that the signal intensity may be enhanced, its stability is usually poor and the results become irreproducible.[143,145]

A very sensitive back-extraction method used for the sequential indirect determination of P and As in pure water has been described by Rozenblum.[142] The method relies on the use of butyl acetate as the extractant for the molybdophosphoric acid and the determination of Mo in ammonia solution is then carried out in a graphite furnace. As low as 25 pg ml^{-1} of P may be determined. Other schemes have also been devised for the sequential determination of P and Si[144,145] and have been applied to rock analysis.[145] This last procedure created a controversy in relation to its unsuitability for the analysis of Si in rocks.[146,147]

1.1.3.1.*c*. *Precipitation of molybdophosphoric acid.* Melton *et al.*[149] have used the gravimetric quinolinium molybdophosphate method of phosphate precipitation and dissolution in ammonia solution for determining P in fertilisers (5.51–48.07% P_2O_5 content). The determination of Mo is carried out in an air - acetylene flame at its 320.9-nm secondary resonance line. The method for the determination of macro-amounts of P is rapid and simple and its accuracy compares favourably with the AOAC method.[149a]

1.1.3.2. *Ternary heteropolyacids*

These methods are based on the formation of molybdovanadylphosphoric[150] or molybdoantimonylphosphoric[151] acids followed by their extraction into isobutyl methyl ketone or butyl acetate, respectively. In the former, the determination of the V absorbance at the 318.5-nm line in a dinitrogen oxide - acetylene flame is related quantitatively to the P content. The detection limit is 0.0005% of P. In the latter, the atomic absorption of Mo at 313.3 nm or of Sb at 217.6 nm is measured in a graphite furnace. The working graph for P is found to be linear over the range 0.01–0.15 μg (Mo measurements) or 0.1–2 μg (Sb measurements). The molybdovanadylphosphoric acid method[150] has been applied satisfactorily to the determination of P in steel and iron. Elements usually present in these samples do not interfere. The molybdoantimonylphosphoric acid method[151] has been applied to the determination of trace amounts of P in sulphur and in phosphosilicate glass with satisfactory results. Interferences from Bi, Ca, Co, Fe(III), Mn(II), Pb, Se(IV), Si, Te(IV) and Zn at a 100-fold mass excess are almost negligible, but As(III), Ge and Cr(VI) interfere seriously.

1.1.4. Redox Reactions

Oxidising or reducing substances may sometimes be determined by reaction with either one or two reagents (one of which is a metal ion) that can be oxidised or reduced by the substances involved. A separation procedure is then used to isolate either the reduced or the oxidised form of the added metal ion. In general, these methods are not very selective, because complete absence of other oxidising or reducing agents is required. They are divided into inorganic anions and organic compounds, according to the chemical nature of the analyte.

1.1.4.1. *Inorganic anions: determinations of iodide, iodate, nitrate and chlorate*

Iodides (up to 5×10^{-3} mequiv.) have been determined by their reaction with Cr(VI) in an acidic medium and then extraction of the unreacted Cr(VI) into isobutyl methyl ketone from a 3 M HCl medium. The increase in the atomic signal of the Cr(III) in aqueous solution or the decrease in the atomic absorption of the Cr(VI) in the organic phase may be quantitatively related to the iodide concentration.[6] The reduction of Se(IV) to elemental Se by iodide (up to 10^{-3} mmol) in an acidic medium followed by AAS of Se has been also proposed.[153,154]

Iodate (up to 3×10^{-3} mequiv.) has been determined by oxidation of Fe(II) to Fe(III) and extraction of the latter into diethyl ether from 9 M HCl solution, followed by flame AAS of Fe in the organic layer.[6] The presence of air in the aqueous solution is critical for an accurate method and it is necessary to deaerate all solutions with nitrogen to prevent air oxidation of the Fe(II).

Hassan[155] has proposed an indirect method for determining nitrates (0.2–2 mg of nitrate-nitrogen) by reduction with Cd metal in a 0.05–0.1 M HCl medium. The dissolved cadmium is aspirated into an air - acetylene flame and measured at its 228-nm line. The reaction of nitrate under the prescribed conditions proceeds through a four-electron reduction process.

$$2NO_3^- + 4Cd + 10H^+ = N_2O + 4Cd^{2+} + 5H_2O$$

No interferences occur in the presence of up to a 100-fold mass excess of Cl^-, SO_4^{2-} $C_2O_4^{2-}$, CO_3^{2-}, PO_4^{3-} and NH_4^+. The method has been applied with excellent results to inorganic and organic nitrates.

Mitsui and Fujimura[156] proposed a simple and rapid method for the indirect determination of chlorates. The method is based on the reduction of chlorate (0.012–2.24 μg ml^{-1} of ClO_3^-) to chloride with Fe(II), precipitation of silver chloride and its dissolution with ammonia. The method is not very selective.

1.1.4.2. *Organic compounds*

Some organic compounds have also been determined indirectly by redox reactions. Two types of reactions have been employed. One involves the reduction of the analyte with a metal in solution and the metal precipitate is dissolved in nitric acid[99,157–159] and determined by AAS, or the unreduced metal[160] is determined by AAS. The other is based on initial oxidation with periodic acid[99,161] or potassium permanganate,[162] precipitation[99,161] or complexation[162] with a metal ion solution and determination by AAS of the metal precipitate after dissolution[99,161] or liquid - liquid solvent extraction.[162] In general, the reported procedures have been applied to functional groups (Table IX).

TABLE IX

DETERMINATION OF ORGANIC COMPOUNDS BY REDOX REACTIONS

Compound	Matrix	Measured metal	Quantitative relationship	Characteristics of the method	Reference
Aldehydes	Water	Ag	Add Tollen's reagent and dissolve Ag precipitate in HNO_3	0.25–4 μmol ml^{-1} of compound can be determined. Recovery is 95–103%	157
Acetaldehyde ..	Ethanol	Ag	Sample is treated with Tollen's reagent; the precipitated Ag is filtered and dissolved in HNO_3	Limit of detection is 0.0019 mg of acetaldehyde	99
Polyhydric alcohols	Ethanol	Ag	Alcohols react with HIO_4 to yield iodate which is precipitated with silver nitrate. Precipitated Ag is dissolved in ammonia	Limits of determination are (mg): glycerol, 0.16; lactose, 0.82; saccharose, 1.93; glucose, 0.28; tartaric acid, 1.22; benzoin, 1.07	99
Aliphatic and aromatic 1,2-diols ..	Water	Pb	Diols are oxidised with HIO_4. Iodate is then precipitated with Pb(II) and this Pb dissolved in nitric acid	0.4–4 μmol ml^{-1} can be determined. Method is rapid and selective, but precision is poor. Recovery 93.3–101.3%	161
Nitro compounds ..	Water	Ag	Nitro compounds are reduced with Zn. Tollen's reagent is added and the precipitated Ag dissolved in HNO_3	Metal ions interfere strongly, but their effect can be avoided by extraction of nitro compounds into benzene. Resorcinol, benzoin, *p*-aminophenol and ninhydrin also interfere	159
Sugar	Plant materials	Cu	Cu(II) is added in alkaline medium, Cu_2O removed and unreacted Cu(II) determined	0.1–0.5 mg ml^{-1} of dextrose can be determined. Recovery 99.6–102.4%. Method compares favourably with AOAC method	160
Folic acid	—	Ni	Acid is oxidised with MnO_4^-, the product complexed with Ni and extracted into IBMK	Linear range is 1.2–20 μg of Ni per mole of folic acid. No interference is observed from some organic substances	162

1.2. Methods Based on the Formation of Compounds in the Atomisation Cell

These methods are based on the fact that some anions form refractory compounds with metal elements at the atomisation cell temperature. They are divided in two groups, depending on whether the absorption measurements are monitored on either atoms or molecules. An important characteristic of these methods, as compared with those described previously, is that the chemical reaction used to establish a quantitative relationship between the metal and anion is carried out in the atomisation cell itself and not in the solution. Therefore, they are, in general, more rapid as no prior separation of the chemical species of the metal to be determined is required.

1.2.1. Suppression or Enhancement of the Atomic-absorption Signal of a Metal

This type of method involves measurement of the suppression or enhancement of the atomic signal of a given metal by its reaction in the atomisation cell with the anion to be determined. These methods are rapid, but their selectivity is affected by the presence in the analyte-containing solution of other species that might suppress or enhance the absorbance of the metal added. However, in order to overcome interferences from metal cations, the sample should be treated previously with a cation-exchange resin.[163–169] Similarly, in some instances, potentially interfering anions should be removed either by an anion-exchange resin[167] or by precipitation.[165]

The methods are classified into two groups, according to the addition of a constant or variable concentration of metal ion to the anion-containing solution.

1.2.1.1. *Constant concentration of the metal added*

As a rule, the calibration graph is constructed using a suitable concentration of metal to obtain a linear change of absorbance (with negative slope) in the presence of increasing amounts of the analyte, at the concentration level expected to be present in the samples. The anion concentration in the sample solution is determined by adding the same concentration of metal as in the calibration graph, measuring the absorbance by AAS and relating this measurement to the calibration graph.

In this indirect method, the described procedures have been classified according to the nature of the metal ion added.

1.2.1.1.*a*. *Alkali metals: determination of fluorine.* Gutsche *et al.*[170] described a rapid micro-method (0.1 µl of sample is employed) for the indirect determination of fluorine by reacting sodium vapour with fluorine-containing compounds at temperatures of about 800 °C. The decrease in the atomic Na concentration gives a relative and specific (Cl^-, Br^- and I^- do not interfere practically) value for the amount of fluorine present. The method is also very sensitive (detection limit 0.8 ng) and may be employed as the basis of a fluorine detector device in the gas-chromatographic determination of trifluoroethanol.

1.2.1.1.*b*. *Alkaline earth metals: determinations of phosphate, sulphate, fluoride and organic compounds.* Phosphates (4–20 µg ml^{-1} of P) and sulphates (10–30 µg ml^{-1} of S) can be determined by the depressing effect they have on the atomic absorption of 20 µg ml^{-1} of Ca at the 422.7-nm line in an air - acetylene flame.[1] El Shaarawy[171] pointed out that the sensitivity is highest at P to Ca ratios lower than 0.5 and, although the sensitivity increases on using an air - hydrogen flame, an air - acetylene flame is preferred because interferences are fewer. The method has been satisfactorily applied to the analysis of P in foods[171] and rock phosphate.[163]

A practical method for the determination of phosphate (up to 10 µg ml^{-1} of P) in aqueous and biological media has been proposed by Ezhova[172] employing a constant concentration of added Sr and keeping a Sr to P ratio of greater than 1.7. Absorbance measurements are made at the 460.7-nm Sr line. The method has been used for determining P in rock phosphate.[164]

Bond and O'Donnell[165] have utilised the depressing effect of F^- ions on the Mg atomic signal to determine fluoride (0.2–20 µg ml^{-1} of F^-) in an air - coal gas flame. The method is subject to interferences mainly from phosphate, sulphate and a high concentration of mineral acids. Aluminium, lanthanum, acetate and oxalate also interfere at concentrations greater than 1000-fold the fluoride concentration. Few other cations interfere at a significant level, their interference being compensated for by the addition of an excess of cation to both the sample and the standard solutions.

Christian and Feldman[6] have reported that glucose ($<10^{-6}$ M) and ribonuclease (<3 µg ml^{-1}) may be determined by their depressive action on the absorbance of 25 and 14 µg ml^{-1} of Ca, respectively.

1.2.1.1.*c*. *Transition metals: determinations of fluoride, sulphate and ammonia.* A procedure based on the enhancement of Zr atomic absorption at 360.1 nm (500 or 2000 µg ml^{-1} of Zr are employed) by fluoride in the dinitrogen oxide - acetylene flame has been reported by Bond and O'Donnell.[165] The method is less sensitive (5–200 µg ml^{-1} of F^-) than the Mg-based method described previously, but allows a higher degree of freedom from interferences. In the presence of phosphate, which interferes in the Zr method, a similar enhancement of Ti atomic signal allows the determination of fluoride in the range 40–400 µg ml^{-1} by addition of 400 µg ml^{-1} of Ti and measuring at the 364.3-nm Ti line.[165]

Kunishi and Ohno[173] have developed an atomic-absorption inhibition - release method for the determination of the sulphate in rhodium-plating baths. The method involves a decrease of the Fe(III) atomisation in the plating solutions and a corresponding increase in Fe absorbance when a standardised La(III) solution is added. The authors propose the following mechanism:

$$Rh(SO_4)_n^{(2n-3)-} + Fe^{3+} \rightleftharpoons Rh(SO_4)_n^{(2n-3)-} - Fe^{3+}$$

$$3La^{3+} + 3SO_4^{2-}{}_{(free)} \rightleftharpoons La_2(SO_4)_3$$

$$Rh(SO_4)_n^{(2n-3)-} - Fe^{3+} + (2n/3)La^{3+} \rightleftharpoons (n/3)La_2(SO_4)_3 + Fe^{3+} + Rh^{3+}$$

At the point where La(III)/SO_4^{3-} is approximately 2/3, the Fe absorbance increases steeply and sharp breaks occur. The amount of total sulphate is quantitatively determined by extrapolation at the position of these breaks.

The enhancement of Zr absorbance in a dinitrogen oxide - acetylene flame at its 360.1-nm line by ammonia has been employed by Bond and Willis[174] for determining ammonia. The calibration graph covers 1.7–85 µg ml^{-1} of NH_3. There are no interferences from NO_3^- and SO_4^{2-}, but PO_4^{3-} does interfere. Mitsui and Fujimura[175] reported an interesting method for the indirect determination of trace amounts of ammonia (up to 20 µg ml^{-1} of NH_4^+) by the enhancement effect on the atomic absorption of silver in an air - acetylene flame. The recovery ranged from 98 to 100%. Calcium and zinc interfere.

1.2.1.2. *Variable concentration of the metal added*

In recent years, new indirect determinations based on sharp shifts in the magnesium atomic absorption have been developed. These methods are divided into two groups: atomic absorption inhibition titration (AAIT) and atomic-absorption inhibition - release titration (AAIRT).

1.2.1.1.*a*. *Atomic-absorption inhibition titration: determinations of sulphate and phosphate.* The inhibition titration experiment involves the addition of an Mg(II) titrant solution to a stirred solution of the anion from which metal cations have been removed. The titrated solution is simultaneously aspirated into an air - hydrogen flame and the atomic signal of the magnesium is monitored. Typical calibration graphs are given in Fig. 4. In the AAIT method the experimental conditions, such as a relatively cool flame, the hydrogen - air flow ratio and the beam height, are optimised. However, the most critical parameters are the flame temperature and the anion to metal molar ratio.[166,169] Magnesium is selected as the titrant metal owing to both its atomic-absorption sensitivity and the large inhibition that can be brought about by anions forming Mg refractory compounds. Important advantages of this method are speed, simplicity and sensitivity. However, the devices used proved to be suitable for studying analytical interference effects and flame reactions.[177,178]

A rapid and sensitive method for the determination of sulphate [Fig. 4(*a*)] at trace levels (1–20 μg ml^{-1} of SO_4^{2-}) has been described by Looyenga and Huber.[166] In the absence of trace amounts of interfering ions (*e.g.*, phosphate and silicate) the method is applicable to

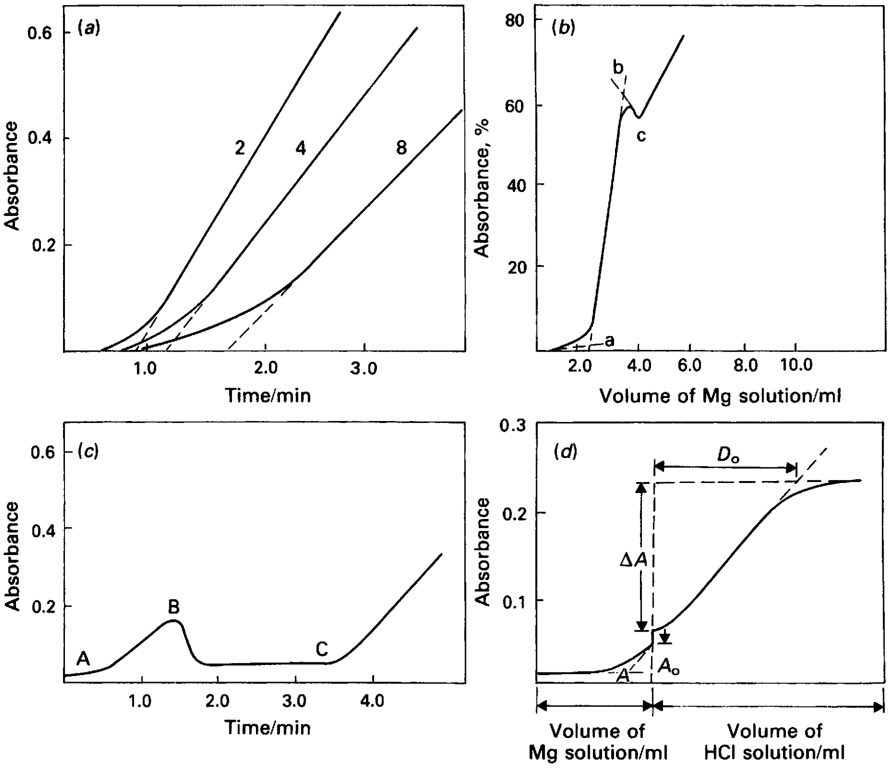

Fig. 4. Typical graphs recorded in AAIT (a^{166}, b^{167} and c^{176}) and AAIRT (d^{169}). (*a*) Titrations of 2.0, 4.0 and 8.0 μg ml^{-1} SO_4^{2-} with 50 μg ml^{-1} Mg solution; titrant flow-rate, 1.49 ml min^{-1}. (*b*) Titration of 8 μg ml^{-1} PO_4^{3-} with 200 μg ml^{-1} Mg solution; for a, b and c see text. (*c*) Titration of 1.0 μg ml^{-1} SiO_2, 4.0 μg ml^{-1} PO_4^{3-} and 20 μg ml^{-1} SO_4^{2-} with 50 μg ml^{-1} Mg solution; titrant flow-rate, 2.03 ml min^{-1}; for A, B and C see text. (*d*) Titration of 2.0 μg ml^{-1} F^- with 50 μg ml^{-1} Mg solution, followed by 0.001 M HCl. Aspiration rates: $MgCl_2$, 2.0 ml min^{-1}; HCl, 1.05 ml min^{-1}. ΔA, fluoride analytical signal; solid line, smoothed recorder trace.

concentrations as low as 0.1 μg ml^{-1} of SO_4^{2-}. Crawford *et al.*[167] studied an Mg-based AAIT method for ortho-, pyro-, tri-, tetra- and hexaphosphates. The shape of the calibration graph for orthophosphate [Fig. 4(*b*)] suggests the formation of refractory compounds with 2, 3 and 4 Mg atoms for each atom of P. At points a, b and c, the Mg to PO_4^{3-} ratio remains essentially constant and any of these points may serve as an end-point for the titration even in the presence of sulphate. Silicate must be removed or previously determined. The procedure has been used to determine phosphate satisfactorily in river water and detergents. A similar method has been used by Nyangababo and Hamya[168] for determining phosphate in fresh waters.

A very rapid, sensitive and selective method for the simultaneous titration of silicate, phosphate and sulphate has been reported.[176,179] The titration graph shows three distinct rectilinear segments (A, B and C) with different slopes [Fig. 4(*c*)], corresponding to silicate, silicate and phosphate and silicate, phosphate and sulphate, respectively. The method is sensitive enough to determine these three anions in most waste waters, as well as silicate and sulphate in surface and drinking waters.

1.2.1.1.*b*. *Atomic-absorption inhibition - release titration*: *determination of fluoride*. Fong and Huber[169] have developed a magnesium-based AAIRT method for the determination of fluoride (0.1–10 μg ml^{-1} of F^-) in solution. It is based on the distinctive pH dependence of the MgF_2 inhibition reaction [Fig. 4(*d*)]. The sample is adjusted to pH 5.2 ± 0.2 and an excess of $MgCl_2$ is added, until a pre-determined signal magnitude is obtained [A_0 in Fig. 4(*d*)]. The addition of Mg is then stopped and the addition of 0.001 M HCl is begun. With decreasing pH, a distinct upward shift in the Mg atomic-absorption signal is obtained, corresponding to the amount of Mg released from the inhibition of fluoride [ΔA in Fig. 4(*d*)]. This effect permits the determination of fluoride in the presence of equal or larger amounts of sulphate and other anions. It has even been suggested that the procedure can also be employed for the standardisation of an acid solution. The numerical value of D_0 (the number of milliequivalents of the acid solution added that are necessary to reach a constant value in the Mg atomic signal) is inversely proportional to the acid concentration and is obtained from the Mg absorbance *versus* volume of reactants, as observed in Fig. 4(*d*).

1.2.2. Molecular-absorption Spectrometry: Determination of Halogens

Molecular-absorption spectrometry (MAS) has seldom been applied to the determination of anions.[180,181] In this section those MAS methods are described which are based on the formation of stable metal - halogen molecules in the atomisation cell by nebulisation of the anion-containing solution to which a metal ion in excess has been added. The molecular absorption of the compound formed is then measured at the absorption peak by means of a deuterium lamp. An important drawback of these indirect methods is the serious background absorption.[180]

Tsunoda *et al.*[180] have determined nanograms of Cl^- and Br^- by means of molecular absorption of AlCl at 261.4 nm (sensitivity 0.12 ng of Cl^-) and AlBr at 279.0 nm (sensitivity 1.1 ng of Br^-) in a carbon-rod furnace. Aluminium solutions containing Fe(III) + Sr(II) or Co(II) + Sr(II) may be employed to decrease background absorption as well as a two-channel spectrophotometer. The method is rapid, simple, sensitive and relatively free from interferences of foreign ions. However, interferences from Br^- or I^- on the AlCl absorption and I^- on the AlBr absorption are not reported. These workers have applied this method, with good results, to the determination of chlorine in NBS orchard leaves and chlorine or bromine in solutions containing trace amounts of organo-oxychlorine and bromine compounds. A similar procedure has also been described[181] for the determination of chloride (up to 28.6 μg ml^{-1} of Cl^-) by molecular absorption of InCl at 267.2 nm.

1.3. Methods Based on the Formation of Volatile Compounds: Determination of Halogens

In this section, the methods associated with the formation of gaseous compounds fed into the atomisation cell are described. The methods involving the formation of PH_3 are not considered here, as they have been reviewed widely in the literature on volatile hydrides.

Gutsche *et al.*[182] developed a method for the specific determination of trace amounts of fluoride via gaseous SiF_4. The atomic absorption of Si is measured at its 251.6-nm resonance line using either a dinitrogen oxide - acetylene flame (detection limit 30 μg of F^-) or a graphite furnace (detection limit 0.17 μg of F^-).

A rapid but not very sensitive and selective method has been employed for determining chloride (50–200 μg ml^{-1} of Cl) in minute volumes of inorganic and organic compounds in solution by means of gaseous CuCl.[183]

Iodides (1×10^{-6}–5×10^{-5} M) have been determined by heating solutions containing I^- and $Hg(NO_3)_2$ in a graphite tube. Two Hg absorption peaks appear because the decomposition temperature of HgI_2 is higher than that of $Hg(NO)_3)_2$.[184] Cyanide, S^{2-} and $S_2O_3^{2-}$ interfere, but in the presence of H_2O_2 do not. Interfering cations may be removed by extraction as metal quinolin-8-olates.

2. DIRECT METHODS

In these methods, the direct atomic signal measurement of an element is related to its concentration. They are divided into methods based on non-metallic elements (inorganic anions) and on metallic elements (organometallic compounds and metal chelates), according to the nature of the measured element.

2.1. Non-metallic Elements

The direct determination by AAS of non-metallic elements (halogens, O, S, N, P and C) involves special difficulties. Some of these problems arise from the fact that these elements exhibit their principal resonance in the vacuum ultraviolet region, where an intense absorption by the atmosphere and the flame itself is observed (Table X). Therefore, measurements in this spectral zone requires an atomic-absorption spectrophotometer whose optical system and instrumental assembly can be evacuated or purged with an inert gas. Although a vacuum monochromator has been employed, a nitrogen or argon purged monochromator of greater luminosity can be used as well.[185] Such instruments are not readily available in many analytical laboratories. However, because of the very high absorption in the ultraviolet region, particular attention should be paid to desorption processes that can distort the analytical signal. Linked with this is the strong non-specific absorption to be expected in this range, which must certainly be taken into account in measuring. Therefore, background correction is essential, which may be carried out by alternative measurement of the radiation from a line source and that of either a continuous source or a non-resonance line.

TABLE X

MAIN RESONANCE LINES AT WAVELENGTHS OF LESS THAN 200 nm OF NON-METALLIC ELEMENTS *

Element	Line/nm	Element	Line/nm
F	95.2, 95.5	O	130.22
Cl	134.7, 138.0	S	180.7, 182.4, 182.6
Br	145.0, 148.9, 157.6	N	119.96
I	178.3, 183.0	P	177.5, 178.3, 178.8
		C	156.1, 165.7

* From references 3, 4 and 190.

Other difficulties arise from the tendency of O, P, N, S and C to form molecular species even at high temperatures.[186–190] Nevertheless, this fact may be made use of for the determination of non-metallic elements.[186,187]

With a conventional instrument, non-metallic elements can be determined in the region of the spectrum above 200 nm by either atomic or molecular absorption using a non-resonance line of the element or an adequate band of the molecular species of the analyte. However, the sensitivity under these conditions is generally lower than that obtained measuring at wavelengths below 190 nm. In addition, the sensitivity is highly temperature dependent in some instances.[189]

Apart from the problems connected with the analytical line, difficulties are also encountered in finding intense and stable emission sources for non-metallic volatile elements, such as halogens, S and P.

Hollow-cathode lamp (HCL) sources do not have sufficient intensity to permit their use for non-metallic elements with the existing optical arrangement.[191] Also, it is difficult, with elements of high volatility, to ensure the manufacture of reproducible stable sources.[192]

Although electrodeless discharge lamp (EDL) sources have circumvented some drawbacks of the sealed-off HCLs for these elements, in relation to the emission intensity, signal to background intensity ratio, stability and limited operating lifetime, other problems still exist. For example, there is an appreciable self-absorption when EDLs are employed. As reported by Kirkbright and co-workers,[185,192,193] some difficulty has been experienced in achieving intense emission at the resonance lines below 200 nm for P, S and I, particularly if source line broadening owing to self-absorption is to be minimised. This self-absorption can be partly eliminated by operating the source at lower power[192] or at low pressure.[194]

TABLE XI

SENSITIVITIES, DETECTION LIMITS AND TOLERANCE LIMITS OF PHOSPHORUS, SULPHUR AND IODINE FOR SOME ANALYTICAL LINES EMPLOYED IN DIRECT METHODS BY FLAME AAS

Element	Source *	Wavelength/ nm	Flame type	Sensitivity †	Detection limit †	Tolerance limits for foreign ions ‡	Reference
P ..	DDL	246.0	N_2O - C_2H_2	—	20	NH_4^+, Na, K, Mg, Ca, Mn, Cu, Zn (1:1.2)	186
P ..	HCL	213.5/213.6	Air - C_2H_2	290	—	Many cations interfere	197
P ..	HCL	214.9	Air - C_2H_2	540	—	As above	197
P ..	-	213.5/213.6	N_2O - C_2H_2	—	130	Al, Ca, Cu, Fe, K, Na (1:1)	198
P ..	EDL	177.5	N_2O - $C_2H_2(N_2)$	4.8	29	I^-; not reported for other ions	191
P ..	EDL	178.3	N_2O - $C_2H_2(N_2)$	5.4	21	Al, Ba, Ca, Cd, Cu, K, Li, Mg, Mo, Na, Ni, Zn, Cl, Br, F, NO_3^-, SO_4^{2-}, BO_2^-, CO_3^{2-}, EDTA (1:40)	191
P ..	EDL	178.8	N_2O - $C_2H_2(N_2)$	8.8	37	I^-; not reported for other ions	191
S ..	DDL	207	Air - H	10	—	§	187
S ..	DHCL	182.6	N_2O - $C_2H_2(N_2)$	5	10	§	192
S ..	DHCL	182.0	N_2O - $C_2H_2(N_2)$	3	5	§	192
S ..	DHCL	180.7	N_2O - $C_2H_2(N_2)$	1	5	§	192
S ..	EDL	180.7	N_2O - $C_2H_2(N_2)$	9	30	Al, Cu, K, Mg, Mn, Mo, Na, Ni, Zn, F, Cl, Br, PO_4^{3-} (1:5)	185
I ..	EDL	206.2	N_2O - C_2H_2	1300	600	§	199
I ..	DHCL	183.0	N_2O - $C_2H_2(N_2)$	14	22	§	192
I ..	EDL	183.0	N_2O - $C_2H_2(N_2)$	12	25	Cu, Co, Cr, K, Na, Ni, Mg, Mo, Zn, Al, Hg(1:50); F, Cl, Br, NO_3^-, PO_4^{3-}, SO_4^{2-} (1:100)	195
I ..	CDL	183.0	N_2O - C_2H_2	6	9	§	200

* DDL, deuterium discharge lamp; CDL, capillary discharge lamp of He - I vapour.
† Definitions and units are given in Table IV.
‡ In parentheses, P to foreign ion mass ratio, except for reference 186, which is molar ratio.
§ Not reported.

Kirkbright and Wilson[192] described a type of demountable hollow-cathode lamp (DHCL) as an alternative sharp line source for P, S and I, and compared it with the corresponding microwave excited EDLs for the same elements. The most significant improvement in performance characteristics is observed for the sulphur DHCL source. However, using a DHCL, the resonance lines for P in the 177–179 nm spectral range are rather weak, but the 213.5 - 213.6 nm and 252.5 nm lines show appreciable intensity.

From the elements given in Table X, it is to be noted that physical conditions are not favourable for the determination by AAS of certain gases (N and O) and C.[190] Because of the low degree of dissociation, an unwanted high theoretical detection limit is expected for these elements. A particularly high experimental cost is to be expected for elements with resonance lines below 105 nm (*e.g.*, F) as for this range there are no materials for windows.[190]

These methods are classified into two groups: flame and electrothermal methods, according to the procedure used to obtain the atom population.

2.1.1. Flame Methods

The strong radiation absorption in vacuum ultraviolet by the atmosphere and most flames made the use of wavelengths above 200 nm in the early stages of the direct determination of non-metallic elements by flame AAS compulsory and until recently it has been assumed that only poor sensitivity could be attained.

However, since the description by Kirkbright and co-workers[185,193,195,196] of the N_2-separated dinitrogen oxide - acetylene flame, the determination of these elements at their more sensitive resonance lines, shorter than 200 nm, became possible. This flame shows a remarkable transparency at these wavelengths owing to the absence of absorbing oxygen species in the interconal zone of the flame and the separation of the oxidising outer mantle by N_2 shielding. Although the dilution effects are less severe with other flames, such as air - acetylene and nitrogen - hydrogen entrained air, these latter flames show a transparency too low to be used below 190 nm. In addition, chemical and physical interferences are more serious in these cooler flames.[185,191,195] A correlation of sensitivities, detection limits and tolerance limits of foreign ions for P, S and I using different flame types is given in Table XI.

2.1.1.1. *Atomic-absorption spectroscopy: determinations of phosphorus, sulphur and iodine*

It can be seen that the most suitable lines for the direct determinaion of P are in the spectral region between 177 and 179 nm. No background emission is detected at this spectral zone.[191] In order to circumvent the difficulties arising from work in the vacuum ultraviolet, the less sensitive non-resonance lines at the 213.5 - 213.6 nm doublet have also been employed (Table XII). The determination of P by AAS does not exhibit the severe interferences that are given in flame emission, but it is considerably less sensitive.[198]

TABLE XII

ANALYTICAL APPLICATIONS OF DIRECT ATOMIC-ABSORPTION TECHNIQUES FOR DETERMINATION OF NON-METALS

Sample	Element determined	Wavelength/ nm	Atomisation cell	Standard used	Concentration of element in analysed sample	Reference
Nucleotides	P	246.0	N_2O - C_2H_2	H_3PO_4	3.39–574 mg ml^{-1} of P	186
Foodstuffs	P	178.3	N_2O - $C_2H_2(N_2)$	$(NH_4)_2HPO_4$	0.73–1.34% (*m/m*)	191
Detergents	P	214.3	N_2O - C_2H_2	H_3PO_4 *	13.8 and 18.7% (*m/m*)	201
NBS orchard leaves	P	213.6	HGA 2100	$CaHPO_4$ †	0.21% (*m/m*)	202
Biological materials (NBS)	P	214.9; 213.6	Graphite profile tubes	KH_2PO_4 †	0.19–1.10% (*m/m*)	203
Gasoline	P	214.2	HGA 2100	Triphenyl phosphate ‡	0.005–0.01 g gal^{-1} of P	204
BCS steels	P	213.6	Graphite profile tubes	$NH_4H_2PO_4$	0.010–0.062% (*m/m*)	205
BAM steels	P		Graphite furnace	$(NH_4)_2HPO_4$ †,§	Down to 0.002% (*m/m*)	206
Oils, fats	P	213.5/213.6	HGA 76B	Ammonium phosphate¶	1–100 µg ml^{-1} of P	207, 208
Gasoline	P	213.6	HGA 2100	Tricresyl phosphate ‡	3–65.2 µg ml^{-1} of P	209
Amino acids and derivatives	S	207	Air - H	H_2SO_4	1–12 mol of S per mole of compound	187
Oils	S	180.7	N_2O - $C_2H_2(N_2)$	Dibenzyl disulphide‖	0.106–2.68% (*m/m*)	193
Rat thyroid	I	183.0	Graphite furnace	KI	94–117 mg of I per 100 g	210

* Matrix interference is compensated for by the addition method.
† A solution of $La(NO_3)_3$ is previously injected into the graphite furnace.
‡ Standard dissolved in P-free gasoline.
§ Zeeman correction is used.
¶ Standards and samples are ashed with $MgSO_4$ and P is converted into $Mg_2P_2O_3$ and dissolved in HNO_3.
‖ Standards dissolved in IBMK.

Sulphur and iodine are determined at their 180.7- and 183.0-nm resonance lines, respectively (Table XII). Although a higher sensitivity is obtained for iodine at 178.2 nm, the recorded emission intensity from the EDL source is lower at this line than at 183.0 nm, and the precision of the measurements thus becomes lower.[211] On the other hand, the Leipert amplification procedure, based on the reactions

$$\mathrm{I}^- \overset{\mathrm{Br}_2}{\rightleftharpoons} \mathrm{IO}_3^-$$

$$\mathrm{IO}_3^- + 5\mathrm{I}^- + 6\mathrm{H}^+ \rightleftharpoons 3\mathrm{I}_2 + 3\mathrm{H}_2\mathrm{O}$$

provides a 38-fold increase in sensitivity as reported by Kirkbright *et al.*[196] There is, however, a loss of selectivity when substances capable of oxidising iodide to elemental iodine are present. Nevertheless, interfering cations may be removed by cation exchange.

The sensitivity for both sulphur and iodine can be enhanced by solvent extraction[195,196] or by addition of a miscible organic solvent to the aqueous solution.[185] This fact is fully accounted for by the improved nebuliser efficiency obtained with the organic solvent.

2.1.1.2. *Molecular-absorption spectroscopy: determinations of phosphorus and sulphur*

Both P[186,189] and S[187,188] show a great tendency to form molecular species with oxygen in most atomisation - excitation media, the determination of these elements at the 246.0 nm (PO) and 207 nm (SO_2) molecular bands also being possible (Table XII).

TABLE XIII

SENSITIVITIES, DETECTION LIMITS AND TOLERANCE LIMITS OF PHOSPHORUS, SULPHUR, IODINE AND BROMINE FOR SOME ANALYTICAL LINES EMPLOYED IN DIRECT METHODS BY ELECTROTHERMAL AAS

Element*	Wavelength/nm	Atomisation device	Sensitivity†	Detection limit†	Tolerance limits for foreign ions‖	Reference
P ..	177.5	Graphite furnace	1.3×10^9 ‡	—	§	214
P ..	213.6	HGA 2100	0.075 ¶	0.3 ¶	Mg, Na, K, As (1:100); Si (1:50)	202
P ..	213.5/213.6	HGA 2100	0.075 ¶	0.1 ¶	§	217
P ..	214.2	HGA 2100	—	0.2 ¶	§	204
P ..	213.5/213.6	HGA 76B	—	0.2¶	§	207
P ..	213.5/213.6	HGA 76	—	2 ng	§	218
S ..	180.7	Graphite furnace	5.4×10^7 ‡	—	§	214
S ..	180.7	Graphite furnace	0.42 µg	—	§	219
S ..	182.0	Graphite furnace	0.68 µg	—	§	219
S ..	182.6	Graphite furnace	1.5 µg	—	§	219
S ..	216.9	Microwave discharge in quartz cell	—	0.3 µg as H_2S or 0.7 µg as SO_2	§	188
I ..	178.2	Graphite tube	0.02	—	§	211
I ..	183.0	Graphite tube	0.04	—	$NaNO_3$ (1:1000); KCl, Na_2SO_4, NaCl, Na_2HPO_4 (1:100)	211
I ..	183.0	Graphite furnace	1.2×10^8 ‡	—	§	214
I ..	183.0	HGA 2000	0.1	0.4	Cl, Br, Na (1:100)	210
I ..	183.0	Cathode sputtering cell	12	6	Cl, Br, F, NO_3^- (1:50)	221
I ..	183.0	Platinum loop	9	18	Interfering cations are removed by cation exchange and some anions via oxidation of iodide to iodine and solvent extraction followed by reduction of iodine to iodide	220
I ..	206.1	HGA 2000	3.5	10	§	210
I ..	206.16	Graphite cuvette	—	2 ng	§	215
Br ..	148.86	Special graphite furnace	—	1.5 ng	§	190

* An EDL source is used in all instances.
† Definitions and units are given in Table IV.
‡ Sensitivity given in absorbance per gram.
§ Not reported.
¶ $La(NO_3)_3$ solution is employed for correcting matrix interferences.
‖ Values in parentheses are the P to foreign ion mass ratio.

2.1.2. Electrothermal Methods: Determination of Phosphorus, Sulphur and Iodine

The first attempts to determine P by electrothermal AAS were made by Walsh[212] in the early 1960s and later by L'vov and Khartsyzov[213] in their experiments with a graphite cuvette. The direct determinations of S and I by electrothermal techniques were reported by L'vov and Khartsyzov[214,215] and by Berezin.[216]

In a fuel-rich N_2-separated dinitrogen oxide - acetylene flame three problems arise[211]: (i) a relatively large volume of sample is required for nebulisation; (ii) the sensitivity is limited by the difficulty of achieving high sample concentrations in the cell, owing to dilution by the support gas; and (iii) at short wavelengths a degradation of the signal to noise ratio occurs owing to fluctuating absorption at the flame - atmosphere interface. Therefore, the use of non-flame atomisation devices overcomes the limitations imposed by the nature of the flames: the absorption by flame gases is eliminated and, compared with flames, reduced noise levels as well as higher sensitivities can be achieved[189,211] (Table XIII).

The graphite furnace is the most widespread technique of electrothermal atomisation. As the inert purge gas either nitrogen or argon can be utilised. However, argon has been reported to produce a two-fold increase in sensitivity for P with respect to nitrogen.[207] On the other hand, the sensitivity is greatly affected by temperature and tube conditions.[189,204,207] The use of graphite profile tubes has been proved to increase the sensitivity of many elements by a factor of 3–5 over that of standard cylindrical tubes.[205]

TABLE XIV

COMBINATION OF CHROMATOGRAPHIC AND ATOMIC-ABSORPTION SPECTROMETRIC TECHNIQUES FOR ANALYSIS OF ORGANIC COMPOUNDS

Compound	Matrix	Chromatographic* method	AAS	Comments	Reference
Lead alkyls ..	Gasoline	HPLC	Pb; flame	Determination at µg level	226
Metallothionein	Protein	HPLC	Cd, Zn or Cu; flame	Gel-permeation column is used	227, 228
Tin tetraalkyls, alkyltin chlorides		HPLC or GC	Sn; flame	Detection limit 11–19 µg. Sensitivity 0.9–1.5 µg	229
Triphenyltin ..	Biological Samples	LC	Sn; flame	Column packed with Al_2O_3. Compound to be determined is previously extracted into $CHCl_3$ - methanol	230
Tetraalkyl lead ..	Gasoline	LC	Pb; flame	Detection limit *ca.* 10 µg of Pb	231
Tributyltin oxide (I), triphenyltin chloride (II) ..	Synthetic resin emulsion paints	TLC	Sn; electrothermal	Detection limit 0.2 $\mu g\ g^{-1}$. Average recovery for 1 g of paint containing 10 mg of compound (I) or (II) was 74.7–82.1 and 87.1–90.1%, respectively	232
Alkyl selenium ..		GC	Se; flame		233
Tetraalkyl lead ..	Air	GC	Pb; electrothermal	Determination at µg level	234, 235
Alkyl mercury ..	Fish tissue	GC	Hg; electrothermal	Detection limit 0.3 $\mu g\ ml^{-1}$ for 0.5-g samples	236
Ga and In organometallic compounds ..		GC	Ga or In; flame	Determination at µg level. Standard deviation 0.06%	237

* HPLC, high-performance liquid chromatography; GC, gas chromatography; LC, liquid chromatography; TLC, thin-layer chromatography.

Other electrothermal atomisation devices are the platinum loop[220] and the cathode sputtering cell.[212,221] This latter offers the advantage of a longer retention time for the atom cloud, so that the absorption peak can be measured with standard equipment. For iodine[221] good reproducibility may be obtained and interferences may be compensated for by matching the composition of both samples and standards.

The analytical applications of the determination of P and S in different samples are summarised in Table XII.

2.2. Organic Compounds

Organic substances can be determined by direct AAS methods if they contain a metal element in their molecule.

Vitamin B_{12} contains one atom of cobalt per molecule. Therefore, a method has been proposed for the determination of this vitamin in pharmaceutical dosage forms, based on the atomic absorption of cobalt at the 242.5-nm line.[222,223]

Dimethylpolysiloxanes have been determined in fats and oils[224] and juices and beer[225] via atomic signal measurement of Si at its 251.6-nm resonance line.

However, direct AAS methods for the determination of organic compounds are widely employed for the rapid analysis of organometallic compounds by a hybrid analytical technique based on the GC - AAS coupling. In Table XIV some procedures based on this principle are summarised.

3. CONCLUSIONS

A comparative study of the relative analytical utilisation of the described methods is presented in Table XV. From this table the following conclusions can be drawn.

TABLE XV

COMPARATIVE STUDY ON THE APPLICABILITY OF THE DESCRIBED METHODS

Method	Inorganic anions	Organic compounds
Indirect—		
Precipitation	17.3	4.4
Complex formation	12.9	16.9
Heteropoly compounds	10.4	—
Redox reactions	2.4	2.8
Direct atomisation	0.3	0.4
Volatile compounds	1.2	—
	Total: 53.5	Total: 24.5
Direct—		
Flame	5.6	6.8
Electrothermal	9.3	—
	Total: 14.9	Total: 6.8
	Overall total: 68.4	Overall total: 31.3

1. Most investigations have been devoted to the determination of inorganic anions, as can be concluded readily from the publication of twice as many papers related to their determination, as those devoted to organic compounds.
2. The indirect methods have found much greater application than direct methods in the determination of both inorganic and organic anions. They are more tedious and time consuming than the direct methods, but their methodology is much better established.
3. For the indirect methods, precipitation reactions have been used most for determining inorganic anions while organic compounds have been determined mainly by means of complex formation reactions, and a large number of indirect methods are suitable for the determination of organic functional groups.
4. The direct methods are used a third less than the indirect ones. They were developed in the early 1970s and are still faced with many research and technical problems. Their use for organic analysis is a consequence of the employment of the atomic-absorption spectrophotometer as a chromatographic detector.

We have attempted to prove how powerful a tool AAS is for the analysis of inorganic anions and organic compounds. However, much effort has to be made is the future to increase the applicability of AAS methods to the fast-growing field of organic analysis and to improve further the development of the direct methods in connection with recent advances in instrumentation.

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