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Functional Group Analysis of Nitrogen- and Sulphur-containing Organic Compounds

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Data published during the last 7-9 years on problems concerning the determination of nitrogen- and sulphur-containing functional groups in organic compounds are surveyed.
The bibliography includes 281 references.

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I. INTRODUCTION

Methods of functional group analysis are of indepenent important both in industry, for the analysis of various industrial mixtures, and in the study of newly synthesised compounds. During recent years, three monographs have been published[1-3] on advances in analytical chemistry in the field of functional group analysis of organic compounds. However, they deal only with studies published up to 1967. This paper represents a review of studies on the analysis of various amines, amides, hydrazines, hydrazides, oximes, nitro- and nitroso-compounds, thiols, sulphides, disulphides, sulphonic acids, etc., carried out in 1968 to 1977.

Studies on analysis in recent years have been carried out with the following main aims: (1) the improvement of known analytical methods, their application to more complex systems, and detailed investigation of reaction mechanisms; (2) automation of methods involving the use of electrometric methods for the determination of the titration end point (amperometry, potentiometry, and coulometry); (3) the application of new chemical reagents; (4) the development of new analytical methods.

II. TITRIMETRIC METHODS FOR THE DETERMINATION OF NITROGEN- AND SULPHUR-CONTAINING ORGANIC COMPOUNDS

1. Acid–Base and Oxidation–Reduction Titration Methods

(a) Determination of amines. Acid–base titration is one of the classical methods for the analysis of nitrogen-containing organic compounds, but it has not been used on a sufficiently large scale until the non-aqueous titration technique became popular[4]. At present organic bases are widely determined by acid–base titration in research and in industry[5,6]. Comparatively recently a review has been published on methods for the determination of aromatic amines[7], which shows that the most general and easiest method for determining amino-groups is non-aqueous potentiometric titration. Thus a procedure has been proposed[8,9] for the non-aqueous potentiometric titration of polyethyleneamines and pyridyl-containing carbamates using a solution of $HClO_4$ in glacial acetic acid as the titrant. Solutions of neutral salts ($CaCl_2$, LiCl, NaCl, etc.) are sometimes used in the potentiometric determination of weak bases. The effectiveness of the above salts is determined by their influence on the hydrogen ion activity and entails an increase of the width and sharpness of the potential jumps. Kreshkov et al.[10] investigated certain features of potentiometric titration in solutions of alkali and alkaline earth metal chlorides and developed methods for the determination of amines; they also studied the influence of the salt solution on the pH shift. According to the authors[10], the best salts are LiCl and $CaCl_2$. Thus *m*-, *p*-, and *o*-phenylenediamines were titrated using $CaCl_2$ solutions; comparison of titration curves in a salt solution with the corresponding curves for the same substances in water shows that the use of a salt solution greatly improves the titration conditions. The error of the method is 0.3%.

Titration in a non-aqueous medium has been used for the joint determination of higher aliphatic amines and quaternary ammonium salts[11]. The method is as follows: the quaternary ammonium salt is converted into the perchlorate or iodide and the remaining amine is determined by titration with $HClO_4$. After the titration of the amine, mercury(II) acetate is added in order to convert the quaternary ammonium perchlorate or iodide into the highly basic quaternary ammonium acetate and the undissociated HgI_2:

$$2\,(R_4\overset{+}{N}\overline{I}) + Hg(CH_3COO)_2 \rightarrow 2\,(R_4\overset{+}{N}CH_3COO^-) + HgI_2 \ .$$

HgI_2 is then dissolved in an excess of the mercury(II) acetate solution and the quaternary ammonium acetate is titrated with $HClO_4$:

$$R_4\overset{+}{N}CH_3COO^- + H^+ + ClO_4^- \rightarrow CH_3COOH + R_4\overset{+}{N}ClO_4^- \ .$$

Since the basicity of all the compounds titrated is high, the final titration point is readily determined visually. For specimens with a ratio of tertiary amine to quaternary ammonium salt of 1 : 40, the results of the determination of the amine were reproducible to within 3–5% and those of the determination of the quaternary ion were reproducible to within 1–2%.

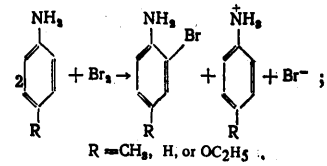
Potentiometric titration of a 0.1 *N* $HClO_4$ solution using differentiating non-aqueous solvents has been used to determine amine *N*-oxides. The methods for a quantitative determination of amine *N*-oxides are based mainly on their reduction to amines and the determination of the excess reductant. $SnCl_2$, $TiCl_3$, and HCl have been

recommended as reductants[1]. However, these methods suffer from many limitations. Methods involving the direct titration of the *N*-oxides as bases are more promising[12].

Comparison of the ionisation constants of amines and *N*-oxides showed that aliphatic and saturated heterocyclic amines and their *N*-oxides with $pK = 4-5$ can be determined separately by potentiometric titration with $HClO_4$ in differentiating non-aqueous solvents. The interaction of amine *N*-oxides with protic acid solutions in dioxan, ethyl methyl ketone, and acetonitrile proceeds via a stage involving the formation of anomalous salts in which there are two molecules of the base per acid molecule. The method proposed[12] has been used to analyse mixtures of amine *N*-oxides and amides, hydrogenated aromatic heterocyclic bases, and the corresponding amines. Kwiatkowski et al.[13] used potentiometric titration in dimethyl sulphoxide (DMSO) with the aid of glass electrodes to analyse di-(n-butyl)amine, tri-(n-butyl)amine, piperidine, *N*-ethylpiperidine, allylamine, isobutylamine, diethanolamine, etc.

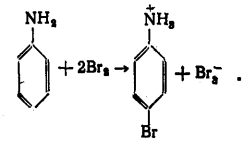
Careful studies of potentiometric titration in non-aqueous media are being continued and the influence of the titrant concentration, temperature, and amine structure is being investigated. Apart from $HClO_4$, the titrants used in the determination of amines are HCl, H_2SO_4, and toluene-*p*-sulphonic acid, dissolved in DMSO.[13] However, in many instances, particularly in the analysis of the products of synthesis, precipitates or tarry substances are formed during the titration, coat the electrodes, and interfere with a clear-cut determination of the titration end point. The high-frequency titration method, which is free from this disadvantage, was therefore used in the determination of certain aromatic amines[15]. This procedure has been used successfully for the overall and separate determination of primary and secondary amino-groups in polyethylenepolyamines and products of synthesis based on them. A TV-61 high-frequency titrator was employed; the determinations were carried out mainly by the back-titration method, since the equivalence point is then determined more clearly. A suitable solvent, ensuring the most distinct inflections in the titration curve, was selected for each compound.

The bromination method is frequently used for the quantitative determination of amines. The bromide–bromate system, which evolves bromine in an acid medium, has come to be employed as a source of bromine. However, this method requires the use of aqueous solutions which has limited its applications to the determination of amines. In recent years a number of studies have been made on titration with bromine in non-aqueous solutions[16–19]. Krause and Kratochvil[16] determined a number of aromatic amines to within 1% using propylene carbonate as the solvent. Propylene carbonate is a convenient medium for the bromination of amines, is resistant to the action of the halogen, has a high dielectric constant which increases the rate of reaction, is soluble in water, colourless, and non-toxic. The majority of amines are soluble in propylene carbonate. In many cases the bromination takes place in the presence of bases such as pyridine (in order to bind the evolved protons). Like the hydroxy-group, the amino-group activates the *ortho*- and *para*-positions in electrophilic aromatic substitution. Since primary amines are proton acceptors, the bromination of certain amines in propylene carbonate is possible without the addition of a base. In the titration of *p*-phenetidine, *p*-toluidine, and aniline the potential increases sharply when 1-2 equivalents of bromine has been added. This can be explained by the reaction

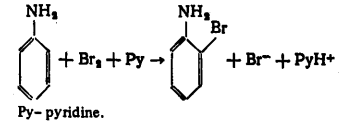


R = CH_3, H, or OC_2H_5.

Since the monobrominated aromatic amine is a weaker base than the non-brominated amine, the protons produced in the substitution stage apparently combine with the non-brominated amine. The protonated amine is not brominated subsequently, since the protonated amino-group hinders electrophilic substitution. The second potential jump in the absence of pyridine occurs after the addition of two moles of bromine per mole of aniline:

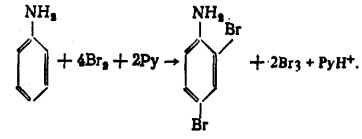


When pyridine is present in the reaction mixture, two potential jumps also occur. The first takes place after the addition of one equivalent of bromine:



Py – pyridine.

The second occurs after the addition of four moles of bromine per mole of aniline:



p-Toluidine behaves similarly to aniline. The introduction of a third bromine atom in the free *ortho*-position of aniline is apparently difficult, although after the addition of six moles of bromine a very small potential jump does appear[16].

Analysis of *m*-phenylenediamine by titration with bromine is possible both in the presence of pyridine and in its absence. The bromide–perbromide system in pyridine[17] (PBPB, $C_5H_5N.HBr.Br_2$), each molecule of which readily evolves one molecule of free bromine, may be used as the source of bromine. The greater availability of crystalline PBPB compared with the bromide–bromate solution and high reaction rates with minimal side reactions make this method more suitable in both preparative and analytical chemistry. The above system had been used previously to brominate substituted phenols and aromatic amines and aliphatic and alicyclic ketones in acetic acid[18]. The system has been used[17] to determine aniline and various monosubstituted anilines. The majority of reactions were rapid (over a period of 10–15 min); the concentration of the amine analysed was 10^{-4} M and the error of the method was <1%. The end point was determined spectrophotometrically; photometric titration is possible only for colourless or slightly coloured products, which is a significant disadvantage of this method.

Sotsenko et al.[19] modified the bromide–bromate method for the determination of aromatic amines in various solutions. The essential feature of their procedure reduces to analysis in a specially designed diffusion apparatus with

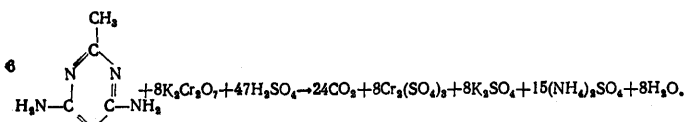
addition of a known excess of a standard bromide–bromate solution. In an acid medium the free bromine evolved brominates, for example, aniline to tribromoaniline and its excess is absorbed by a potassium iodide solution deposited on a porous material (filter paper or synthetic water-soluble paper). The titration of the iodine, evolved in an amount equivalent to that of the absorbed bromine, is carried out in the same apparatus with sodium thiosulphate solution; the time required for the analysis is 10 min at 40°C or 17 min at room temperature, and the accuracy of the determination is to within 1.5%. This method can be used to analyse dark or intensely coloured solutions. Sotsenko et al.[19] analysed *m*-toluidine, anthranilic acid, sulphanilic acid, and anilinium chloride. In the determination of semicarbazide hydrochlorides Campbell et al.[20] used successfully titration with potassium bromate in the presence of metal ions (nickel, cobalt, and manganese). Semicarbazides are determined with $KBrO_3$ in accordance with the following scheme:

$$3NH_2\underset{\underset{O}{\|}}{C}NHNH_2 + 2BrO_3^- \rightarrow 2N_2 + 3CO_2 + 3NH_3 + 2Br^- + 3H_2O \quad .$$

Iodometric titration combined with various procedures for the detection of the titration end point is widely used in the determination of organic compounds. A thermometric titration method, in which alicyclic and aliphatic amines and hydrazines are titrated with iodine in non-aqueous solutions containing alkyl vinyl ethers, which polymerise exothermically in the presence of an excess of iodine, has been described[21]; the titration end point is determined on the basis of the exothermic polymerisation reaction. This method has an accuracy to within 1% in most cases.

In the above study iodine was used both as the titrant and as the catalyst of the cationic polymerisation and ethyl vinyl ether was employed as the monomer. Among organic bases, aliphatic and alicyclic amines have been determined by this procedure, namely n-butylamine (3.6), benzylamine (3.7), piperidine (3.6), tris(hydroxymethyl)-methylamine (4.3), 2-*N*,*N*'-diethylaminopropionitrile (4.4), *N*-methylmorpholine (4.6), etc.; pyridine derivatives, namely pyridine (4.1), α-picoline (3.8), pyridine-2,6-dicarboxylic acid (0.09), pyridine *N*-oxide (2.2), 3-picoline *N*-oxide (2.2), etc.; aniline derivatives, namely aniline (1.3), *o*-toluidine (1.5), diphenylamine (0), triphenylamine (0), etc.; and heterocyclic nitrogen-containing compounds, namely hexamethylenetetramine (5.0), phthalazine (3.5), quinoline (0), and benzimidazole (4.0). The number of iodine atoms consumed per molecule of the test compound is indicated in brackets. It is believed[21] that the number of iodine atoms reacting with the molecule of the base may be used as a measure of the strength of the base.

The titrimetric method involving oxidation by $K_2Cr_2O_7$ has been used successfully[22] to determine acetoguanamine in the presence of melamine and guanidine; the excess oxidant was determined iodometrically:



$$+8K_2Cr_2O_7 + 47H_2SO_4 \rightarrow 24CO_2 + 8Cr_2(SO_4)_3 + 8K_2SO_4 + 15(NH_4)_2SO_4 + 8H_2O.$$

A method of direct potentiometric titration of various amines by hypobromite, based on the hydrogen substitution reaction in the amino-group has been proposed[23]:

$$RNH_2 + 2BrO^- \rightarrow R{-}NBr_2 + 2OH^- \quad ,$$
$$R_2NH + BrO^- \rightarrow R_2{-}NBr + OH^- \quad .$$

The authors[23] tested the method on 40 different compounds.

(b) Determination of hyrazine and its derivatives. A monograph[24], which describes a comparative analysis of all the existing methods and examines in detail the reaction mechanisms and the influence of various factors on analytical results, is devoted to various methods for the determination of hydrazine and its derivatives. Malone[25] proposed an acid–base isocyanate method for the determination of mixtures of hydrazine with 1,1-dimethylhydrazine and monomethylhydrazine. The method is based on the difference between the rates of reaction of isocyanate with the corresponding hydrazines in anhydrous acetic acid solution; the rate of reaction decreases in the sequence hydrazine > monosubstituted hydrazine ≫ disubstituted hydrazine. An alcoholic HCl solution was used as the titrant, the accuracy of the method being to within 0.1 to 0.5%. A method involving direct non-aqueous titration in dimethylformamide (DMF) by strong bases has been proposed for the determination of *N*,*N*'-diacylhydrazines[26]. Tetrabutylammonium hydroxide or potassium t-butoxide were proposed as titrants in the presence of 2-nitroaniline as the indicator.

Titration with a solution of ICl in 5 *N* HCl has been used recently[27] to determine hydrazine, phenylhydrazine, *p*-nitrobenzoic hydrazide, semicarbazide, and isonicotinic acid hydrazide; the oxidation is in all cases rapid and quantitative. Amperometric titration methods for the determination of certain mono- and di-substituted hydrazines with a permanganate solution at pH 6–7 have been described[28]. The relative standard error in ten replicate experiments was 3%. Subsequently the method was improved[29], using as the medium an aqueous acetone solution in which the potentials of the onset of the oxidation of hydrazine and dimethyl hydrazine at a platinum anode differ sharply. The reaction mechanism is based on the difference between the rates of oxidation by potassium permanganate of the products of the interaction of hydrazine and dimethylhydrazine with acetone in the presence of $Na_4P_2O_7$. A solution of potassium dichromate may be used as the oxidant; the accuracy of the method is to within 0.5%.[30]

(c) Determination of amides and nitriles. A review has been devoted to the determination of amides and nitriles[31]; the authors discuss the principal methods for the determination of amides: hydrolysis (alkaline, acid, and catalytic), potentiometric and amperometric titration, reduction with $LiAlH_4$, and colorimetry. For nitriles, there are as yet no specific analytical methods, which makes it very difficult to determine them chemically in mixtures with nitrogen-containing compounds. Hydrolysis yields satisfactory results only for primary aliphatic nitriles. Reports have been published recently about new methods for the determination of organic compounds of this class, which are discussed in detail in Section IV.

(d) Determination of oximes and their derivatives. The principal methods for the determination of compounds of this class are given in a monograph[1]. The latest studies[32,33] were devoted to potentiometric non-aqueous titration of mono- and di-oximes and benzohydroxamic acids with a 0.1 *N* solution of tetrabutylammonium hydroxide. In all cases a clear-cut end point, corresponding to one mole of base for one mole of oxime, was obtained. The influence of the solvent on the change in potential at the end point has been discussed[32,33]. An

attempt [34] to modify the iodometric method for the determination of hydroxylamines (Blom's method) was unsuccessful; the authors studied the oxidation reaction in detail and proposed a mechanism:

$$RCH_2NHOH \xrightarrow{I_2} RCH{=}NOH \quad ,$$
$$RCH{=}N{-}OH \underset{}{\overset{H_2O}{\rightleftarrows}} RCHO + NH_2OH,$$
$$NH_2OH \xrightarrow{I_2} NO_2^- \quad .$$

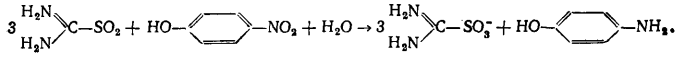
The amount of nitrite formed from hydroxylamine derivatives depends on the rate of hydrolysis of the intermediate oxime; if the latter is low, the quantitative determination of nitrite is difficult. For this reason, the method is used only for qualitative analysis.

(e) Determination of nitro-compounds, nitroso-compounds, and nitrosamines. Aromatic nitro- and nitroso-compounds are determined by reduction either with Fe^{2+} in an acid or alkaline medium [35,36] or with an excess of titanium chloride solution [37]. An interesting method, involving the aquametric determination of nitro-compounds, based on their reduction by $SnCl_2$ in anhydrous acetic acid to the amine and water and subsequent determination of the evolved water with Fischer's reagent, has been proposed [38]:

$$RNO_2 + 3SnCl_2 + 6HCl \rightarrow RNH_2 + 3SnCl_4 + 2H_2O \quad .$$

The excess $SnCl_2$ was titrated with an anhydrous solution of iodine in DMF. Thus the content of NO_2 groups was estimated simultaneously by both potentiometric and aquametric methods. The titration end point was in both cases established biamperometrically using the $I_2 \rightleftarrows 2I^-$ system; the accuracy of the method is to within 0.5%.

It has been suggested that thiourea dioxide (TUD) be used for the determination of nitro-groups in phenols [39]. The essential feature of the method consists in the quantitative reduction of the nitro-groups to amino-groups:



The aminophenols formed were determined spectrophotometrically.

Methods for the determination of nitrosamines are described in detail in reviews [41,42], where the chemical properties, biological activities, and methods of analysis of compounds of this class are considered. A sensitive method for the determination of nitrosamines consists in their reduction by $LiAlH_4$ to hydrazine and condensation of the latter with anthracene-9-aldehyde or phenanthrene-9-aldehyde, which leads to the formation of highly fluorescent hydrazones. After their isolation, the hydrazones are identified spectrophotometrically or mass-spectrometrically [43]. Mention should also be made of a new interesting reagent used to determine various functional nitrogen-containing groups, namely 1-chloro-3-ethylpent-1-en-4-yn-3-ol (Placidyl) [44]. This reagent can be used in various solvents (C_2H_5OH, $CHCl_3$, CCl_3CCl_3) to test for ureas, primary aromatic amines, *sym*-alkylhydrazines, and indole derivatives.

(f) Determination of thiols. One of the most frequently used methods for the determination of thiols is oxidative titrimetry. Direct and back titration with iodine, accompanied by the visual or potentiometric indication of the end point, are used [45-48]. The mechanism of the oxidation of thiols to disulphides has been studied in detail comparatively recently [48] and may be represented schematically as follows:

$$2RSH + 2H_2O \rightleftarrows RSSR + 2H_3O^+ + 2e^- \quad ,$$
$$2e^- + (I_2)_{aq} \rightleftarrows 2I^- \quad ,$$
$$2RSH + (I_2)_{aq} + 2H_2O \rightleftarrows RSSR + 2I^- + 2H_3O^+ \quad .$$

In an anhydrous medium the reaction does not go to completion owing to the reverse protolytic reaction

$$2H_3^+O + 2I^- \rightleftarrows 2HI + 2H_2O \quad .$$

The reducing effect of HI predominates. The reaction involving t-butylmercaptan proceeds to the sulphenyl iodide:

$$R_3CSH + I_2 \rightleftarrows R_3CSI + HI \quad .$$

The side reaction

$$R_3CSI + RSH \rightleftarrows R_3CSSR + HI$$

is suppressed with lead(II) nitrate, which forms the mercaptide and then lead iodide:

$$(RS)_2Pb + I_2 \rightleftarrows RSSR + PbI_2 \quad .$$

It has been shown [48] that there is a tendency towards further oxidation to higher oxidation states of sulphur, so that errors in the determination of certain thiols are possible.

Together with iodine, bromine or a bromide–bromate solution are used [49-51]. They are stronger oxidants than iodine and increase the degree of oxidation of the disulphide. The titration with bromide–bromate, proposed previously for the determination of sulphides and disulphides in acetic acid, has been used to determine thiols with potentiometric indication of the end point using platinum or graphite electrodes [49]. The potential jump corresponds to the reaction

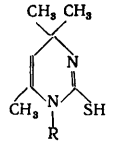
$$RSH + 3Br_2 + 7H_2O \rightleftarrows RSO_2Br + 5H_3O^+ + 5Br^- \quad .$$

Aromatic thiols are oxidised quantitatively to sulphonyl bromides, while the reaction involving aliphatic thiols proceeds with difficulty. The sensitivity of the method is to within 5×10^{-8} M thiol. Apart from the bromide–bromate system, a study was made of the $Pb(CH_3COO)_4/Pb(CH_3COO)_2$ system [49], which has a still higher standard oxidation potential, but the oxidation of thiols to the sulphonic acids in anhydrous acetic acid was not observed. This is probably caused by the solvolysis in this medium. Only the following reaction takes place:

$$2RSH + (CH_3COO)_4Pb \rightleftarrows RSSR + (CH_3COO)_2Pb + 2CH_3COOH \quad .$$

The reaction is used in both potentiometric and visual titration with an indicator to determine primary aliphatic thiols with a long chain and aromatic and heterocyclic thiols [51].

Potassium or sodium periodate in dilute sulphuric acid has been used for the quantitative determination of primary and secondary thiols [52]. Thiocarbonyl compounds and sulphocyanamide ions interfere with the determination. The same method has been used [53] to determine 2-mercaptopyrimidines of the type



R = H, CH_3, n-C_4H_9, iso-C_4H_9, C_6H_5, 3-$NO_2C_6H_4$, or 2-NO_2-4-$CH_3C_6H_3$.

One of the oldest methods for the determination of thiols involves their oxidation with copper(II) salts. Nowadays the reaction is usually carried out in DMF with potentiometric indication of the end points, using platinum, graphite, or copper electrodes[54]. The oxidation of thiols by potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$ proceeds quantitatively only in an alkaline medium[54,55], but, since the oxidation of thiols is accelerated in air under these conditions, the determination must be carried out in an inert gas atmosphere; in the back titration ascorbic acid must be used to determine the excess $[Fe(CN)_6]^{3-}$. The accuracy of the method is to within 1.5%.

Iodine chloride and bromide and iodine and bromine cyanides are used very frequently to determine thiols[56-58]. The method is based on the oxidation of thiols to disulphides:

$$2RSH + IX \rightleftarrows RSSR + HI + HX;$$
$$X = Cl, Br, \text{ or } CN.$$

The reaction is carried out in an aqueous or anhydrous medium with potentiometric or visual indication of the equivalence point. The somewhat unstable results obtained when iodine cyanide is used[57] are associated with the formation of hydrogen iodide, which is a powerful oxidant. Its influence can be eliminated by adding benzene, because HI is soluble in water and thiols are soluble in benzene. Bromine cyanide is more convenient than iodine cyanide, because HBr is a weaker reductant. The accuracy of the method is to within 0.25%. Thiocarbonyl compounds, sulphides, and thiocyanate ions interfere with the determination. It has been found recently[59] that, in the presence of acetic acid, thiols are readily and quantitatively oxidised to disulphides by *N*-bromosuccinimide. However, this method is inconvenient owing to the low solubility of *N*-bromosuccinimide in water and the changes in its solutions with time.

A number of methods for the determination of thiols are based on the formation of insoluble or undissociated mercaptides. These are primarily reactions with silver and mercury ions. Silver salts had been frequently used previously to determine thiols by amperometric titration[2], but, in view of the difficulty of determining the end point, potentiometric determinations have come to be used. During recent years, methods have been developed for the determination of thiols using silver electrodes[60-64] with solutions of mercury salts and silver nitrate as titrants. Apart from mercury salts, organomercury compounds, which are more selective for the thiol group, are frequently employed. *p*-Dimethylaminophenylmercury acetate and *p*-diethylaminophenylmercury acetate[65,66] have been proposed for the visual, potentiometric, and amperometric titration of thiols (the error of the method is $<1.5\%$).

Qualitative tests for the mercapto-group must also be mentioned. Thus the reaction of thiols with 2,2-dithiobis-(5-nitropyridine) leads to the appearance of a yellow colour due to the formation of 5-nitropyridine-2-thione[67]. This reaction is used for the detection of thiols in paper and thin-layer chromatography. Another sensitive test for the SH group is reaction with $Hg(CN)_2$,[68] which leads to the formation of mercury mercaptide and HCN. The evolution of the latter may be detected from the appearance of a blue colour in filter paper impregnated with a solution of tetrabase or copper ethylacetoacetate in chloroform. The minimum amount of thiols which may be determined is 1–5 μg.

(g) Determination of sulphides and disulphides. The principal methods for the determination of sulphides and disulphides have been described fairly completely in a monograph[1] and in conference proceedings[3,6]; during recent years, few studies have been published on the analysis of compounds of this class. Thus a method involving acid–base potentiometric titration with sodium hydroxide in DMF has been proposed for the analysis of bis-(2-carboxyphenyl) disulphide[69]. Potentiometric titration (using a silver sulphide electrode) by silver salts has been employed for the separate determination of thiols and disulphides in a mixture[48]. The thiol is titrated initially and then sodium sulphite is added, the latter reacting with the disulphide as follows:

$$RSSR + SO_3^{2-} \rightarrow RS^- + RSSO_3^- .$$

The mercaptan produced is titrated with silver salts. The disulphide group is frequently reduced to the mercapto-group and all the analytical methods for the determination of thiols can be used. Many reagents have been proposed for the reduction of disulphides[64,70,73], but none of them are universal. Best results have been obtained for the solution $LiAlH_4$ in tetrahydrofuran (THF).

Wronski[64] proposed a new reagent—sodium aluminium bis-(2-methoxyethoxide) dihydride (70% solution in benzene):

$$NaAlH_2(OCH_2CH_2OCH_3) + RSSR \rightarrow NaAl(SR)_2(OCH_2CH_2OCH_3) + H_2 .$$

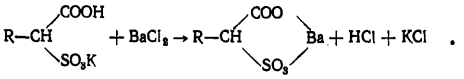
Decomposition with water yields thiols, hydrogen sulphide, sodium hydroxide, aluminium hydroxide, and α-methoxyethanol. The method is applicable to aliphatic and aromatic disulphides and its accuracy is to within 5%. Sulphides and disulphides are usually determined by methods based on their oxidation with periodate to the corresponding sulphoxides[71]. A solution of phenyliodoso acetate in dilute acetic acid has been proposed as the oxidant[72]:

$$RSSR + 4PhI(OCOCH_3)_2 + 4H_2O \rightarrow RSO_2SO_2R + 4PhI + 8CH_3COOH .$$

The excess of phenyliodoso acetate is reduced with ascorbic acid and titrated with a solution of iodine. The method can be used also for the analysis of a mixture of thiols, sulphides, and disulphides; it is accurate, rapid, and does not require special conditions.

(h) Determination of sulphonic acids, sulphinic acids, thioureas, and dithiocarbamates. The principal method for the analysis of sulphonic acids is alkalimetry. In recent years many technological products have been analysed by this procedure, and mixtures of isomeric sulphonic acids have been determined. Thus an attempt has been made[74] at the separate determination of toluene-*o*- and toluene-*p*-sulphonic acids by high-frequency titration in non-aqueous media. Kreshkov and coworkers[75] developed a differential titration method (with the aid of KOH) for the determination of a mixture of aminobenzenesulphonic acids, the accuracy of the method being to within 2–6%. Certain substituted aromatic sulphonic acids are determined by potentiometric titration with sodium methoxide in pyridine or acetone[76], but the accuracy is low. In the determination of a mixture of isomeric sulphonic acids the latter are frequently subjected to preliminary separation on a column with cation-exchange resins[77]; the accuracy of the method is to within 1%. A specific method[78] for the determination of α-sulphocarboxylic acids is based on their ability to cyclise readily to form a six-membered

ring with alkaline earth metal ions, particularly the barium ion:



Thus the determination of α-sulphocarboxylic acids can be reduced to the determination of hydrochloric acid. The titration is carried out in a 1 : 1 water–isopropyl alcohol medium with strong bases.

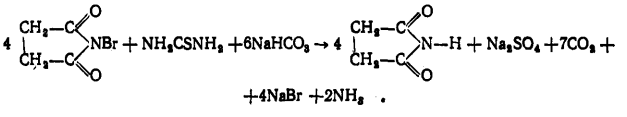
Iodometric titration has been used to determine sodium noramidopyrinemethanesulphonate [79].

A method for the quantitative determination of sulphinic acids [80,81] is based on the reaction with nitrous acid:

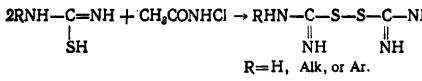
$$2RSO_2H + HONO \rightarrow (RSO_2)_2NOH + H_2O \quad .$$

The reaction is carried out in a strongly acid medium, the end point being determined potentiometrically or amperometrically; the accuracy is to within 0.8%.

Thiourea and its derivatives are readily determined by oxidative titrimetry. A method for the determination of thiourea by its direct titration with $KMnO_4$ in sulphuric acid has been described [82]; the end point is distinct and stable. Thiourea can be oxidised quantitatively to the sulphate with potassium dichromate in sulphuric acid [83]. The excess dichromate is titrated with ferrous ammonium sulphate; it is noteworthy that, under these conditions, thiocyanates are also oxidised; the accuracy of the method is to within 0.5%. It was shown subsequently that [84] the presence of copper(II) ions greatly accelerates the reaction. It has been suggested recently that *N*-bromosuccinimide be used as an oxidant for thiourea [85,86] (the reaction is carried out in the presence of sodium bicarbonate):

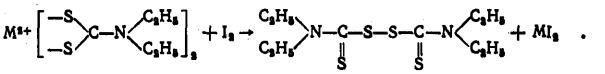


N-Chloroacetamide has also been proposed as a thiourea oxidant [87] (for potentiometric and visual titration):



Potassium iodate is used successfully to oxidise thiourea to the disulphate [70,88]. One of the old methods for the oxidation of thiourea consists in its titration by silver salts in an ammoniacal medium in the presence of dithizon [89]. This procedure is also used for the joint determination of thiourea and thiocyanates [90]. The ability of thiourea to form stable insoluble compounds with silver ions has been used to make silver halide membrane electrodes, which are employed for the potentiometric determination of thiourea [91,92].

In view of the great practical importance of dithiocarbamates (as fungicides), a review was published comparatively recently by Halls [93], which the principal method for the determination of compounds of this class are analysed. The majority of the methods are based on the decomposition of dithiocarbamates in an acid medium and the determination of carbon disulphide. Oxidative methods of determination are also discussed. The determination of water-insoluble bivalent mercury, lead, cadmium, and zinc ions as the diethyldithiocarbamates by titration with a solution of iodine and chloroform has been proposed [94]:



The end point is determined visually or spectrophotometrically. Iodine chloride [95] and iodine and bromine cyanides [96] are also used as oxidants for dithiocarbamates; the accuracy of the method is to within 0.5%. The influence of the pH of the medium, the nature of the solvent, and the nature of extraneous ions has been investigated [95]. Methods have been proposed for the determination of dithiocarbamates with the aid of the iodine–azide reaction [97] and potentiometric titration with perchloric acid in an anhydrous medium [96]. A method involving the direct titration of dialkyl and diaryl phosphorodithioites with dimethyl- and diethyl-aminophenylmercury acetates has been developed [99]. Mention should be made of studies [5,100] in which a method has been proposed for the coulometric analysis of a technical mixture of sulphenamides and dibenzothiazolyl sulphide, based on the oxidation of solutions in acetic acid with bromine. The separate determination of the mixture components is based on their different solubilities in the organic solvent.

2. Titration with Preliminary Chemical Reactions

a. Determination of nitrogen-containing organic compounds. A widely used method for the determination of tertiary amines in the presence of secondary and primary amines is titration in glacial acetic acid with a solution of perchloric acid after preliminary acylation with acetic anhydride [101]. However, quantitative acylation of certain amines by acetic anhydride requires severe conditions. It has been suggested [102] that trifluoroacetic anhydride be used as the acylating agent. The acylation reaction proceeds at room temperature; the error is 0.4%. Isopropenyl acetate can be used successfully as the acylating agent [103], its acylating capacity being superior to that of keten and acetic anhydride; the compound is of interest for the acylation of readily enolised compounds; the accuracy of the method is to within 0.1–0.4%. The formaldehyde–sodium bisulphide complex reagent is frequently used in the iodometric determination of amines [104-106]; it reacts with the amino-group to form methanesulphonates, which are titrated with a solution of iodine in an aqueous acid medium. Aniline and its derivatives [104], toluidines, and xylidenes [105] have been determined by this method; its accuracy is to within 0.5%.

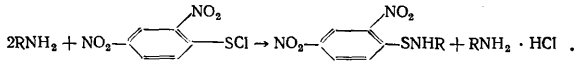
The cyanoethylation reaction has been used for the determination of primary and secondary amines [107]; the amines react with acrylonitrile in accordance with the equations

$$RNH_2 + CH_2{=}CHCN \rightarrow RNHCH_2CH_2CN,$$
$$R_2NH + CH_2{=}CHCN \rightarrow R_2NCH_2CH_2CN .$$

The reaction is accelerated by catalysts (water and acids) and takes place at room temperature for the majority of amines. The excess acrylonitrile is titrated by the sulphite method.

Obtemperanskaya and Kalinina [108] suggested that 2,4-dinitrobenzenesulphenyl chloride be used for the determination of aliphatic and aromatic amines; it reacts over a period of 10–15 min with the amine in benzene solution,

forming 50% of the amide and 50% of the amine hydrochloride:



The employment of pyridine greatly accelerates the reaction and improves the yield of the product. The determining factor in the reaction is the change in the pK_b of the amine; one should note that amines with $pK_b \geq 11$ do not react (diphenylamine); the error is $<1\%$. Since the reagent is highly hygroscopic, the authors subsequently replaced it by 2-nitrobenzenesulphenyl thiocyanate [109]. The method [109] is based on the reaction of these compounds in the presence of a small amount of alkali:

$$RNH_2 + NO_2C_6H_4SSCN \xrightarrow{NaOH} NO_2C_6H_4SNHR + NaSCN + H_2O \quad .$$

The excess reagent is decomposed with an aqueous solution of alkali. The sulphenamide formed reacts with hydrochloric acid to form sulphenyl chloride, which interacts quantitatively with potassium iodide to form iodine:

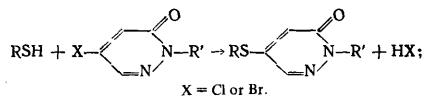
$$NO_2C_6H_4SNHR + 2HCl \rightarrow NO_2C_6H_4SCl + RNH_2 \cdot HCl \quad ,$$
$$2NO_2C_6H_4SCl + 2KI \rightarrow (NO_2C_6H_4S)_2 + I_2 + 2KCl \quad .$$

The liberated iodine is titrated with sodium thiosulphate; the accuracy of the method is to within approximately 1%. The application of these reagents in analytical chemistry has many advantages over methods based on the acylation reaction and acid–base titration.

Primary and secondary amines may be determined quantitatively by reaction with 1-(isothiocyanatomethyl)-isatin, in which crystalline urea derivatives are formed readily [110]. Phenyl isocyanate has been suggested [111] for the determination of primary and secondary amines. The thiourea derivatives formed are titrated with potassium iodate in an acid medium at room temperature.

Among the titrimetric methods for the determination of amino-compounds used at the present time, mention should be made of titration with bivalent metal (Cu^{II} and Mn^{II}) salts. For example, α-amino-acids have been determined [112] by titration with a solution of copper(II) sulphate, the maximum error being 0.3%. Aminopolycarboxylic acids are analysed by titration with Mn^{2+} salts [113–115]. A solution of *N*-chlorosuccinimide in the presence of Methyl Red as the indicator has been suggested for the determination of microamounts of hydrazines and their salts [116]. The end point is determined from the disappearance of the colour of the indicator. A 0.1 *N* solution of *N*-chloroacetamide has been used for the potentiometric analysis of hydrazine derivatives [117], the error of the method being $\pm 0.8\%$. Potentiometric oxidative titration of oximes is carried out with $K_7Cu(HTeO_6)_2$. [118] The reagent is prepared by oxidising copper(II) to copper(III) with $K_2S_2O_8$ in KOH solution in the presence of $K_2Te_2O_7$ as the complex-forming agent.

b. Determination of organic sulphur compounds. Many methods for the determination of thiols involving phenylation by various reagents have been proposed. It has been suggested that 3-phenothiazinone in 80% acetic acid be used for the back titration of thiols [119]; the excess is titrated with sodium thiosulphate. The same reagent is suitable for the determination of thiourea and thiosemicarbazides. The titration of thiols with 4,5-dibromo-6-pyridazinone or 4,5-dichloro-6-pyridazinone in aqueous or organic media takes place quantitatively with elimination of an equivalent amount of the hydrogen halide [120]:



Side reactions with other nucleophiles, amines, phenols, sulphides, and alcohols were not observed. In a series of studies for the determination of thiols [121–126] new reagents have been proposed and analytical methods devised. We believe that vinyl sulphones are interesting reagents [112]. Owing to the presence of the electron-accepting sulpho-group, they readily react with nucleophiles via the terminal carbon atom attached to the double bond:

$$R{-}SO_2{-}CH{=}CH_2 + R'SH \rightarrow RSO_2CH_2CH_2SR' \quad .$$

A three-fold excess of a solution of the vinyl sulphone in dioxan is added to the thiol being analysed, the excess being titrated by the sulphite method. Aliphatic, aromatic, and heterocyclic mercaptans may be determined by this procedure. A method, which had been used earlier for the analysis of aliphatic and aromatic mercaptans and is based on nucleophilic addition to acrylonitrile, has been suggested for the quantitative determination of heterocyclic thiols [121]; the accuracy is to within 0.5%.

Arenesulphenyl halides are highly reactive in relation to thiols [123–126]; the reaction results in the formation of asymmetric disulphides:

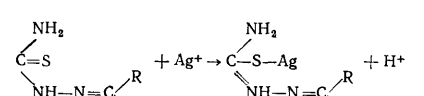
$$RSH + ClSC_6H_3(NO_2)_2 \rightarrow RSSC_6H_3(NO_2)_2 + HCl \quad .$$

It is carried out in acetic acid, the excess reagent being determined iodometrically. Aliphatic and aromatic thiols containing OH, NH_2, and CCOH groups can be determined by this method In the reaction with heterocyclic thiols it is necessary to add pyridine in order to bind the hydrogen chloride. The error of the method does not exceed 1%. In the potentiometric titration of thiols with tetraethylammonium hydroxide, it is necessary to add 1-chloro-2,4-dinitrobenzene, which leads to a sharp increase of the potential jump [125].

Chloramine-T has been suggested as the oxidant for the analysis of thiosemicarbazides [127]; the reaction takes place quantitatively under the usual conditions:

$$NH_2NHCSNH_2 + 6[CH_3C_6H_4NCl]^- + 6H_2O \rightarrow 6CH_3C_6H_4SO_2NH_2 +$$
$$+ 6Cl^- + CO_2 + N_2 + \overset{+}{N}H_4 + H^+ + SO_3^{2-} \quad .$$

The excess chloramine-T is determined iodometrically. Thiocyanates and hydrazines interfere with the determination of thiosemicarbazides. Despite the enormous importance of thiosemicarbazones in pharmacology, until recently there were no suitable methods for their quantitative determination. Comparatively recently Campbell et al. [128] proposed a simple and rapid method for the quantitative determination of aromatic monothiosemicarbazones by the potentiometric titration of the protons liberated on formation of the complex with silver ions:



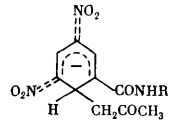
The accuracy of the method is to within 0.5%, but the procedure cannot be extended to all types of thiosemicarbazones and requires further development. The same workers [129] used copper(II) instead of silver for the determination of alkylbisthiosemicarbazones by an analogous procedure, the accuracy of which is to within 0.5%.

III. PHOTOMETRIC METHODS FOR THE DETERMINATION OF NITROGEN- AND SULPHUR-CONTAINING ORGANIC COMPOUNDS

A method widely used in recent years for the determination of nitrogen-containing organic compounds has been photometric analysis [3,24]. A number of investigators have developed new procedures for the determination of amines, amides, hydrazines, oximes, azo-compounds, etc. by colorimetric methods using various chemical reagents, which can be nitro-compounds, aromatic halogeno-derivatives, dyes, metal ions, etc. Most of these are readily available, and the analytical methods are simple and highly sensitive. There have been few studies in recent years on the photometric analysis of sulphur-containing organic compounds.

1. Photometric Analysis Using Organic Reagents

a. Determinations with nitro-compounds. Various aromatic nitro- and polynitro-derivatives, which give rise to intensely coloured solutions in acetone in the presence of strong alkalis, are fairly frequently used for the quantitative determination of nitrogen-containing compounds. The procedure is based on the Janowsky reaction, in which acetone interacts with the dinitro-compound in the enolic form, forming a quinonoid structure of the following type:



Comparatively recently Malone [130] investigated the interaction of hydrazine and amine derivatives with 20 different nitro-compounds and established that all the nitro-compounds which he proposed are suitable under certain conditions for the quantitative analysis of nitrogen-containing compounds. Bartos showed [131,132] that nitromethane, which forms red compounds in the presence of alkylamines or their quaternary bases, can be used successfully instead of acetone in reactions of polynitro-compounds (1,3,5-trinitrobenzene, picric acid). Bartos determined by this method many alkylamines and their hydrochlorides. Arylamines are less reactive and several hours are required for the appearance of the colour. The same workers [133] proposed a method for the photometric analysis of primary and secondary amines using 1-fluoro-2,4-dinitrobenzene and nitromethane in DMF. In order to obtain a more intense colour in solutions, Bartos introduced in addition potassium hydrogen borate. The addition of potassium hydrogen borate in DMF to the organic phase leads to an intense violet colour, a green-violet colour, and a green colour in the presence of primary alkylamines, secondary alkylamines, and aromatic amines respectively. The microanalysis of aromatic amines via the Janowsky reaction has been investigated [134] and its conditions have been discussed in detail.

It has been suggested that *sym*-trinitrobenzene be used for the determination of certain aromatic amines [135]. The authors regard this reaction as a charge-transfer process which leads to the formation of $\pi-\pi$ complexes absorbing in the ultraviolet or in the visible region, λ_{max} depending on the nature of the amine (primary, secondary, or tertiary). Thus aniline and toluidine (primary amines) can be readily distinguished from *N*-methylaniline (a secondary amine) and *N*,*N*-dimethyl- and *N*,*N*-diethyl-anilines (tertiary amines).

Legradi [136,137] suggested that aliphatic amines and amino-acids be determined with the aid of 2,4-dinitrobenzene in the presence of hydroxylamine hydrochloride as the catalyst. Obtemperanskaya and coworkers [138,139] also used 2,4- and 3,5-dinitrobenzenes to analyse primary and secondary aromatic and heterocyclic amines and hydrazines. The majority of aromatic primary amines and hydrazines are phenylated quantitatively at room temperature. The appearance and development of the colour of the solutions over a period of time and its stability depend on the nature of the functional substituents in the benzene ring of the amine or hydrazine. The sensitivity of the method is to within $10^{-5}-10^{6}$ M and the accuracy of the determination if to within 0.13–2.8% for aliphatic amines, 0.8–6.0% for aromatic amines, 0.5–4.7% for heterocyclic amines, and 0.6–4.0% for substituted hydrazines.

A method has been proposed for the photometric microdetermination of certain biogenic amines in the presence of amino-acids and amino-alcohols, based on the reaction with 3,5-dinitrobenzoyl chloride [140]. The sensitivity and accuracy of the method are to within 1×10^{-6} M and 2% respectively. The same workers used 2,4-dinitrobenzoyl chloride for the analysis of aromatic, aliphatic, and acyclic amines. The reaction takes place quantitatively at room temperature, its sensitivity and accuracy being to within 1.3×10^{-6} M and 0.2–2.8% respectively. Obtemperanskaya et al. [141] made a comparative assessment of 3,5-dinitrobenzoyl and 2,4-dinitrobenzoyl chlorides. The latter reagent is more sensitive and in addition can be used for a test in the qualitative analysis of aromatic, aliphatic, and acyclic amines, since it forms solutions having different colours. 1-Fluoro-2,4-dinitrobenzene can be employed successfully for the analysis of aromatic and aliphatic amines [142]. The reaction takes place quantitatively at room temperature for aliphatic amines and at 60°C for aromatic amines, its accuracy being to within 0.5–6.0%.

b. Determination using other chlorine-containing reagents. Fickentscher [143] and Tashima et al. [144] used chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) as the reagent for the photometric determination of nitrogen-containing compounds. On interaction with aromatic amines it gives rise to bluish violet solutions. Fickentscher determined by this method microamounts of dimethylamine in DMF; Tashima et al. [144] used this reagent for the analysis of methylcellosolve solutions of various aniline derivatives. The accuracy of the method is satisfactory.

Quinone dichloroimide has been proposed for the separate determination of aliphatic and aromatic amines [145]; 53 compounds have been studied by this procedure. The ability of many aromatic amines and heterocycles to react with polyhalogeno-compounds (with CBr_4 or CHI_3) and to give rise to coloured solutions under the influence of ultraviolet light served as the basis for their colorimetric analysis [146]. Apart from CBr_4 and CHI_3, di- and trichloroethylenes, hexachloroethane, and isopropyl iodide may be used; however, one should note that the method requires further development. There are several analytical procedures for hydroxylamines, including thin-layer chromatography [147,148].

Stewart and coworkers [149,150] proposed a new photometric method for the determination of microamounts of arylhydroxylamines with the aid of 9-chloroacridine. The sensitivity and accuracy of the method are to within 0.8 to 3.0 mg ml^{-1} and 1.6–3.6% respectively. Hydroxylamines can be determined by the same method in the presence of primary aromatic and aliphatic amines, amides, aromatic nitro-compounds, and phenols.

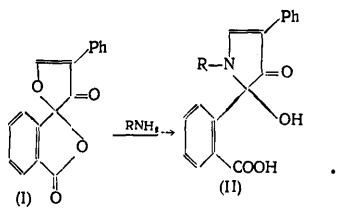
c. Determination using organic dyes. Organic bases and their salts may be determined by an extraction-photometric method using acid dyes as the reagents. The employment of dyes, whose solutions have high molar extinction coefficients, makes it possible to determine quantitatively amines in very dilute solutions. Two reviews [151,152], which discuss in detail the choice of dye and solvent, the influence of the pH of the medium, and the influence of various factors on the extraction constants of the complexes formed, have been devoted to the development of this method. A number of determinations have been made of the extraction constants [153–159]. It is recommended that Bromothymol Blue or the ethyl ether of tetrabromophenolphthalein be used for the analysis of quaternary ammonium salts [160,161]. Among all the solvents investigated, chloroform, a chloroform–alcohol mixture, or a benzene–isopentyl alcohol mixture proved to be most effective [162]. In the analysis of amines in the presence of Bromophenol Blue [163] the complexes formed were isolated and identified; the colour of the complex can be accounted for by the quinonoid structure of the dye. Bromophenol Blue, Bromocresol Purple, Bromocresol Blue, and Bromochlorophenol Blue have also been used as reagents for the determination of amines [164–167]. Korenman [164] used Bromophenol Blue for the quantitative determination of aromatic amines to within 0–6%.

Amines have been determined [165] by their extraction with chloroform using Bromocresol Purple and Bromothymol Blue. The authors established that the dyes react as singly-charged anions, which are responsible for the colour of the extracts of the amine compounds. The accuracy of the extraction-photometric analysis may be increased severalfold by adding C_1–C_4 alcohols to the reaction mixture [166] or by extraction with ternary nitrobenzene–chloroform–benzyl alcohol mixtures [167].

d. Determination of amines by the azo-coupling reaction. Azo-coupling is widely used for the determination of aromatic amines [3]. Diazotised dinitroaniline has been used [168] as a reagent for the determination of various aromatic amines; the reaction is carried out in highly acid solution and its accuracy is to within 0.5–5.9%. The method involving diazotisation with subsequent coupling to an H^+ acid and colorimetric determination of the resulting dye has been employed [169]; the authors determined toluidines, chloramines, and nitroanilines; the accuracy of the analysis is to within 1–1.5%. Bromonitrosol (3-bromo-2-nitroso-1-naphthol) can be used for the analysis of amines and hydrazines [170]; the reaction leads to the formation of coloured azo-compounds, which can be determined photometrically, but the accuracy of the analysis is comparatively low.

e. Other methods of colorimetric analysis. An interesting photometric method for the determination of *p*-phenylenediamine has been proposed by Corbett [171], its sensitivity and accuracy being to within 10^{-4}–10^{-5} M and 2% respectively. Aliphatic primary and secondary amines, α-amino-acids, sulphamides, hydrazines, and other compounds containing the amino-group condense in an alkaline medium with 1,2-naphthoquinone-4-sulphonic acid to form red, orange, and yellow derivatives of 1,2-naphthoquinonemonoimines [172]. The method is simple and highly sensitive, but suffers from limitations in the determination of secondary arylamines. The method involving the coulometric titration of amines is of definite interest [173]. Biphenyl radical-anions are used as the titrant. At a low rate of conversion it is possible to measure the absorption due to intensely coloured radical-cations generated from the amines in the course of the reaction; the accuracy is to within 1.7 to 3.0%.

Fluorescamine (I), [174] which forms coloured compounds (II) with amines, is an effective reagent in the colorimetric analysis of primary amines:



The pH of the medium and the concentration of reagent (I) are important for the reaction. The sensitivity of the method is to within between 0.01 and 0.1. M.Legradi [175,176] used successfully phenylacetonitrile in an alkaline medium and diazotised sulphanilic acid for the analysis of nitro-compounds. The method described by Mordovina et al. [177] may be used for the microdetermination of nitrobenzenes in aqueous solution. Thiourea dioxide $(NH_2)_2CSO_2$ in an alkaline medium has been suggested for the microdetermination of the nitro-groups in aromatic compounds; the sensitivity of the method is high and its accuracy is to within 1–4%.

2. Photometric Analysis Using Inorganic Reagents

Quantitative photometric analytical methods, based on reactions with simple and complex metal salts, are widely used in the analysis of nitrogen-containing organic compounds [3]. Many fundamental studies devoted to a detailed investigation of the structures of the complex formed and the determination of various factors influencing the reaction have been published in recent years. For example, a study has been made [178] of 15 different aromatic amines in the presence of 13 metal ions [178]: Cr^{3+}, Cu^{2+}, Fe^{3+}, Bi^{3+}, Ag^+, Ni^{2+}, etc. It was shown that, in the presence of hydrogen peroxide and alkali, coloured complexes are formed and that the colour of the solution depends on the concentration of the amine. A method based on the reaction with $Fe(NO_3)_3$ in the presence of acetyl chloride is highly sensitive in the determination of aliphatic and aromatic amines [179]. The influence of temperature, the concentration of the salt and acetyl chloride, and the pH of the medium on the formation of the complexes has been studied, and a mechanism has been proposed for the formation of the complexes; the accuracy is to within at least 3%.

Connors and Albert [180] used successfully the Hamilton reagent for the analysis of 15 aromatic amines, including α-methylbenzylamine. The reaction with the copper(II) ion in ammonia solution has been used in the determination of isomeric aminophenols in mixtures [181]; the reaction led

to the formation of coloured complexes, which were extracted with 1-butanol and determined colorimetrically. Copper and nickel salts in the presence of salicylaldehyde have been used to analyse amines[182]; the reaction results in the formation of coloured complexes: yellow for aromatic amines and yellow-green for aliphatic amines. Mitsui and Fujimura[183] used this method to determine primary amines but, instead of salicylaldehyde, they employed nitrosalicylaldehyde; the accuracy of the method is to within 0.5–1.5%.

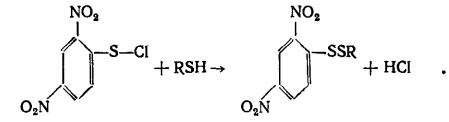
Legradi[184] developed an interesting drop method for the determination of amines and hydrazines with the aid of silver nitrate in the presence of alkalis; a drop of an ethanol solution of the amine (or hydrazine), a drop of silver nitrate solution, and a drop of 0.1 *N* NaOH are deposited on filter paper, which results in the appearance of an intense colour. This method may be used to determine *p*-, and *o*-phenylenediamines, *o*-aminophenol, anisidines, and toluidines. Sodium nitroprusside, which forms solutions with a characteristic colour, is fairly frequently used to determine amino-compounds[1,2]. Sodium nitroprusside was used comparatively recently[185] in a mixture with acetaldehyde for the quantitative determination of secondary aliphatic amines in a mixture with primary amines. The same method can be employed also for the determination of *N*-methylated amino-acids to within 3%. Marco and Mecarelli[186] used sodium nitroprusside together with ferrocyanate for the determination of guanidine and arginine derivatives. The employment of a mixed solvent containing isopropyl alcohol and water prevents the formation of insoluble deposits and gives rise to a high intensity of the colour of the solution.

Reactions involving oxidation by potassium peroxydisulphate, potassium hexacyanoferrate, potassium bromate, sodium perchlorate, etc. are frequently used in the photometric analysis of amines[187–189]. Korotkova and Noskov[189] used $K_3[Fe(CN)_6]$ as the oxidant for the determination of certain aromatic amines and, in order to establish the optimum conditions for the photometric determination, they employed the Box–Wilson mathematical experimental design method.

In conclusion, one should note that each of the methods described for the quantitative colorimetric determination of nitrogen-containing compounds has its advantages, disadvantages, and limitations. Certain methods are applicable only to the simplest representatives of compounds of the class indicated and are not applicable to more complex systems; in many instances difficulties arise in carrying out the experiment. However, sometimes the colorimetric method of analysis is the only suitable procedure among all the known methods of functional group analysis for compounds of the given class.

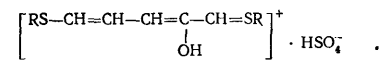
3. Photometric Analysis of Sulphur-containing Organic Compounds

Photometric methods for the determination of thiols are based on the following reactions: phenylation reactions, reactions with disulphides, and reactions with organomercury compounds. The first type includes primarily the dinitrophenylation reaction proposed[190] for the determination of aliphatic and aromatic thiols. The method proposed by the same workers[191] for the determination of thiols using 2,4-dinitrobenzoylsulphenyl chloride is based on the Janowsky and *sym*-phenylation reactions. The reaction of a thiol with an excess of the reagent by a factor of 2–3 is quantitative over a period of 3–5 min at 50°C:

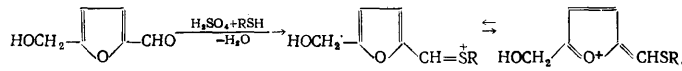


After the Janowsky reaction has been carried out, photometric measurements are made on the solutions at $\lambda = 480$ nm.

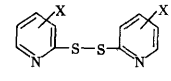
Another interesting reaction has been suggested by Unorits[192]. Furfural reacts with thiols in sulphuric acid at room temperature to form a red-violet substance ($\lambda max = 505$ and 535 nm), which consists of the hydrolytically cleaved furan ring:



In the reaction with hydroxymethylfurfural ring opening does not occur, and the colour arises as a result of the formation of cations having the following structure:

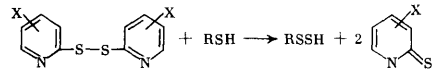


The use of heterocyclic disulphides of the type



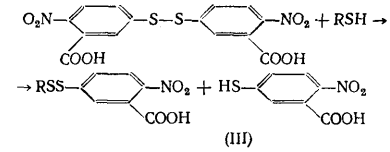
X = NO_2, NH_2, or COOH.

has been proposed for the photometric determination of thiols[193]. The reaction proceeds in accordance with the equation



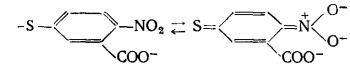
The thiopyridone formed absorbs in the range 240–430 nm. We may note that the accuracy of the method is low.

4,4′-Bisdimethylaminophenylmethanol, which forms intensely blue cations at pH 5.0, is also used as an alkylating agent[194]. The addition of a thiol causes the disappearance of the colour. This method is widely used in the analysis of proteins. Photometric methods for the determination of thiols mixed with disulphides have been described[195,196], 5,5′-dithiobis-(2-nitrobenzoic acid), reacting via the mechanism



(III)

being used as the reagent. An intense yellow colour ($\lambda max = 412$ nm) arises owing to the formation of the aromatic mercaptide (III). The generation of the colour due to this mercaptide has been demonstrated by the detection of the quinonoid mesomeric structure



Reactions with organomercury compounds are widely used in photometry[64,196]. *p*-Dimethylaminophenylmercury acetate and *p*-diethylaminophenylmercury acetate are

used for the extraction-photometric determination of thiols. It is suggested[64] that organomercury compounds form chelates with diphenylcarbazone which has a bright violet colour in benzene. The accuracy of the method is to within 4–8%; thioureas, sulphates, nitrates, and phosphates do not interfere with the determination. The results of the photometric method agree satisfactorily with those of titrimetric analysis where the given reagents are used as titrants.

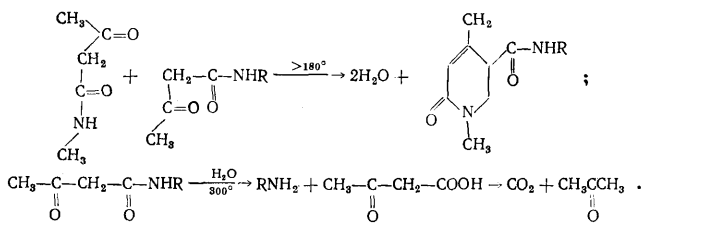
Only one paper has been published in the last six years on the photometric determination of sulphides and disulphides, involving the determination of thiuram disulphide in fungicides in the course of the analysis of industrial preparations; the method is based on the reaction with copper acetate[73]. Basic dyes of the type of rhodamine C, Acridine Orange, and Chrysandine [chrysoidine? (Ed. of Translation)] have been proposed as reagents for the determination of sulphonic acids[46,52]. Some of the main factors which determine the interaction between basic dyes and sulphonic acids are the pH of the medium and the concentration of acid. Quinone derivatives are used in the colorimetric determination of thiourea. Thus 1,4-diamino-5-nitroanthraquinone has been used in anhydrous acetic acid[200]; the measurements were made at 565 nm. Thioureas, thiosemicarbazides, monothiosemicarbazides, and isothiocyanates react with 2,3-dichloro-1,4-naphthoquinone in an ethanol solution of ammonia, forming an intense violet colour[201]. Apart from ammonia, pyridine, quinoline, ethylamine, and aniline may be used as the bases. The sensitivity of the method decreases in the sequence thiosemicarbazones > thiosemicarbazides ≫ thioureas > isothiocyanates. We believe that the method requires further development. Wronski[202] suggested a method based on the reaction of thiourea with an alkaline solution of *o*-(hydroxymercuri)benzoic acid with heating.

It has been noted that aromatic substituents increase while aliphatic substituents decrease the rate of desulphonation; tri- and tetra-substituted and cyclic thioureas are extremely resistant to this reaction. Attempts have been made[88,203] to reduce the reaction time by employing dipolar aprotic solvents—dimethylformamide and dimethyl sulphoxide. An interesting photometric method has been proposed for the determination of xanthates[204]: acetone and then the xanthate are added to a solution of nickel nitrate in acetic acid; photometric measurements are then made at 420 nm on the resulting intensely yellow solution. The error of the method is to within less than 0.5%. Dixanthates are determined with the aid of an excess of potassium thiocyanate[205]; the amount of potassium thiocyanate is determined photometrically on treatment with $(NH_4)_2SO_4.Fe(SO_4).24H_2O$ in nitric acid. A comparative assessment of all the methods for the analysis of sulphur-containing compounds permits the conclusion that the potentiometric titration procedures are the most suitable, being simplest and most accurate.

IV. OTHER METHODS

One should consider in the first place certain new analytical methods devised in recent years. A definite interest attaches to the method for the determination of aliphatic nitriles based on catalytic hydrogenation with subsequent titration in a non-aqueous medium[206]. The authors[206] devised a special apparatus for the hydrogenation of nitriles, which occurs in the presence of platinum oxide as the catalyst in acetic acid. The amines formed are determined by potentiometric titration with 0.1 *N* $HClO_4$ solution in dioxan. The standard deviations do not exceed 0.003–0.006.

Two methods for the determination of amides are noteworthy: the ion-exchange method[207] and analysis of *N*-substituted amides by the thermal cleavage method[208]. The latter procedure is based on brief (1–2 min) heating of amides at 300–400°C, amides being readily decomposed under these conditions to the amines and acids (or their decarboxylation products). The reaction products are identified chromatographically (by TLC or paper chromatography). More than one hundred compounds have been studied by this method; a mechanism has been proposed for the cleavage reaction and may be represented schematically as follows[208]:



A highly sensitive colorimetric method[209], in which the amide group is oxidised with bromine, the excess bromine is decomposed by sodium formate and the products are oxidised further with iodine until the formation of a pale-blue complex (the "tri-iodine–starch" complex), may be used to determine trace amounts of various amides in aqueous solutions; photometric measurements are made on the complex at 610 nm. The accuracy of the method is to within 3.0%.

A rapid and convenient micro-gas-volumetric method for the determination of the hydrazino-group in organic and inorganic compounds by oxidation of the group with *p*-benzoquinone in 5% Na_2HPO_4 solution has been reported[210]. Hydrazine derivatives may be determined by this procedure in the presence of ammonium salts; the accuracy is to within 0.2%. A method for the quantitative determination of dimethylhydrazine in solution by classical and a.c. polarography has been developed recently[6]. The method may be used in the dimethylhydrazine concentration range 10^{-3}–10^{-6} M and the error is 4%.

A very interesting analytical method has been developed for the determination of a mixture of α-amino-alcohols (primary, secondary, and tertiary) by treatment with an excess of potassium periodate in a weakly alkaline medium[211]. The method is rapid and accurate; the presence of α-amino-acids and α-diamines does not interfere with the analysis. It should also be mentioned that, following the development of the technique of ion-selective electrodes[213,216], potentiometric methods have come to be even more widely used for the determination of various nitrogen and sulphur-containing compounds. These methods may be used to determine many substances belonging to the classes noted above[5,6,212,214,215]. The polarographic method is used on a fairly wide scale in the analysis of complex organic sulphur-containing compounds[5,198].

The experimental data presented in this review indicate the great interest of investigators in the problem of the functional group analysis of nitrogen- and sulphur-containing organic compounds. At the same time one should note that there are still too few universal methods for the chemical analysis of mixtures of compounds belonging to different classes. The problems to be solved in the immediate future apparently involve the search for new

reagents and greater use of mathematical experimental design methods for the selection of optimum reaction conditions.

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During the preparation of the manuscript for the press, a number of new publications appeared. There are several reviews devoted to general problems of functional group analysis[217-220]. Titrimetric methods for the determination of nitrogen- and sulphur-containing compounds have been described[221-225] and accounts of photometric methods have appeared[256-266]. Other analytical methods have also been described[267-281].

REFERENCES

1. N. D. Cheronis and T. S. Ma, "Organic Functional Group Analysis by Micro and Semimicro Methods" (Translated into Russian), Izd. Khimiya, Moscow, 1973.
2. S. Siggia (Editor), "Instrumental Methods of Organic Functional Groups Analysis" (Translated into Russian), Izd. Mir, Moscow, 1974.
3. I. M. Korenman, "Fotometricheskii Analiz" (Photometric Analysis), Izd. Khimiya, Moscow, 1975.
4. J. J. Lagowski, Analyt. Chem., 112, 305R (1970).
5. "VI Vsesoyuznoe Soveshchanie po Polyarografii" (The VIth All-Union Conference on Polarography), Izd. Zinatne, Riga, 1975.
6. "III Vsesoyuznaya Konferentsiya po Analiticheskoi Khimii" (The IIIrd All-Union Conference on Analytical Chemistry), Izd. Nauka, Moscow, 1976.
7. N. N. Mikhailova, L. M. Lazorenko, G. S. Leonova, T. A. Rubtsova, G. N. Stepanyan, and E. S. Sytova, "Modern Methods of Analysis in the Production of Chemical Additives" [?], NIITEKhIM, Moscow, 1971.
8. M. Zgoda and S. Petri, Chem. Analit., 16, 175 (1971).
9. E. G. Novikov and V. K. Kondratov, Zhur. Anal. Khim., 23, 955 (1968).
10. A. P. Kreshkov, L. N. Shvetsova, G. P. Svistunova, and E. A. Emelin, Zhur. Anal. Khim., 26, 369 (1971).
11. St. J. H. Blackeley and V. J. Zatka, Analyt. Chim. Acta, 74, 139 (1975).
12. N. N. Bezinger, G. D. Gal'pern, N. G. Ivanova, and G. A. Semeshkina, Zhur. Anal. Khim., 23, 1538 (1968).
13. E. Kwiatkowski, H. Plucinska, and I. Nikel, Chem. Analit., 14, 1295 (1969).
14. M. Martka and Y. Pipalova, Chem. prumysl., 23, No. 3, 149 (1973).
15. Z. M. Demidova and N. F. Budyak, Zhur. Anal. Khim., 24, 1253 (1969).
16. R. D. Krause and B. Kratochvil, Analyt. Chem., 45, 844 (1973).
17. T. R. Williams and S. Wakeham, Analyt. Chim. Acta, 52, 152 (1970).
18. C. Djerassi and C. R. Sholz, J. Amer. Chem. Soc., 70, 417 (1970).
19. N. K. Sotsenko, A. I. Yurzhenko, and V. D. Osadchii, Zhur. Anal. Khim., 28, 2459 (1973).
20. M. I. M. Campbell, R. Grzeskowiak, and B. Perrett, Talanta, 18, 943 (1971).
21. E. J. Greenhow and L. E. Spencer, Analyst, 99, 82 (1974).
22. I. N. Stan'kov and E. V. Lysenko, Zavod. Lab., 40, 261 (1974).
23. P. Norkus and G. Simkeviciute, Zhur. Anal. Khim., 26, 2002 (1971).
24. H. E. Malone, "The Determination of Hydrazino–Hydrazine Groups", Oxford, 1970.
25. H. E. Malone, Analyt. Chim. Acta, 47, 363 (1969).
26. S. Ehrlich-Rogorinski and M. Wilchek, Analyt. Chim. Acta, 74, 449 (1975).
27. P. N. Krishnan Nambisan and C. G. Ramachandran Nair, Indian J. Chem., 10, 665 (1972).
28. A. A. Usvyatsov, A. R. Sudakov, Yu. A. Krylov, and E. V. Fronchek, Zavod. Lab., 37, 150 (1971).
29. A. A. Usvyatsov, A. R. Sudakov, Yu. A. Krylov, and N. K. Agasyan, Zhur. Anal. Khim., 29, 170 (1974).
30. B. P. Pant and S. P. Singh Dhakarey, Indian J. Appl. Chem., 32, 197 (1969).
31. V. G. Borodina and N. A. Kolchina, Zhur. Anal. Khim., 26, 2031 (1971).
32. G. Rourt and J. Cardia-Monjo, Inf. Quim. analyt. pura apl. Ind., 27, No. 2, 72 (1973).
33. J. K. Aggrawal, Analyst, 97, 578 (1972).
34. G. Tomlinson, W. H. Cruickshank, and T. Viswanatha, Analyt. Biochem., 44, 670 (1971).
35. W. I. Awad, S. S. Hassan, and M. T. Zaki, Analyt. Chem., 44, 911 (1972).
36. Z. G. Szabo and L. G. Bartha, Magyar Kém. Folyóirat., 78, 325 (1972).
37. L. S. Bark and P. Bate, Analyst, 98, 103 (1973).
38. R. A. Dubinskii and V. A. Klimova, Izv. Akad. Nauk SSSR, Ser. Khim., 1476 (1970).
39. S. I. Obtemperanskaya, A. P. Terent'ev, and V. K. Zlobin, Vestnik Moskov. Gos. Univ., No. 1, 119 (1974).
40. S. I. Obtemperanskaya and V. K. Zlobin, Zhur. Anal. Khim., 29, 609 (1974).
41. J. G. Sebranck and R. G. Cassens, J. Milk and Food Technol., 36, 76 (1973).
42. I. A. Wolff, J. Environmental. Sci., 35, 114 (1972).
43. F. Fiorese, J. Pirl, P. R. Manio, and A. Carella, Analyt. Chem., 45, 388 (1973).
44. K. W. Jang and E. V. Brown, Analyt. Letters, 5, 293 (1972).
45. A. Gottfursht, Metal. Finish., 67, No. 5, 50 (1969); Anal. Abs., 19, 1429 (1970).
46. L. G. Torstensson, Talanta, 20, 1319 (1973).
47. K. G. Housler, R. Geger, and S. Rennhok, Z. Chem., 12, 339 (1972).
48. I. P. Daneky, Int. J. Sulfur. Chem., 6, 159 (1971).
49. K. G. Housler, R. Geger, and S. Rennhok, Z. Chem., 14, 198 (1974).
50. N. A. Kolchina and G. M. Kondrat'eva, Zhur. Anal. Khim., 24, 1884 (1969).
51. K. K. Verma and S. Bose, Analyt. Chim. Acta, 65, 236 (1973).
52. J. Ahmed and S. Bose, J. Indian Chem. Soc., 50, 505 (1973).
53. A. M. Blotti, S. M. Sondhi, and N. K. Ralhan, J. Indian Chem. Soc., 50, 406 (1973).
54. K. G. Housler, R. Geger, and S. Rennhok, Z. Chem., 13, 196 (1973).
55. K. Verma and S. Bose, Talanta, 22, 74 (1975).
56. B. C. Verma, S. M. Ralhan, and N. K. Ralhan, Zhur. Anal. Khim., 30, 195 (1975).
57. A. Srivastava and S. Bose, J. Indian Chem. Soc., 51, 736 (1974).
58. P. Rom, P. Aggarwal, R. Chond, and K. Naresh, Indian J. Chem., 12, 986 (1974).

59. J.M.Bachharwat, N.S.Ramegowda, and A.K.Koul, Indian J.Chem., 11, 614 (1973).
60. J.Toribara and L.Koval, Talanta, 17, 1003 (1970).
61. H.Wenck, E.Schwabe, F.Schreider, and L.Flohe, Z.analyt.Chem., 258, 267 (1972).
62. F.Peter and R.Rosset, Analyt.Chim.Acta, 64, 397 (1973).
63. A.Cernenko and F.Crisan, Material Plast., 11, 239 (1974); Anal.Abs., 29, 2079 (1975).
64. M.Wronski, Talanta, 21, 776 (1974).
65. A.I.Busev and L.I.Teternikov, Zhur.Anal.Khim., 24, 918 (1969).
66. A.I.Busev, N.B.Shemjakina, and L.I.Teternikov, Analyt.Letters, 1, 763 (1968).
67. D.R.Grosseti and Y.E.Murrey, J.Chromatogr., 41, 121 (1969).
68. F.Feigl, D.Goldstein, and E.K.Libergott, Analyt. Chim.Acta, 47, 553 (1969).
69. S.P.Agathangelon, D.R.Brown, A.G.Fogg, and D.Burns, Labor.Pract., 20, 115 (1971).
70. B.C.Verma and S.Kumar, Zhur.Anal.Khim., 29, 1240 (1974).
71. H.Mochrle and G.Hempel, Arch.Pharm., 306, 903 (1973).
72. K.K.Verma and S.Bose, J.Indian.Chem.Soc., 50, 542 (1973).
73. W.Sztark, Nahrung, 19, 312 (1975); Analyt.Abs., 29, 4618 (1975).
74. T.M.Filimonova and B.F.Filimonov, Zhur.Anal. Khim., 24, 773 (1969).
75. A.P.Kreshkov and S.V.Vazhileva, Zhur.Anal. Khim., 28, 2029 (1973).
76. T.Jasinski and R.Korewa, Chem.Analit., 13, 1919 (1968).
77. B.G.Gnedin, M.A.Spryskov, and G.P.Chudinova, Izd.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 13, 262 (1970).
78. Yu.A.Nesterenko, I.S.Azhmedzhanov, and V.D.Lisitskaya, Zavod.Lab., 38, 283 (1972).
79. M.Gachon, G.Maire, and F.Eloy, Annal.pharm. France, 32, 697 (1974).
80. I.P.Danehy and V.I.Elia, Analyt.Chem., 44, 1281 (1972).
81. M.Matrka, Z.Sagner, and Q.Spevak, Chem. prumysl, 22, 551 (1972).
82. A.Kurian and C.V.Suryanarayana, Analyst., 97, 576 (1972).
83. V.R.S.Roo, Z.analyt.Chem., 249, 189 (1972).
84. B.Jakuszewski, W.Jedrzejewski, and J.Badecka-Jedrzejewska, Chem.Analit., 17, 349 (1972).
85. R.J.Thibert and M.Sarwar, Microchem.J., 14, 271 (1969).
86. R.D.Tiwari and U.C.Rande, Analyst., 94, 813 (1969).
87. B.Singh, S.C.Nistndra, and B.C.Verma, Z.analyt. Chem., 257, 348 (1971).
88. B.C.Verma and N.S.Kumar, Analyst, 98, 900 (1973).
89. D.M.Czakis-Sulikowska, Chem.Analit., 17, 345 (1972).
90. A.M.Bhatti and N.K.Ralhan, Z.analyt.Chem., 260, 370 (1972).
91. A.V.Gordievskii, O.A.Zemskaya, and N.I.Savin, Zhur.Anal.Khim., 29, 164 (1974).
92. G.Berthon and C.Zuca, Chim.Analyt., 51, 385 (1969).
93. D.J.Halls, Mikrochim.Acta, 1, 62 (1969).
94. A.F.Grand and M.Tamrer, Analyt.Chem., 40, 1904 (1968).
95. P.N.Krishnan Nambison and C.G.Ramanchandran, Analyt.Chim.Acta, 52, 475 (1970).
96. R.C.Roul, N.C.Sharma, K.K.Chouhan, and R.Rarkosh, Indian J.Chem., 10, 227 (1972).
97. Z.Kurzawa and E.Kubasewski, Chem.Analit., 19, 263 (1974).
98. M.A.Bernarg, M.-M.Borel, and G.Chauvenet, Bull.Soc.chim.France, 4, 1663 (1972).
99. A.I.Busev and L.I.Teternikov, Zhur.Anal.Khim., 23, 1134 (1968).
100. B.I.Isaeva, M.I.Lebedeva, and M.B.Organesyan, Trudy Moskov.Khim.-Tekhnol.Inst., No.71, 290 (1972).
101. N.K.Mathur, Talanta, 13, 1601 (1966).
102. E.A.Gribova and V.V.Dyatlova, Zavod.Lab., 36, 29 (1970).
103. M.A.Volodina and I.V.Kon'kova, Vestnik Moskov. Gos.Univ., 1, 123 (1968).
104. W.Grabowicz, Chem.Analyt., 24, 533 (1969).
105. W.Grabowicz and G.Mikolajczyk, Chem.Analyt., 17, 357 (1972).
106. W.Grabowicz, Chem.Analyt., 14, 21 (1969).
107. S.I.Obtemperanskaya and Nguen Dyk-Khoe, Vestnik Moskov.Gos.Univ., 5, 116 (1969).
108. S.I.Obtemperanskaya and N.N.Kalinina, Zhur. Anal.Khim., 26, 2252 (1971).
109. S.I.Obtemperanskaya and M.N.Sizoi, Zhur.Anal. Khim., 28, 399 (1973).
110. F.Knotz, Sci.pharm., 38, No.1, 26 (1970); Analyt. Abs., 20, 1705 (1971).
111. B.C.Verma and S.Kumar, Analyst, 99, 498 (1974).
112. Y.A.Gawargious, A.Besada, and M.Hassam, Mikrochim.Acta, 6, 1003 (1974).
113. H.A.Mottola and H.Freiser, Analyt.Chem., 39, 1294 (1967).
114. H.A.Mottola, Talanta, 16, 1267 (1969).
115. H.A.Mottola, Analyt.Chem., 42, 630 (1970).
116. M.Z.Barakat, M.Abou-El-Mararem, and M.Abd El-Racuf, Analyt.Chem., 46, 777 (1974).
117. B.Singh, S.C.Nistandra, and B.C.Verma, Z. analyt.Chem., 258, 366 (1972).
118. J.P.Gonzales and C.M.Feranandez, Inf.Quim. analit.pura apl.Ind., 23, No.5, 139 (1969).
119. M.Roileanu and E.Dobre, Rev.Roum.Chim., 15, 823 (1970).
120. W.Schruber, Z.analyt.Chem., 254, 345 (1971).
121. S.I.Obtemperanskaya, G.P.Kareva, and O.S.Zhukovskaya, Zhur.Anal.Khim., 28, 2066 (1973).
122. S.I.Obtemperanskaya, G.P.Kareva, and O.S.Zhukovskaya, Zhur.Anal.Khim., 29, 174 (1974).
123. S.I.Obtemperanskaya, N.N.Kalinina, T.N.Speranskaya, and N.M.Solov'eva, Zhur.Anal.Khim., 29, 946 (1974).
124. S.I.Obtemperanskaya and T.A.Egorova, Vestnik Moskov.Gos.Univ., Ser.Khim., No.5, 115 (1969).
125. S.I.Obtemperanskaya and T.A.Egorova, Zhur. Anal.Khim., 24, 1439 (1969).
126. S.I.Obtemperanskaya and N.N.Kalinina, Zhur. Anal.Khim., 26, 1407 (1971).
127. D.S.Mahadevappa and A.C.Ananda Murthy, Talanta, 17, 431 (1970).
128. M.I.M.Campbell, R.Grzeskowiak, and I.D.M.Turner, Analyst, 96, 286 (1971).
129. M.I.M.Campbell, R.Grzeskowiak, G.G.Jenkinson, and Y.D.M.Turner, Analyst, 97, 70 (1972).
130. H.E.Malone, Talanta, 22, 97 (1975).
131. J.Bartos, Talanta, 16, 551 (1969).
132. J.Bartos, Chim.analyt., 53, 18 (1971).

133. J. Bartos, Analysis, 2, 479 (1973).
134. T. Severin, J. Loske, and D. Scheel, Chem. Ber., 102, 3909 (1969).
135. I. P. Sharma and R. D. Tiwari, Microchem. J., 17, 151 (1972).
136. L. Legradi, Mikrochim. Acta, 3, 517 (1971).
137. L. Legradi, Mikrochim. Acta, 2, 222 (1970).
138. S. I. Obtemperanskaya and V. N. Likhosherstova, Vestnik Moskov. Gos. Univ., No. 3, 130 (1969).
139. S. I. Obtemperanskaya, E. G. Chalenko, and N. S. Moroz, Vestnik Moskov. Gos. Univ., No. 2, 83 (1969).
140. S. I. Obtemperanskaya and V. N. Likhosherstova, Zhur. Anal. Khim., 26, 158 (1971).
141. S. I. Obtemperanskaya, V. N. Likhosherstova, and A. P. Terent'ev, Zhur. Anal. Khim., 25, 2033 (1970).
142. S. I. Obtemperanskaya, A. P. Terent'ev, Yu. A. Tikhonov, and I. Ya. Tsypkina, Vestnik Moskov. Gos. Univ., No. 3, 117 (1969).
143. K. Fickentscher, Arch. Pharm., 302, 119 (1969).
144. I. Tashima, H. Hasegawa, H. Juki, and K. Takiura, Japan Analyst, 19, 43 (1970).
145. U. Toyozo and M. Jamamoto, Japan Analyst, 17, 306 (1968).
146. K. Wrabets, Z. analyt. Chem., 246, 258 (1969).
147. H. B. Hucker, Drag. Metal. Disposition, 1, 322 (1973).
148. A. H. Beckett and S. Al-Sarraj, J. Pharm. Pharmacol., 24, 916 (1972).
149. J. T. Stewart, T. D. Shaw, and A. B. Ray, Analyt. Chem., 41, 360 (1969).
150. R. E. Gammans, J. T. Stewart, and L. A. Sternson, Analyt. Chem., 46, 620 (1974).
151. C. W. Ballard, J. Isaacs, and P. G. Skott, J. Pharm. Pharmacol., 6, 971 (1954).
152. V. D. Gupta, Indian J. Pharm., 35, 77 (1973).
153. B. A. Persson, Acta Pharm. Suecica, 7, 337 (1970).
154. B. A. Persson, Acta Pharm. Suecica, 7, 343 (1970).
155. B. A. Persson, Acta Pharm. Suecica, 7, 353 (1970).
156. R. Modin and G. Schill, Acta Pharm. Suecica, 7, 585 (1970).
157. V. D. Gupta and J. B. Reed, J. Pharm. Sci., 59, 1683 (1970).
158. B. A. Persson, Acta Pharm. Suecica, 8, 193 (1971).
159. E. R. Carrett and J. Tsau, J. Pharm. Sci., 61, 1404 (1972).
160. M. Tsubouchi, J. Pharm. Sci., 60, 943 (1971).
161. K. O. Borg, Acta Pharm. Suecica, 8, 1 (1971).
162. F. Matsui, J. R. Watson, and W. N. French, J. Chromatog., 44, 109 (1969).
163. K. Kigasawa, Yakugaku Zasshi, 90, 182 (1970).
164. I. M. Korenman and N. A. Shemareva, Zhur. Anal. Khim., 29, 2032 (1974).
165. L. S. Mikhailova and Z. I. Chalaya, Zhur. Anal. Khim., 29, 2036 (1974).
166. G. L. Starobinets, D. Z. Luk, and E. Rakman'ko, Zhur. Anal. Khim., 30, 1812 (1975).
167. T. S. Burenko and R. S. Kripenina, Zavod. Lab., 39, 152 (1973).
168. S. I. Obtemperanskaya, A. P. Terent'ev, and Yu. A. Tikhonov, Vestnik Moskov. Gos. Univ., Ser. Khim., No. 12, 369 (1971).
169. L. V. Kuritsyn and V. M. Kuritsyna, Izd. Vys. Ucheb. Zavod., Khim. i Khim. Tekhnol., 15, 461 (1972).
170. I. M. Korenman, N. V. Kurina, and T. Ya. Peshcherkova, Trudy po Khim. i Khim. Tekhnol., Gor'kovsk. Gos. Univ. im. Lobachevskogo, No. 2 (23), 136 (1969).
171. I. F. Corbett, Analyt. Chem., 47, 308 (1975).
172. J. Bartos and M. Peser, Bull. Soc. chim. France, 4, 1627 (1970).
173. P. Wuelfing, E. A. Fitzgerald, and H. H. Richtol, Analyt. Chem., 42, 299 (1970).
174. V. Toome, S. De Bernardo, K. Manhart, and M. Weigele, Analyt. Letters, 7, 437 (1974).
175. L. Legradi, Mikrochim. Acta, 6, 1170 (1969).
176. L. Legradi, Mikrochim. Acta, 3, 544 (1970).
177. L. P. Mordovina, V. I. Korotkova, and V. V. Noskov, Zhur. Anal. Khim., 29, 580 (1974).
178. K. R. Manolov and V. T. Stamatova, Mikrochim. Acta, 2, 222 (1970).
179. J. P. Rawal and J. P. Singh, Analyt. Chem., 47, 738 (1975).
180. K. A. Connors and K. S. Albert, Analyt. Chem., 44, 879 (1972).
181. W. Rzeszutko, Acta Polon Pharm., 31, 323 (1974).
182. Ya. I. Korenman and N. G. Sotnikova, Zhur. Anal. Khim., 28, 2063 (1973).
183. T. Mitsui and Y. Fujimura, Japan Analyst., 23, 1309 (1974).
184. L. Legradi, Mikrochim. Acta, 3, 472 (1969).
185. C. Wagner, Analyt. Biochem., 60, 278 (1974).
186. A. D. Marco and E. Mecarelli, Mikrochim. Acta, 1, 135 (1970).
187. R. C. Gupta and S. P. Srivastava, Z. analyt. Chem., 257, 275 (1971).
188. L. Legradi, Mikrochim. Acta, 1, 198 (1969).
189. V. I. Korotkova and V. V. Noskov, Zhur. Anal. Khim., 27, 580 (1972).
190*. S. I. Obtemperanskaya and Yu. N. Tikhonov, Vestnik Moskov. Gos. Univ., Ser. Khim., No. 6, 95 (1966).
191. S. I. Obtemperanskaya and Nguen Kim Kan, Zhur. Anal. Khim., 29 (10), 2069 (1974).
192. K. Kunorits, Analyt. Chim. Acta, 55, 221 (1971).
193. D. R. Grossetti and J. F. Murrey, Analyt. Chim. Acta, 46, 139 (1969).
194. M. S. Pohrbach, B. A. Humphries, F. I. Jost, W. G. Rhodes, S. Boatman, R. G. Hiskey, and J. H. Harrison, Analyt. Biochem., 52, 127 (1973).
195. J. Mourice, Erdöl und Köhle, 26, 140 (1973).
196. A. I. Busev and L. I. Teternikov, Analyt. Letters, 4, 53 (1971).
197. T. Takashi, H. Kozuo, and K. Akinori, Japan Analyst, 23, 650 (1974).
198. F. E. Powelle and C. J. Snowden, Analyst, 100, 1192, 502 (1975).
199. Z. I. Chalaya and L. S. Mikhailova, Zhur. Anal. Khim., 25, 1829 (1970).
200. F. Garcia, E. Monuel, and M. I. Ruedos, Quim. anal., 29, 27 (1975); Analyt. Abs., 29, 3 (1975).
201. M. B. Devani, C. J. Shishoo, and M. G. Shah, Analyst, 98, 759 (1973).
202. M. Wronski, Chem. Analit., 14, 83 (1969).
203. I. A. Vinson, Analyt. Chem., 41, 1661 (1969).
204. L. F. Roo and S. Singh, Indian J. Chem., 11, 1072 (1973).
205. I. G. Higgins and L. M. Mukherjce, Chem. Ind., 7, 317 (1974).
206. Z. Goral and M. Jaworski, Chem. Analit., 15, 629 (1970).
207. M. Qureski, S. Qureski, and S. C. Singhal, Indian J. Analyt. Chem., 40, 1781 (1968).

*See also Yu. N. Tikhonov, Candidate's Thesis, Moscow State University, Moscow, 1970.

208. J. Skutil and J. Gasparic, Mikrochim. Acta, 6, 828 (1972).
209. M. W. Scoggins and J. W. Miller, Analyt. Chem., 47, 152 (1975).
210. S. S. M. Hassan and M. T. M. Zaki, Microchem. J., 15, 470 (1970).
211. A. Besada and I. A. Gawargious, Talanta, 21, 1247 (1974).
212. J. M. Ross and M. S. Frant, Analyt. Chem., 41, 967 (1969).
213. K. Cammann, Beckman Rept., 21 (1970); Ref. Zhur. Khim., 21G4270 (1971).
214. R. P. Buck, Analyt. Chem., 46, 28 (1974).
215. W. Selig, Microchim. Acta, 3, 515 (1974).
216. B. P. Nikol'skii and E. A. Mazherova, Vestnik Leningrad. Gos. Univ., 84 (1975).
217. F. Pallrin, Pure Appl. Chem., 44, 3, 579 (1975).
218. T. Jr. Smith and J. M. Patterson, Analyt. Chem., 48, 5, 83 (1975).
219. B. Kratochvil, Analyt. Chem., 48, 355 (1976).
220. R. L. Parry-Jones, Educ. Chem., 13, 76 (1976).
221. W. F. Koch, W. C. Hoyle, and H. Diehl, Talanta, 22, 717 (1975).
222. L. A. Chazova, B. A. Lopatin, and G. L. Loshkarev, Trudy Krasnodar. Politekh. Inst., No. 70, 49 (1976).
223. L. N. Balyatinskaya, Yu. F. Milyaev, and L. G. Babankova, Zhur. Anal. Khim., 31, 963 (1976).
224. G. A. Sal'nikova, N. I. Simonova, T. A. Eremina, B. M. Babkin, and V. Ya. Katsobashvili, Zavod. Lab., 46, 156 (1976).
225. C. G. R. Nair and P. Indrasenan, Talanta, 23, 239 (1976).
226. H. Saad, M. T. Zaki, and K. A. Tollan, Microchim. Acta, 1, 521 (1976).
227. M. Bos, S. T. Ljpma, and E. A. Dahmen, Analyt. Chim. Acta, 83, 39 (1976).
228. L. S. Bark and P. Prachuabpaibul, Analyt. Chim. Acta, 84, 207 (1976).
229. L. J. Bjelica, V. J. Vajgand, T. J. Pastor, and D. V. Palić, Z. anal. Chem., 280, 382 (1976).
230. O. F. Raizullaeva and L. A. Shvyrkova, Trudy Samarkand. Univ., No. 280, 24 (1975).
231. W. Selig, Microchem. J., 21, 92 (1976).
232. B. C. Verma and S. Kumar, Microchem. J., 21, 237 (1976).
233. G. P. Balabanov, Yu. I. Mushkin, M. G. Ivanov, and T. I. Maslova, USSR P. 555 338 (1977).
234. F. F. Gaal, B. F. Abramovic, F. B. Szebenyi, and V. D. Canic, Z. analyt. Chem., 286, 222 (1977).
235. N. Duc Hue, Hóa hoc., 3, 29 (1976).
236. E. J. Greenhow, Analyst, 102, 1217, 584 (1977).
237. B. C. Verma and S. Kumar, J. Indian Chem. Soc., 52, 528 (1975).
238. K. K. Verma and S. Bose, Philipp. J. Sci., 103, 3, 187 (1974).
239. K. C. Tseng and W. F. Gutknecht, Analyt. Chem., 47, 13, 2316 (1975).
240. K. K. Verma, J. Ahmed, and S. Bose, Z. analyt. Chem., 278, 2, 128 (1976).
241. K. K. Verma, Talanta, 22, 3, 920 (1975).
242. A. Cedergren, Talanta, 22, 12, 967 (1975).
243. K. K. Verma, J. Ahmed, and S. Bose, Z. analyt. Chem., 278, 367 (1976).
244. V. G. Luk'yanitsa, G. D. Gal'pern, and T. Yu. Filippova, Symposium, "Organicheskie Soedineniya Sery" (Organic Sulphur Compounds), Riga, 1976, Vol. 1, p. 81.
245. B. C. Verma and S. Kumar, Talanta, 23, 241 (1976).
246. B. C. Verma and S. Kumar, Microchim. Acta, 1, 209 (1976).
247. A. M. Bond, Z. Sczajer, and G. Winter, Analyt. Chim. Acta, 84, 37 (1976).
248. V. N. Byr'ko, T. I. Tikhonova, and G. I. Pavlova, Zhur. Anal. Khim., 31, 1089 (1976).
249. K. Häusler and S. R. Geyer, Z. Chem., 16, 232 (1976).
250. M. Wronski and B. Mazurkiewicz, Chem. Analit., 21, 949 (1976).
251. A. Zdúnska, W. Kwapizewski, and B. Dulowska, Chem. Analit., 21, 681 (1976).
252. B. C. Verma and S. Kumar, Talanta, 23, 612 (1976).
253. H. P. Stivastava, J. Indian Chem. Soc., 53, 400 (1976).
254. M. N. Krishna, R. K. Rama, and R. J. Pulla, Z. analyt. Chem., 286, 247 (1977).
255. B. C. Verma and V. Sharma, J. Indian Chem. Soc., 53, 1190 (1976).
256. M. Qureshi and I. A. Khan, Analyt. Chim. Acta, 86, 309 (1976).
257. S. I. Obtemperanskaya, T. N. Speranskaya, and L. N. Bukhtenko, Vestnik Moskov. Gos. Univ., Khimiya, 17, 621 (1976).
258. J. A. Plaizer, J. G. Van Damme, and R. E. De Néve, Analyt. Chem., 48, 1536 (1976).
259. T. S. AlGhabsha, S. A. Rahim, and A. Townshend, Analyt. Chim. Acta, 85, 189 (1976).
260. A. Mizukami and T. Amano, Japanese P. 502 595 (1975); Ref. Zhur. Khim., 13G234 (1976).
261. H. Kenjiro, S. Yoshiaki, T. Shoji, and V. Fumiko, Bunseki Kagaku, 26, 511 (1977).
262. J. T. Stock and L. M. Doane, Analyt. Chim. Acta, 86, 317 (1976).
263. V. P. Fadeeva and N. F. Zaslavskaya, Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim., No. 3, 155 (1976).
264. M. P. C. Ip and R. J. Thibert, Microchim. Acta, 1, 599 (1976).
265. Z. Przybylski, Chem. Analit., 21, 263 (1976).
266. R. Knapek and Z. Chmiel, Nahrung, 20, 165 (1976).
267. W. A. Aue and V. Paramasigamani, Int. Symp. Microchim. Techn., Davos, 210 (1977).
268. R. V. Golovnya, E. A. Mistryukov, and A. L. Samusenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1632 (1977).
269. H. Sohr and K. Wienhold, Analyt. Chim. Acta, 83, 415 (1976).
270. G. Srivastava, M. Gopal, U. C. Pande, and R. D. Tiwari, Z. analyt. Chem., 280, 30 (1976).
271. M. Pribyl and L. Semenkova, Z. analyt. Chem., 278, 347 (1976).
272. L. A. Gribov and V. A. Dement'ev, Symposium, "XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii" (The XIth Mendeleev Congress of General and Applied Chemistry), Moscow, 1975, p. 51.
273. P. Francis and R. Rosset, Analyt. Chim. Acta, 79, 47 (1975).
274. R. G. Baisheva, G. K. Murzatova, and Zh. R. Rakhmetova, Symposium, "Eksperimental'nye Metody Issledovaniya v Khimii i Biologii" (Experimental Research Methods in Chemistry and Biology), Karaganda, 1975, No. 2, p. 79.
275. J. J. Arias, C. Sanchez-Pedreno, and Y. P. Perez Trujillo, Quim. anal., 30, 183 (1976).
276. G. Rauret and J. Garcia-Monjo, Quim. Anal., 30, 29 (1976).
277. R. L. Kaushik, O. P. Vermani, and R. Prosad, Indian J. Chem., 12, 1022 (1976).

278. A. Barbera and D. Canepa, J. Assoc. Offic. Analyt. Chem., 60, 708 (1977).
279. E. Giralt and J. Calmet, Ann. Chim. (France), 2, 97 (1977).
280. K. K. Verma, M. P. Sahasrabúddhey, and S. Bose, Talanta, 23, 725 (1976).
281. P. Chakorova and O. Budevsky, J. Electroanal. Chem., 73, 369 (1976).

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