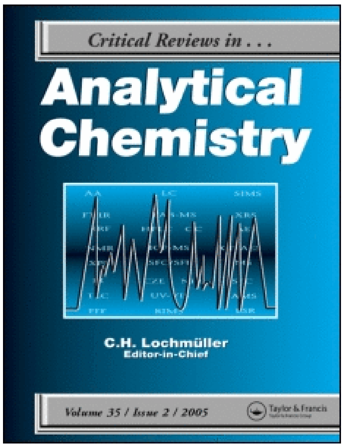
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Spectrophotometric Determination of Trace Elements

Zygmunt Marczenko; Henry Freiser

To cite this Article Marczenko, Zygmunt and Freiser, Henry(1981) 'Spectrophotometric Determination of Trace Elements', Critical Reviews in Analytical Chemistry, 11: 3, 195 — 260

To link to this Article: DOI: 10.1080/10408348108542732
URL: http://dx.doi.org/10.1080/10408348108542732

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROPHOTOMETRIC DETERMINATION OF TRACE ELEMENTS

Author: **Zygmunt Marczenko**
Department of Analytical Chemistry
Technical University of Warsaw
Warsaw, Poland

Referee: Henry Freiser
Department of Chemistry
University of Arizona
Tucson, Arizona

TABLE OF CONTENTS

I. INTRODUCTION

The rapid and continuous progress in trace analysis is associated with the development of several new techniques and industries, the beginnings of which date back to the years following World War II. Their demands for high purity materials are the main driving force, although the idea of microelements has been known for a long time in biological, agrotechnical, and geological studies, as well as in forensic analysis. Trace analysis is also an excellent analytical tool in the food industry and in environmental pollution and archeological research. As recognized recently, trace amounts of many metals and nonmetals are essential for normal biological processes. On the other hand, some elements are toxic if present in too high concentrations. With so many fields of interest and application, trace analysis has become now the major problem of the day in analytical chemistry.

The range of trace analysis comprises element concentrations from $1 \times 10^{-2}\%$ to $10^{-10}\%$ and less. Concentrations up to $1 \times 10^{-4}\%$ (1 to 100 $\mu g/g$) are sometimes called traces, while those below $1 \times 10^{-4}\%$ ($< 1\ \mu g/g$), ultratraces. These concentrations are generally given in parts per million (ppm) and parts per billion (ppb) units (1 ppm = $1 \times 10^{-4}\%$; 1 ppb = $1 \times 10^{-7}\%$).

Many instrumental methods can be applied to the determination of trace elements. Spectrophotometry and emission spectrography have been in common use from the very beginning of trace analysis; atomic absorption spectrometry (flame and electrothermal) has been introduced recently. Because of various reasons polarography, coulometry, fluorimetry, atomic fluorescence spectrometry, X-ray fluorescence spectrometry, mass spectrometry, and neutron activation analysis are less common techniques. Particular techniques cannot be used universally, but they complement one another.

Spectrophotometry, or, strictly speaking, molecular absorption spectrophotometry, is widely applied in trace analysis[1-7] as the necessary equipment is simple and inexpensive. Spectrophotometric methods can be used for precise determination of practically all metals and nonmetals in any material. However, they often call for skilled and experienced operators. Among all instrumental analytical techniques spectrophotometric methods are the most "chemical" ones. They are particularly important as control methods in the preparation of certified standards where high precision and reliability of the results outweigh the disadvantage of the rather time-consuming analytical procedure.

Some difficulties in the application of spectrophotometry to trace analysis are connected with the selection of a suitable, sensitive method. With a vast number of publications reporting new reagents and new spectrophotometric methods the choice is by no means easy. It is, therefore, the aim of this paper to give a critical review of the methods and to recommend the best ones, i.e., the ones that offer high sensitivity and reliability in trace determinations.

II. SPECTROPHOTOMETRY IN TRACE ANALYSIS

A. Sensitivity, Limit of Determination

Objective numerical expression of the sensitivity of spectrophotometric methods is the molar absorptivity or molar (decadic) absorption coefficient (ϵ) at the wavelength (λ_{max}) of maximum absorbance (A) of the colored species ($\epsilon = A/c \times l$) c is the concentration of colored species (mol/l) and l is the thickness of the absorbing layer (cm) (path length).

The value of molar absorptivity (in l.mol^{-1}.cm^{-1}) is an index of the sensitivity. Generally methods in which $\epsilon > 6 \times 10^4$ are considered sensitive[*] those with $\epsilon < 2 \times 10^4$ are considered insensitive.[8] Particularly high sensitivity is generally shown by the methods, discussed below, that are based on ternary systems and amplification reactions.

It is convenient to express and compare the sensitivities of spectrophotometric methods, for elements with very different atomic weights, in terms of the specific absorptivity (a).[9] This is obtained by dividing ϵ by the atomic weight of an element and by 1000

$$a = \epsilon/\text{at. wt} \times 1000$$

The value a (in mℓ.g^{-1}.cm^{-1}) corresponds to the absorbance of a 1 μg/mℓ (= 1 ppm) solution of the determinand in a cuvette of 1 cm path length. The use of the quantity a allows a comparison that is independent of atomic weight of an element.

The sensitivity of spectrophotometric methods is often expressed in terms of the sensitivity index given by Sandell.[2] It represents the number of μg of the determinand per mℓ of a solution having an absorbance of 0.001 for a path length of 1 cm. Sandell's sensitivity (S) is expressed in μg.cm^{-2} ($S = 10^{-3}/a$).

The lowest concentration that can be determined spectrophotometrically can be calculated from the fundamental formula: $A = \epsilon.c.l$. If the minimum absorbance (A) that can be measured is 0.05, the path length (l) is 2 cm, and the molar absorptivity (ϵ) is taken as 5×10^4; the corresponding concentration

---

[*] According to quantum theory, the molar absorptivities of direct spectrophotometric methods (based on simple or chelate complexes) cannot exceed about 1.5×10^5. Higher molar absorptivities (called apparent) are possible in cases of some indirect methods (e.g., amplification, based on some ion associates).

$$c = \frac{0.05}{2 \times 50000} = 5 \times 10^{-7} \text{ M}$$

For the element with relative atomic mass 100, this corresponds to

$$\frac{5 \times 10^{-7}.100}{1000} = 5 \times 10^{-8} \text{ g/m}\ell = 0.05 \ \mu\text{g/m}\ell$$

If the absorbance is to be measured in an ordinary 2-cm cuvette, the minimum volume that can be used is 10 mℓ, which corresponds to a total of 0.5 μg of the element. If we assume that saturated solutions of easily soluble salts average 10%, then 10 mℓ of saturated solution corresponds to 1 g of solute. If the 0.5 μg of the determinand is present in this 1 g of analyzed sample, its concentration in the sample is 5×10^{-5}%. Therefore, the limit of determination by common spectrophotometric methods is 5×10^{-5}%. In other words, concentrations not less than 5×10^{-5}% can be determined directly without preconcentration of trace amounts of elements. Trace concentrations smaller than 10^{-4} to 10^{-5}% are below the sensitivities of most spectrophotometric methods.

The extraction of the color compound can enhance this limit 3 to 4 times. Introduction of an organic solvent to an aqueous medium sometimes gives an increase of sensitivity, e.g., acetone in the case of iron (III)-thiocyanate system. For greater enhancement of the sensitivity of spectrophotometric methods it is necessary to include a preliminary step, such as preconcentration (enrichment). Depending on the sample type and the size of the weighed portion (e.g., 10 g, 100 g, or more) this operation may enhance the sensitivity by one, two, or more orders of magnitude. In this way the "normal" limit of determination is enhanced to 10^{-6} to 10^{-7}%.

A further increase in the sensitivity is practicable by reducing the minimum amount of determinand needed. This may be achieved by using microcuvettes with path lengths of 5 to 20 cm and using only 0.1 to 1 mℓ of color solution.[10,512]

B. Preconcentration of Trace Elements

Preconcentration[11-14] plays a double role in trace analysis: it enhances the relative concentration of the element determined, thereby increasing the sensitivity of the method; it separates the determined trace elements from macrocomponents (matrix) which frequently interfere with the determination.

The matrix is sometimes a single element, as in the analysis of high-purity metals, semiconductors, and reactor materials, but more often is a combination of elements (compounds, mixtures, alloys) as in the case of geological and biological materials.

Two cases can be distinguished: separation of trace elements from the matrix and, vice versa, removal of macrocomponent(s) leaving the trace elements in the mother solution.

The preconcentration of trace elements[1,3,4] can be carried out by solvent extraction, on ion-exchanger columns, by coprecipitation with a collector (scavenger), or by volatilization. The separation of the matrix is carried out by volatilization, solvent extraction, or by precipitation.[13] Electrolysis can be used to separate micro- or macroamounts of some metals.

In the most frequently used extraction separation (preconcentration), simple covalent molecules (e.g., $GeCl_4$, OsO_4, AsI_3), inner chelates and various ion associates (ion pairs), e.g., with use of tri-*n*-butyl phosphate (TBP), tri-*n*-octylphosphine oxide (TOPO), amines, ammonium-, phosphonium-, and arsonium ions are extracted. The precipitation of the matrix is permissible when the operation is carried out in a strongly acidic medium.

If the macrocomponents can be removed by volatilization without introducing large quantities of reagents, the trace elements may be greatly concentrated (e.g., in trace analysis of volatile mineral acids). Wet mineralization and ashing of organic samples, which precede the determination of trace elements, is also an example of separation of the major components by volatilization.

Solvent extraction, coprecipitation with collectors, and ion-exchangers serve also to separate the trace concentrate for particular trace elements before their spectrophotometric determination, e.g., in trace analysis of cadmium,[674] of gold,[701,703] platinum,[702] and of nitric and hydrofluoric acids.[726] In this way a greater number of trace elements can be determined using one large sample. This permits saving the analyzed material (often very expensive) and lowering the limit of determination, because every trace element is determined on the basis of its total content in the sample weight. The disadvantage is the increase of the blank value, particularly for the common elements determined in other parts of the procedure.

C. Contamination, Blank Test

In trace analysis, the effects of contamination from reagents, laboratory air, furnishings, apparatus, and containers have become increasingly important, when very low trace levels of elements need to be determined.[1,15,16]

Parallel to the analysis of the sample, a blank test is performed. The amount of a trace element to be determined must be greater than the total blank value and the blank value variation. It was suggested that a signal (X) could be considered with reasonable confidence to be different from the blank value when it is at least as great as the mean blank value ($\overline{X}$) plus three standard deviations of the blank value ($X = \overline{X} + 3s$).[11]

In order to be able to determine lower levels (it is especially difficult in the case of common elements such as, e.g., Si, Mg, Ca, Al, Fe, Zn, Cu, Pb) it is necessary to reduce the blank value. This can be done by purification of reagents, use of quartz, polyethylene and Teflon® rather than glass vessels. To prevent contact of the sample with laboratory air, certain chemical operations may be conducted in closed chambers (boxes) flushed with purified, filtered air or inert gas. In principle, all stages in the preparation of the sample, including sample-taking, transport, storage, and processing, should be considered in an assessment of the sources of error.

The reagents are usually the greatest source of contamination in the blank test. The water used[17] should be distilled in a quartz apparatus after demineralization with ion-exchangers. Volatile acids[18] can be purified by slow distillation in quartz vessels. Hydrofluoric acid requires fractional distillation in platinum or palladium vessels. Very pure ammonia is obtained by saturation of very pure water in a polyethylene container with gaseous purified ammonia. Solutions of many reagents are usually purified by solvent extraction (e.g., with dithizone, oxine) or by coprecipitation methods with collectors. It is desirable that the concentration of contaminant elements in the reagents be two orders of magnitude lower than in the sample analyzed.

One serious problem in trace analysis is the storage and stability of very dilute standard solutions of elements.[19,20] In addition to the phenomena of adsorption and desorption on and from the container walls, the bacterial action, the effect of exposure to light and to heat should be considered. It is advisable to keep such standard solutions as relatively concentrated stock solutions, and to dilute them by using calibrated pipettes and standard flasks (best made of pure silica) directly before use.

D. Precision, Accuracy, and Selectivity

The precision of spectrophotometric methods[21] depends on the concentration of the determinand, and varies from approximately 0.5 to 2% under suitable measuring conditions. The precision attainable is a function of the absorbance measured. The measuring errors are smaller if the measured absorbance is in the range 0.2 to 1.0.

However, in the determination of trace levels, absorbances <0.2 are often measured, which obviously results in higher measuring errors.

Errors connected with the measurement of absorbance are usually smaller than those associated with the chemical operations in the determination. The overall error of the determination is the summation of the errors committed at each stage of procedure, i.e., in sampling, dissolution, preconcentration, separation of trace elements, and the spectrophotometric measurement. In the course of these operations, a determinand may be introduced from outside the system or may be lost. An accurate blank determination is also of vital importance.

In trace analysis good reproducibility is of course desirable, but a poorer accuracy of determination for very low concentrations must be accepted. In the determination of trace levels of about 10^{-3} to $10^{-4}\%$ an error up to ±10% is usually obtained, whereas in the determination of traces at the 10^{-6} to $10^{-7}\%$ level with preconcentration, the error increases approximately to ±30%.[22]

The error in determining the level of an element by a given method may be estimated by comparing the results with the values considered to be true. There are numerous standard reference materials for trace analysis.[23] If no standard samples of accurately known composition are available, the accuracy of determination is estimated by analyzing the sample with and without a spike of accurately known amount of the determined elements, added to a weighed sample. The amounts of spike added should be close to those contained in the sample itself. The elements to be determined are added in a form which behaves similarly to the form in the sample.

Selectivity of the spectrophotometric methods usually depends on the nature of the reagent used, the oxidation state of the element, the pH of the medium, and the masking agents. If, in spite of use of all these factors, some elements can still interfere in a determination, the species to be determined has to be separated from the interfering elements or vice versa.

The optimum pH range for reaction with a given element is related to the nature of the element and the reagent. For the reagents of the ROH type there is a relation between the color reactions and the hydrolysis of given elements. In strongly acid solutions the color reactions are given by elements having cations which readily hydrolyze, i.e., Zr, Hf, Ti, Th, U(IV). In acid medium the metal ions of the hydrogen sulfide group that form the most stable sulfides react with RSH type of reagents.

Increased selectivity of spectrophotometric methods is mainly obtained by masking the interfering ions. Details on masking can be found in works by Perrin.[24,25] The most often used masking agents are: EDTA, cyanide, citrate, tartrate, fluoride, iodide, and thiosulfate.

High selectivity is obtainable by a suitable combination of masking agents, pH, and appropriate reducing or oxidizing agents. It should be noted that extraction itself also results in an increase of selectivity. In general, the extractive spectrophotometric methods are more selective than methods carried out in aqueous media. Combination of a selective extraction method with a sensitive spectrophotometric method of determination of poor selectivity is an example of an advantageous analytical hybrid solution.

III. COLOR SYSTEMS USED IN SPECTROPHOTOMETRY

A. General

Sensitive spectrophotometric methods are based on color systems formed from reactions of the elements to be determined. The majority are complexation reactions, and rarely other types. Thus, organic complexing reagents play the most important role in trace spectrophotometric analysis.[1,8,26] The presence of some chromophors, such as azo or *p*-quinoid groups, in organic reagents, results in high color intensity of the chelate compounds formed with these reagents. In addition to chelating reagents there exist also color-forming, organic nonchelating reagents, i.e., the basic and acid dyes. These dyes form ion associates with the determined elements, i.e., anionic and cationic complexes. The more sensitive spectrophotometric methods are more and more often based on ternary systems involving basic dyes or some surfactants.

Spectrophotometric inorganic reagents rarely lead to more sensitive methods. These reagents, however, play an important role in sensitive amplification methods. In some cases color systems are due to redox or organic reactions.

In sensitive spectrophotometric methods it is of importance to use reagents of suitable purity. It is generally known that higher sensitivity in the reactions of metals with some reagents (e.g., 1,5-diphenylcarbazide, α-furildioxime) can be attained when the reagents are of good quality.

The course of chromogenic reactions can be considerably influenced by the sequence of mixing the components. The most suitable way of mixing usually evokes the largest value of the absorbance and the best reproducibility of results.[27]

Often one has to deal with solutions which contain the colored complex of the determined element and a color resulting from the excess of the color reagent. For these cases it is especially valuable to use systems with a great contrast of two colors ($\Delta\lambda$), i.e., a great difference between the maxima in the absorption spectra of the complex (MR) and reagent (R)

$$\Delta\lambda = \lambda_{\max}^{MR} - \lambda_{\max}^{R}$$

It is conventionally assumed that a high contrast is when $\Delta\lambda > 80$ nm. Ways of increasing the contrast in color reactions are discussed.[8]

Catalytic methods used in spectrophotometry show high sensitivity. These methods are based on catalytic acceleration of some color redox reactions by elements determined. Catalytic methods are not discussed in this review.

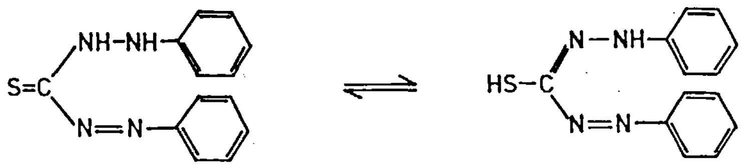
It should be said that in analytical practice one has more and more often to do with automated spectrophotometric methods. Some of these are mentioned in Section V.

B. Binary Systems with Organic Reagents

1. Dithizone and Related Reagents

Dithizone (diphenylthiocarbazone) (H. Fischer, 1925) is a very important, already classical, spectrophotometric reagent. It provides the basis of sensitive methods for such heavy metals as Pb, Zn, Cd, Hg, Ag, Cu, and Bi. Dithizone serves also to determine Pd, Pt, Au, In, Tl, Sn, Te, and Se. The books by Irving[28] and Ivantscheff[29] are excellent monographs devoted to theory and analytical use of dithizone.

In organic solvents dithizone (H_2Dz) exists in the keto and enol tautomeric forms:



(1)

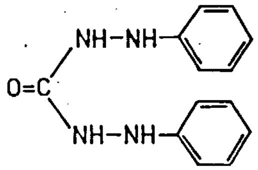
Dithizone forms colored chelates, $M(HDz)_n$, (most often pink) on shaking a green dithizone solution (in CCl_4 or $CHCl_3$) with an aqueous solution of a given metal at a suitable pH. Recent investigations have shown the metal to be bonded to the sulfur atom by replacement of the hydrogen in the thiol group, and also coordinately bonded to a nitrogen atom.

Solutions of metal dithizonates in CCl_4 ($CHCl_3$) are intensely colored, their colors differing considerably from that of dithizone. An exception is the grey-green palladium dithizonate. The molar absorptivities of the metal dithizonates are within the range of 3 to 9×10^4. The most stable dithizonates (Pt, Pd, Au, Ag, Hg, Cu) can be extracted from strongly acidic solutions. Irrespective of their thermodynamic stability the dithizonates of certain metals (Ag, Hg, Pb, Cd) are extracted rapidly, whereas those of other metals (Pd, Cu, Zn) require prolonged shaking with the organic solution of dithizone. This is explicable in terms of the kinetics of dithizonate formation.

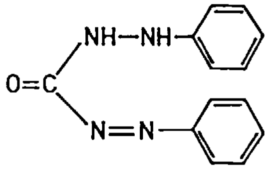
High selectivity in spectrophotometric methods for determining metals with dithizone is attained by controlling the pH of the aqueous medium and using thiosulfate, iodide, and EDTA as masking agents.

Dithizone preparations are always contaminated since atmospheric oxygen oxidizes dithizone to diphenylthiocarbadiazone and other oxidation products that are chemically inactive. The active dithizone content of a reagent diminishes with time.

Reagents related to dithizone are 1,5-diphenylcarbazide (2) and diphenylcarbazone (3):



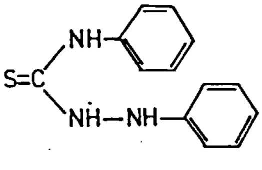
(2)



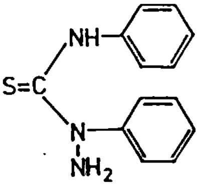
(3)

The products of the reaction of 1,5-diphenylcarbazide with some metals make a basis of sensitive spectrophotometric methods for determining Cr, Os, Cu, and Re. Diphenylcarbazone is used for the determination of, among others, Hg, Zn, Pb, and indirectly for chloride, iodide, and cyanide.

In the same family of reagents belong 1,4-diphenylthiosemicarbazide (4) and 2,4-diphenylthiosemicarbazide (5):



(4)

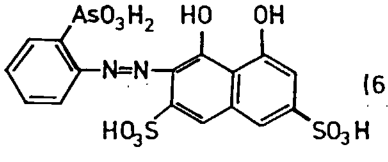


(5)

valuable spectrophotometric reagents for the determination of Ru, Re, Se, and Te.

2. *Azo Reagents*

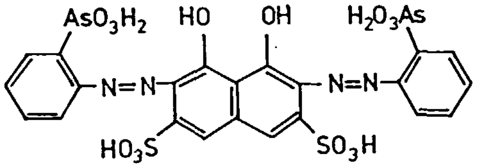
Arsonic azo reagents are the most important from this group of spectrophotometric reagents. They are characterized by the presence of an arsonic acid group in the position ortho to the azo group. Arsenazo I was the first known reagent from this group.



(6)

It is used for spectrophotometric determination of U, Th, Zr, Al, Ti, rare earth elements (REE), and other metals.

Arsenazo III[30] appeared to be a more interesting reagent



(7)

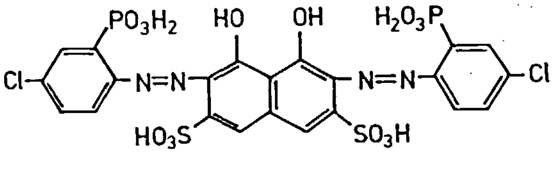
for trace analysis. This arsonic bisazo reagent reacts with Th, Zr, Hf, and U(IV) in strongly acidic solutions (1 to 10 *M* HCl). Arsenazo III methods for these enumerated metals are very sensitive; the molar absorptivities are about 10^5. At pH 1 to 4 arsenazo III reacts with U(VI), Fe(III), Bi, Sc, and REE to form colored chelates. The sensitivity in this case is lower (ϵ about 5×10^4).

The use of arsenazo III in strongly acidic media overcomes difficulties connected with the hydrolysis or polymerization of some multivalent metals. In the determination of Th, Zr, Hf, and U(IV), the high acidity enhances the selectivity of the reagent. Interference from sulfate and phosphate is considerably reduced in the strongly acidic solutions.

The absorbance of the free reagent ($\lambda_{max} = 525$ nm) at the absorption maxima of the metal complexes (λ = 655 to 675 nm) is very slight. The difference between the wavelengths of the absorption maxima of the complexes and of the arsenazo III is very large.

Numerous other spectrophotometric arsonic azo reagents have been suggested.[30]

A related group of reagents comprises azo dyes containing phosphonic acid groups. Chlorophosphonazo III

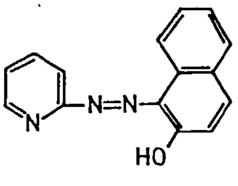


(8)

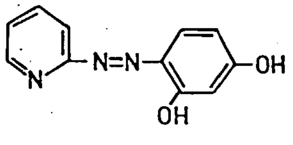
is the well-known example of these reagents. It makes possible the sensitive spectrophotometric determination of Ca, Sr, Ba, Mg, Ti, and other metals.

Complexes of arsonic and phosphonic azo reagents with some metals can be extracted with organic solvents in the presence of such bases as diphenylguanidine, tri-*n*-octylamine, or tribenzilamine.

Principal pyridylazo reagents[31] are 1-(2-pyridylazo)-2-naphthol (PAN) (9) and 4-(2-pyridylazo)resorcinol (PAR) (10)



(9)

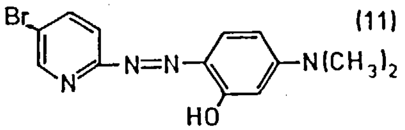


(10)

Between pH 3 and 11 PAN exists as a neutral HR molecule soluble in methanol (ethanol) yielding a yellow color. PAN forms complexes with many metals that are sparingly soluble in water, but soluble in chloroform or benzene. This permits the extractive spectrophotometric determination of Mn, Zn, Cd, Cu, Ni, Co, U, and other metals. The absorption maxima of the complexes are usually very different from that of the reagent. The molar absorptivities of the PAN complexes lie within the range 2 to 6×10^4. Some of the PAN methods are selective when used with masking agents. For example, cyanide enables manganese to be determined in the presence of Ni, Co, Zn, Cd, and Cu, which form stable cyanide complexes. Also, uranium can be determined in the presence of EDTA.

PAR is water-soluble and forms water-soluble chelates. PAR yields color complexes with many multivalent metal ions which form a basis for spectrophotometric determination of metals such as In, Pb, Cu, Pd, Zn, and Hg.

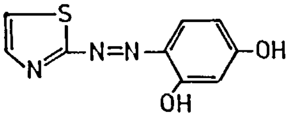
Recently there have been proposed some halogen derivatives of pyridylazo reagents.[32-34] Their complexes with metal ions are more intensely colored and make possible very sensitive determinations. 2-[2-(5-Bromopyridyl)azo]-5-dimethylaminophenol (Br-PADAP)



(11)

is a good example. Molar absorptivities of its complexes are: with copper, 1.0×10^5; zinc, 1.33×10^5; nickel, 1.28×10^5; and cadmium, 1.41×10^5.

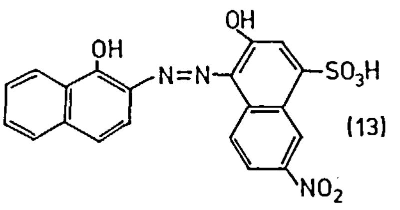
Of the thiazolylazo reagents[35] most often used are 1-(2-thiazolylazo)-2-naphthol (TAN) and 4-(2-thiazolylazo)resorcinol (TAR)



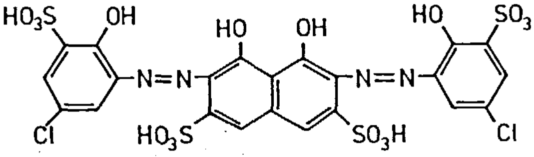
(12)

Their analytical properties are similar to properties of PAN and PAR. In reactions with metal ions they are more selective, mainly due to the lower stability of their complexes.

Azo reagents of other types are used as well, such as eriochrome black T (13) and sulfochlorophenol S (14)



(13)



(14)

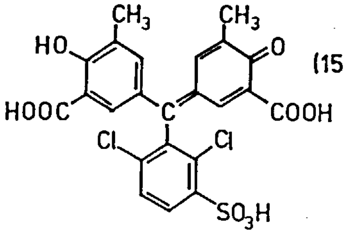
The first is recommended for determining Mg, Ca, Cd, and Th; the second is suggested for Nb, Zr, Sc, and Al.

Azo reagents with sulfonic groups as well as their complexes are water-soluble.

3. Triphenylmethane and Xanthene Reagents

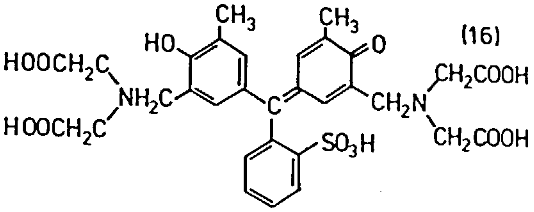
These reagents, derivatives of triphenylmethane and xanthene, and their complexes with metal ions, are intensely colored owing to the presence of the *p*-quinoid group.

Common triphenylmethane reagents are pyrocatechol violet and chrome azurol S (alberon)



(15)

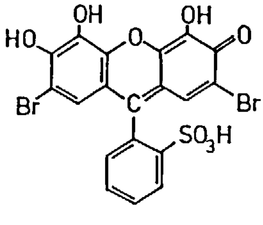
A reagent similar to chrome azurol S is eriochrome cyanine R (solochrome cyanine R). Xylenol orange



(16)

and the related methylthymol blue are characterized by the presence of the iminodiacetic groups. The enumerated reagents are the basis for determining numerous metals, mainly Be, Al, Ga, In, Sc, Cr, Bi, Zr, Th, and Sn. The sensitivity of these methods is good, and vastly increases in the presence of some surfactants. Some complexes of pyrocatechol violet (e.g., with Ga, Sn) can be extracted with organic solvents in the presence of diphenylguanidine.

Well-known xanthene reagents are gallein and bromopyrogallol red

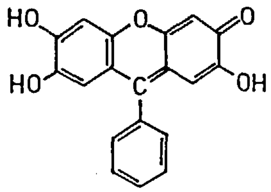


(17)

which make possible the determination of In, Sn, Mo, W, Nb, and REE, among others.

Triphenylmethane and xanthene reagents undergo stepwise dissociation and change their colors according to the pH of the solution. Owing to the presence of sulfonic and iminodiacetic groups the reagents, as well as their complexes with metals, are soluble in water.

Trihydroxyfluorones[36] comprise another class of xanthene reagents. The most common representative of these reagents is phenylfluorone



(18)

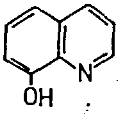
a basis of sensitive spectrophotometric methods for determining germanium and tin. Of the numerous groups of trihydroxyfluorones it is worthwhile to mention: 3-pyridylfluorone (ϵ for tin 1.1×10^5),[37] o-nitrophenylfluorone (ϵ for niobium 1.5×10^5)[38] and quinolylfluorone (ϵ for zirconium 1.65×10^5).[39]

4. *Other Chelating Organic Reagents*

There are also other groups of organic reagents which form chelates with metal ions. The methods based on these reagents are of rather lesser importance in trace analysis, because the molar absorptivities attained in these methods are generally not as high. Since, however, many of these reagents are still used for determining trace elements in various materials (Section V) they are mentioned here.

a. 8-Hydroxyquinoline and Derivatives

8-Hydroxyquinoline (oxine)

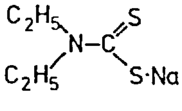


(19)

forms inner chelates with metal ions which are generally soluble in nonpolar solvents. Complexes with Al, Ga, Sc, Ce(IV), Th, Cu, and V(V) are extracted in the range pH 3 to 11, and the obtained molar absorptivities are in the range of 4 to 12×10^3. In the presence of EDTA, hydrogen peroxide, and cyanide, the oxine method is highly selective for aluminum. Derivatives of oxine are: halogenooxines and thiooxine (8-mercaptoquinoline). The sensitivity of these reagents is similar to oxine.

b. Dithiocarbamates

Sodium diethyldithiocarbamate (Na-DDTC)



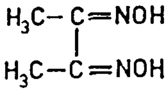
$(C_2H_5)_2N-C(=S)-S\cdot Na$

(20)

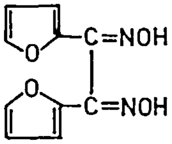
most commonly is used in spectrophotometry. The metal (Cu, Bi, Fe, Ni, Te, Mn, Ru) diethyldithiocarbamates are sparingly soluble in water, but fairly soluble in organic solvents. The methods that use Na-DDTC are rather insensitive: in the well-known method for copper $\epsilon = 1.4 \times 10^4$ (CCl_4 solution); in the case of bismuth $\epsilon = 8.6 \times 10^3$. Other less common dithiocarbamates used in spectrophotometry are dibenzyldithiocarbamate, pyrazolinedithiocarbamate, and pyrrolidinedithiocarbamate.

c. Oximes

Dioximes are today considered as reagents with the highest selectivity.[40,41] The best known are: classical dimethylglyoxime (H_2Dm) (21) and α-furildioxime (22)



(21)

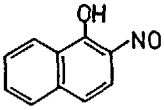


(22)

They form inner chelates with nickel and palladium which are insoluble in water but soluble in $CHCl_3$ (CCl_4). Among other metals that react with dioximes are Re, Cu, Fe(II), and Co. Of the oximes one can mention the simplest oxime, formaldoxime, a highly selective reagent for manganese, and 2,2′-dipyridylketoxime used for determining Co, Pd, Au, and Fe.

d. Nitrosonaphthols

1-Nitroso-2-naphthol and the more recently introduced 2-nitroso-1-naphthol

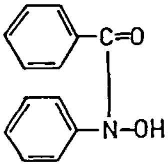


(23)

are highly selective and rather sensitive reagents for cobalt. Of particular advantage is determining cobalt in the presence of nickel. Both reagents react analogously. Respective ε values are 2.9×10^4 at 415 nm and 3.7×10^4 at 365 nm in $CHCl_3$. A related nitroso-R salt (disodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate) and its chelate with cobalt are soluble in water media. Other nitroso compounds worthy of mention are *p*-nitrosodimethylaniline (Pd, Pt, Rh, Ir) and 3-nitroso-2,6-pyridinediol (Os, Ru, Os).

e. Substituted Hydroxylamines

Important spectrophotometric reagents of this group are *N*-benzoyl-*N*-phenylhydroxylamine (BPHA)

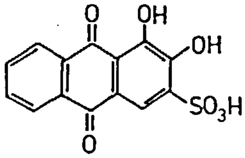


(24)

salicylhydroxamic acid, nicotinohydroxamic acid and *N*-furoylphenylhydroxylamine.[42] These reagents yield extractable chelates and are used for determining such multivalent metals as V(V), Ti, Fe(III), and Nb.

f. Anthraquinone Derivatives

Leading representatives of this class of reagents are alizarin red S,



(25)

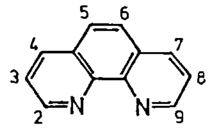
quinalizarin, carmine, and 1,1′-dianthrimide. They are used for determining B, F, Zr, Ge, Se, and Te.

g. Hydroxyflavones

In this class of spectrophotometric reagents, morin and quercetin are the ones most often used (determination of Sn, Zr, V, B, Mo, and Th).[43]

h. 1,10-Phenanthroline and Related Reagents

These reagents[44] contain structural units which react with Fe(II), Cu(I), Zn, Cd, Co, Ru, and Ag. 1,10-Phenanthroline (phen)



(26)

and bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) are highly specific reagents for iron(II) ($\epsilon = 2.2 \times 10^4$ at 533 nm for the bathophenanthroline method). Cuproine (2,2′-biquinolyl), neocuproine (2,9-dimethyl-1,10-phenanthroline), and bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) react specifically with copper(I) ($\epsilon = 1.42 \times 10^4$ at 479 nm for the bathocuproine method). The reagents and their chelates are water-soluble. It should be mentioned that 1,10-phenanthroline as an organic base often takes part in extractable ternary complexes (see Section III.C.4).

C. Ternary Systems with Organic Reagents

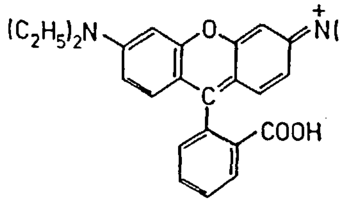
Many of the sensitive and very sensitive spectrophotometric methods are based on ternary (or more complex) systems.[45-47]

The ternary color systems used in spectrophotometry comprise: ion associates formed from nonchelating dyes (basic and acidic) and the elements to be determined that are converted into suitable anionic or cationic complexes, color compounds containing surfactants (cationic or nonionic) and finally, other types of complex compounds.

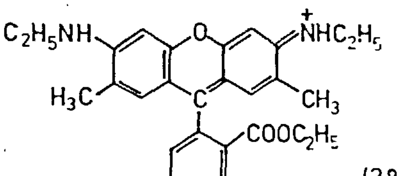
1. Basic Nonchelating Dyes

Xanthene, triarylmethane (mainly triphenylmethane) and azine (thiazine, oxazine, and phenazine) dyes are the ones widely used in spectrophotometric methods. Antipyrine, azo, cyanine, acridine and indamine dyes are less frequently used.[48,49]

Rhodamine B (27), an xanthene dye, has been used in spectrophotometry for a long time and is nowadays commonly used. Of the basic xanthene dyes rhodamine 6G (28),



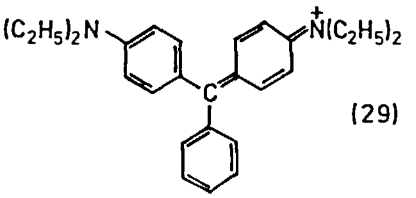
(27)



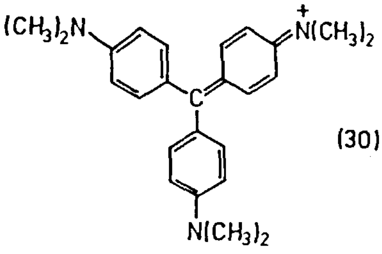
(28)

butylrhodamine B, and ethylrhodamine B (rhodamine 3B), are also of analytical importance.

The main representatives of basic triphenylmethane dyes are: brilliant green (29), malachite green, crystal violet (30),



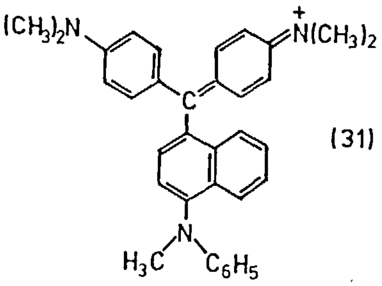
(29)



(30)

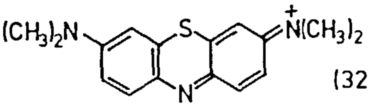
and methyl violet.

The diphenylnaphthylmethane dyes comprise Victoria blue B and Victoria blue 4R



(31)

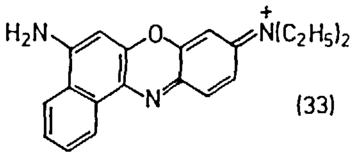
Often used in spectrophotometric methods, methylene blue



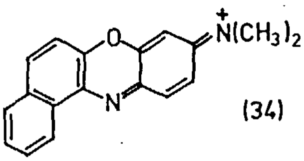
(32)

and methylene green belong to thiazine dyes.

The group of basic oxazine dyes is represented by Nile blue A (33) and Meldola blue (34)



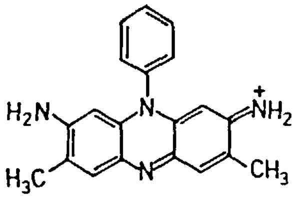
(33)



(34)

Capri blue belongs to this group as well.

The phenazine dye safranine T has the formula



(35)

Table 1
BASIC DYES MOST OFTEN USED IN SPECTROPHOTOMETRIC METHODS

Dyes		
Type	**Example**	**Elements determined**
Xanthene	Rhodamine B	Au, B, Be, Bi, Ca, Cd, Fe, Ga, Hg, In, Mg, P, Re, S, Sb, Sn, Sr, Th, Tl, U, Zn, Zr, REE
	Rhodamine 6G	Bi, Co, Ga, Ge, In, Mn, Ni, S, Sb, Sn, Ta, Te, U, Zn
	Butylrhodamine B	Bi, Co, Ga, I, In, Re, Sb, Sn, Ta, Te
	Ethylrhodamine B	In, Ta, Te
Triarylmethane	Crystal violet	Ag, Au, B, Br, Cl, Ga, Hg, I, N, P, S, Sb, Si, Sn, Ta, Tl, U, V, W
	Brilliant green	Ag, As, Au, B, Cl, Ga, Ge, Hg, In, P, Re, Sb, Sn, Ta, Tl, U, W
	Methyl violet	Ag, Au, B, Cr, I, In, Re, Sb, Ta, Tl
	Victoria blue 4R	Au, Cd, Ga, Re, Ta, Te
Azine	Methylene blue	Au, B, Cl, Ga, Ge, Hg, I, P, Pd, S, Sb, Ta, Tl, U
	Safranine T	P, Re, Sb, Si, Tl
	Meldola blue	B, Ga, Ta, Tl
Antipyrine (chrompyrazols)		Au, B, Ga, Re, Sb, Ta
Azo		Bi, Cd, Hg, Sb, Tl, Zn

The formulas of basic antipyrine dyes (chrompyrazols) and of some basic azo dyes have been given in our previous work.[49]

Anions, containing the elements to be determined, with these dyes form ion associates (ion pairs) which are generally extractable.

Some basic dyes and elements that can be determined with their aid are listed in Table 1. References to the respective spectrophotometric methods can be found in a review paper.[49] As follows from Table 1 a great number of metals and nonmetals can be determined spectrophotometrically using basic dyes. Rhodamine B, crystal violet, brilliant green, rhodamine 6G, and methylene blue are the most frequently used ones.

The anionic forms of the elements determined via ion pairs with basic dyes are presented in Table 2. Anionic halogenide complexes (Cl^-, Br^-, I^-, F^-) are the most important ones. Oxyanion (e.g., ClO_4^-, NO_3^-), heteropolyacid anions as well as anionic thiocyanate, azide and cyanide complexes are used as well. Recently, anionic metal complexes formed with organic chelating reagents are being more and more widely used in ion pair formation with basic dyes, e.g., anionic chelates of oxine and its derivatives, some carboxylic acids, 3,5-dinitropyrocatechol and others.

Ion associates involving basic dyes are generally soluble in nonpolar solvents. Benzene is most frequently used for this purpose, while toluene, dichloroethane, and chloroform are rarely used. Sometimes a small amount (e.g., 10%) of a donor-active oxygen containing solvent (e.g., diisopropyl ether, methyl isobutyl ketone (MIBK), amyl acetate, butanol, tri-*n*-butyl phosphate is added[50] to the nonpolar solvent in order to enhance the extraction for the case of formation of coordinatively unsaturated anionic complexes, e.g., $Zn(SCN)_3^-$, CdI_3^-.

At times the colored ion-associate is not directly extracted. It is then possible to extract the halogenometallic acid (e.g., $HSbCl_6$, $HTlCl_4$, or $HAuBr_4$) with an oxygen-

Table 2
ANIONIC FORMS OF ELEMENTS DETERMINED VIA ION ASSOCIATES WITH BASIC DYES

Anionic forms	Elements determined
Oxy-anions	Br, Cl, Cr, N, Re
Heteropolyanions	As, Ge, P, Si
Halogenide and pseudohalogenide complexes	
Chloride	Au, Fe, Ga, Hg, Sb, Sn, Tl
Bromide	Ag, Bi, Hg, In, Te, Tl
Iodide	Ag, Bi, Cd, Hg, In
Fluoride	B, Ta
Thiocyanate	Co, Mo, W, Zn
Cyanide	Ag, Cu, Hg
Azide	Au, Pd
Complexes with organic ligands	
8-Hydroxyquinoline (oxine)	Ni, U, Zn, REE
Halogeno-oxines	Ca, Co, Mg, Mn, Sr, Th, REE
Thenoyltrifluoroacetone (TTA)	Ca, Mg, U
3,5-Dinitropyrocatechol	Ge, Sn, W, REE
2,4-Dinitro-1,8-dihydroxy-naphthalene	B
4-Nitropyrocatechol	As
Carboxyl acids	B, Be, Co, U, Zr, REE
Alizarin complexone	Ge
2-Nitroso-4-chlorophenol	Fe
4-(2-Pyridylazo)resorcinol	V

containing solvent and then shake the colorless extract with an acidic solution of a basic dye. One can also first extract the ion pair of the anionic complex and quaternary base with a nonpolar solvent. The colorless extract is then shaken with an acidic solution of the dye, e.g., crystal violet.[51] The colorless ion pair of the thiocyanate complex of gold(III) with tetraphenylarsonium ion is first extracted with benzene. An ethanolic solution of brilliant green is then added. The excess of the dye is then removed by shaking with dilute hydrochloric acid.[52]

In the extraction-spectrophotometric methods involving basic dyes the blank is insignificant. It results from the extraction of the simple dye salt, e.g., chloride. It increases with higher concentrations of the ligand (yielding the anion with the metal to be determined) and of the dye and with decreasing acidity.

The basic dyes occur generally as chlorides and bromides. The form in which the dye is able to form the ion-association compound is the monovalent cation. In aqueous solutions the cations are in equilibrium with their protonated forms (the formation of which is favored by increasing the acidity of the solution) and colorless simple molecules or their associates (the formation of which is favored by increasing the pH of the aqueous solution).[53,54] In the extraction-spectrophotometric methods involving nonchelating basic dyes the useful acidity varies in a wide range, from several molar mineral acid solutions to buffered solutions of pH 3 to 6. During the extraction of the ion associate the equilibria shift towards the formation of a reactive simple, monovalent cation of the dye.

The bonding between the anion and the basic dye has an electrostatic character, as indicated by similar absorption spectra of the associate and the dye. The bonding mainly involves dipole-dipole interaction.

The extraction-spectrophotometric methods of determination of elements involving

Table 3
FLOTATION-SPECTROPHOTOMETRIC METHODS WITH USE OF BASIC DYES

Element determined (in form)	Dye	Flotation (solvent)	Molar absorptivity ($\epsilon \times 10^{-5}$)	Ref.
Arsenic (Mo-As-O)	Crystal violet	Cyclohexane (acetone)	3.1	59
Bismuth (Br^-)	Rhodamine 6G	Isopropyl ether (ethanol)	1.5	60
Cadmium (I^-)	Crystal violet	Isopropyl ether (acetone)	1.3	57
Germanium (Mo-Ge-O)	Brilliant green	Butyl acetate (acetone)	1.9	61
(Alizarin complexone)	Rhodamine 6G	Chloroform (ethanol)	2.9	62
Molybdenum (SCN^-)	Crystal violet	Toluene (ethanol)	2.3	63
Osmium (SCN^-)	Methylene blue	Toluene (acetone)	2.2	64
Palladium (Br^-)	Rhodamine 6G	Benzene (dimethylformamide)	3.0	65
Phosphorus (Mo-P-O)	Crystal violet	Butyl acetate (methyl ethyl ketone)	2.7	66
Platinum ($SnCl_2$)	Crystal violet	Benzene (ethanol)	2.1	67
Rhodium ($SnCl_2$)	Malachite green	Isopropyl ether (acetone)	3.4	68
Silicon (Mo-Si-O)	Rhodamine B	Isopropyl ether (ethanol)	5.0	69
	Crystal violet	— (Acetone)	4.3	58
Tellurium (Br^-)	Rhodamine 6G	Benzene (ethanol)	1.7	70
Tungsten (SCN^-)	Crystal violet	Toluene (ethanol)	2.1	71
Zirconium (picramine-epsilon)	Ethylrhodamine B	Benzene (acetone)	3.2	72

basic dyes are very sensitive. The molar absorptivities approach to, and sometimes even exceed, a value of 10^5.

The same ion associate exhibits various ϵ values depending on the nature of the solvent used for the extraction, as a result of various effectiveness of the extraction. The observed differences in ϵ are due to difficulties in keeping the element in the suitable oxidation state. This pertains particularly to antimony(V), thallium(III) and tin(II)[55]. The ϵ value also depends on the quality of the applied dye preparation.[56]

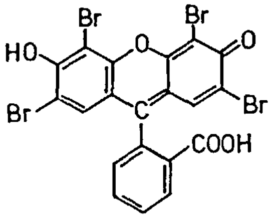
Some ion associates with basic dyes are not extracted when shaking the aqueous phase with solvents of low polarity, but collect at the phase boundary or on the walls of the separatory funnel. In such cases, after removal of the aqueous solution and the organic solvent the precipitate is dissolved in a small amount of a polar solvent (generally acetone or ethanol). The content of the element to be determined is then evaluated on the basis of the absorbance of the obtained polar solution. The above procedure is the basis for flotation-spectrophotometric methods, which are of great value for the determination of minute traces due to their extremely high sensitivity.

The first flotation-spectrophotometric method was proposed by Courtot-Coupez and Guerder.[57] The authors separated, by flotation, the ion pair formed by the iodide cadmium complex and crystal violet by means of diisopropyl ether. After decantation of the aqueous phase, acetone was added to the ether phase and a clear solution was obtained. The sparingly soluble ion associate was also separated by centrifuging and then was dissolved in acetone.[58] So far the number of published works of this type is limited. The known flotation-spectrophotometric methods are listed in Table 3. These methods are highly sensitive and exhibit good selectivity. The molar absorptivities range from 1.3 to 5.0×10^5.

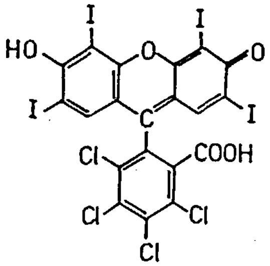
These anions (in the form whereby the elements are determined) have high negative charge and therefore form sparingly soluble associates containing more than one cation of the dye. Due to their high complexity these associates are insoluble in nonpolar solvents.

2. *Acid Nonchelating Dyes*

These dyes are less frequently used in spectrophotometric methods than the basic ones. Acid dyes form extractable ion associates with hydrophobic cationic metal complexes. The dyes used are generally acid-base indicators, known for a long time. The acid xanthene dyes comprise eosine (36), erithrosine and bengal rose B (halogen derivatives of fluorescein) (37)

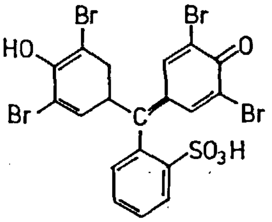


(36)



(37)

The following formula shows the acid triphenylmethane dye, bromophenol blue (tetrabromophenolsulfophthalein)



(38)

The same group also includes bromophenol red, bromophenol green, and cresol purple. The triphenylmethane dyes (sulfophthaleins) are derivatives of phenol red, i.e., phenolsulfophthalein.

Of the acid azo dyes methyl orange has been successfully applied.

The partners in the formation of the ion associates with acid nonchelating dyes are most frequently metal complexes of 1,10-phenanthroline; 2,2′-bipyridyl, cuproine and pyridine have also been used.

The extraction-spectrophotometric methods of the determination of metals (bound into complexes with 1,10-phenanthroline) as ion associates with acid dyes are listed in Table 4. The molar absorptivities in these methods frequently exceed 5×10^4 and sometimes even 1×10^5. Chloroform, toluene, 1,2-dichloroethane, and nitromethane are the commonly used extractants. Sometimes the extraction is carried out with a nonpolar solvent with an addition of a donor-active oxygen-containing solvent.

Metal chelates with 1,10-phenanthroline are generally bivalent cations and react with bivalent anions in the ratio 1:1. Bivalent anions are formed as a result of dissociation of sulfonic, carboxyl and hydroxyl groups of the xanthene and triphenylmethane dyes. Hence the pH values of the aqueous solutions during the extraction are relatively high, and range from 6 to 9, accordingly to the acidity of the dyes and properties of the counterions.

The possibilities of extraction of cationic complex of copper (I) with cuproine and various sulfophthalein dyes have been discussed.[83-85] The molar absorptivity in the method of determining palladium[74] using bengal rose B and pyridine is 1.25×10^5.

Table 4
SOME ACID DYE EXTRACTION-SPECTROPHOTOMETRIC METHODS[a]

Acid dye	Metal determined	Molar absorptivity ($\epsilon \times 10^{-4}$)	Ref.
Bengal rose B	Copper(II)	6.3	73
	Palladium	5.0	74
	Zinc	5.1	75
	Cadmium	6.4	75
	Lead	5.8	76
Eosin	Silver	5.5	77
	Zinc	12.0	78
	Lead	11.0	76
	REE	12.0	79
Erithrosine	Lead	9.6	76
	Cadmium	9.6	76
	REE	16.0	79
Bromophenol blue	Iron(II)	5.9	80
Dibromofluorescein	Zinc	5.0	81
	Cadmium	4.6	81
Methyl orange	Iron(II)	4.8	82

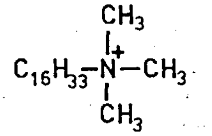
[a] Determined metals in complexes with 1,10-phenanthroline.

Similarly, as in the case of basic dyes, simple salts of acid dyes (e.g., sodium salts) are practically not extracted. Hence, the blank values are negligible.

3. Color Systems with Surfactants

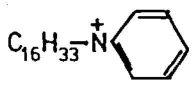
In the presence of some long-chain quaternary bases (showing surface active properties) and chelating triphenylmethane dyes ternary complexes are formed with metal ions. These complexes show more intensive color than the respective simple complexes with the above-mentioned chromophoric reagents.[86-89] In addition to a high increase in the color intensity a bathochromic shift of the absorption maximum takes place. As a result the difference between λ_{max} of the ternary complex and λ_{max} of the chromophore reagent (contrast) is so great ($\Delta\lambda$ = 100 to 200 nm) that the reagent shows no absorption at the λ_{max} of the complex.

The cetyltrimethylammonium (CTA) and cetylpyridinium (CP) ions



$$\begin{array}{c} CH_3 \\ | \\ C_{16}H_{33}-\overset{+}{N}-CH_3 \\ | \\ CH_3 \end{array}$$

(39)



(40)

in the form of salts (chlorides or bromides) are the most frequently used cationic surfactants in spectrophotometric analysis. The action of CTA and CP on the discussed color systems is similar.

Some spectrophotometric methods for the determination of metals using triphenylmethane reagents and CTA or CP are presented in Table 5. In many cases the methods involving CTA and CP exhibit unusual sensitivity. The methods of the determination of beryllium show molar absorptivities 3 to 4 times higher than those obtained in the

Table 5
SOME SPECTROPHOTOMETRIC METHODS BASED ON TERNARY COMPLEXES WITH CHELATING TRIPHENYLMETHANE REAGENTS AND CATIONIC SURFACTANTS (CTA OR CP)

Chelating reagent	Metal determined	Molar absorptivity ($\epsilon \times 10^{-4}$)	Ref.
Pyrocatechol violet	Aluminum	6.5	90, 91
	Germanium	7.0	92, 93
	Tin	7.8	93, 94
	Titanium	7.5	93
Chrome azurol S	Beryllium	10.1	95
	Aluminum	13.1	96, 97
	Gallium	11.4	98
	Indium	12.3	98
	Thorium	14.6	99
	Uranium(VI)	9.9	100, 101
Eriochrome cyanine R	Beryllium	8.7	102, 103
	Gallium	12.0	104
	Indium	10.1	105
	Scandium	15.0	106
	Iron(III)	12.7	107
	Palladium	9.6	108, 109
Chromal blue G	Beryllium	9.4	110
	Palladium	10.1	111
	Scandium	16.5	112
Xylenol orange	Thorium	5.5	113

respective binary systems. A significant increase in sensitivity (though not so high) is also attained for other metals.

As can be seen in Table 5, the reactions of great analytical interest involve metals that easily hydrolyze and show high affinity towards oxygen atoms.

The mechanism of the action of long-chain quaternary bases (being at the same time cationic surfactants) during the formation of intensively colored complexes of metals with chelating triphenylmethane reagents has been discussed by many authors.[88,101,114-117]

It has been shown, using spectrophotometric methods and amperometric titration, that at low concentrations of the quaternary bases ternary complexes which contain few (e.g., 4, 6) CTA or CP molecules (ions) are formed. The color intensity is then miles away from the maximum. As the CTA or CP concentration increases the color intensity of the complexes increases. At the same time small shifts in λ_{max} take place.[102,104,105]

When considering the reaction mechanism in the discussed ternary systems it should be taken into account that cationic surfactants occur in the solution as single ions at low concentrations, and above some concentration they form charged micelles (aggregates of high molecular mass). Since the most intensely colored ternary complexes occur at high excess (50- to 70-fold with respect to metal ions) of quaternary bases, i.e., at their relatively high concentrations, it is obvious that their structures contain micelles of cationic surfactants.

According to Chernova and Savvin et al.[114,115] quaternary bases (CTA, CP) form a kind of ion associate through dissociated or nearly dissociated sulfonic, carboxyl, and hydroxyl groups of the triphenylmethane reagents. Sulfonic groups associate first, then carboxyl and hydroxyl groups. The presence of quaternary bases in the system, particularly as micelles, enhances the dissociation of hydroxyl groups. Since in sulfonic groups the π-electron system is isolated the associates formed through these groups do not affect the color.

The high color contrast in the reactions of the formation of discussed ternary complexes can be explained by the fact that the chromophore reagent (e.g., pyrocatechol violet, chrome azurol S) simultaneously reacts with the metal ion and the quaternary base through two different functional-analytical groups, thereby forming one conjugated system. The mechanism of the formation of these complexes has been discussed in detail by Savvin.[8]

At the same time in these systems, associates of free ions of the triphenylmethane reagent with CTA or CP ions are formed. The absorption spectra of these associates do not differ from those of the chromophore reagents except in an insignificant bathochromic shift.[115,117]

In the reactions of triphenylmethane reagents with metal ions chelates are formed of a reagent ratio (M:R) of 1:1 or 1:2. In the ternary systems involving cationic surfactants the number of molecules (ions) of the chromophore reagent corresponding to one atom of the metal is higher. This is the main reason for the increase in the color intensity of metal complexes when passing from the binary systems to the ternary ones. This fact is ascribed to a weakening hydrolysis of the metal ions in the presence of surfactants. This enables the chromophore reagent to occupy all the coordination sites of the metal.[115]

The optimum pH ranges (4 to 7) for the formation of metal complexes with triphenylmethane reagents in the binary and ternary systems (with CTA and CP) are similar. In the case of some metals (e.g., molybdenum, tungsten, titanium) the reactions take place in relatively acidic media (pH 1 to 2).[93]

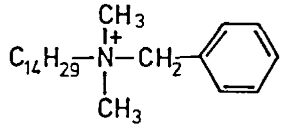
As the excess (concentration) of CTA or CP increases in the intermediate concentration range, the color solutions become turbid and a sparingly soluble compound precipitates (particularly when heating the solution). At higher concentrations of the quaternary bases, the solutions become clear; this is indicated on stepwise formation of complexes. The solubility of the ternary complex containing a larger number of CTA or CP ions (in the form of micelles) is higher. Some authors[116] suppose that the discussed surfactants play the role of a protective colloid.

In the case of some metals, at higher concentrations of CTA (CP) a decrease in absorbance of the ternary complex is observed. This phenomenon can be ascribed to partial blocking of the chelating groups in the molecule of the triphenylmethane reagent by the quaternary base.[104,105,115]

Shaking the solutions containing the ternary complexes in question with organic solvents leads to various results depending on the system and the solvents used. In the case of the beryllium-eriochrome cyanine R-CTA system some oxygen-containing reagents extract the ternary complex as well as the excess of the reagent (the ER-CTA associate). However, the difference between λ_{max} of the complex and that of the reagent is smaller for the extract than for the initial aqueous solution. In addition, the absorbance of the complex is lower (presumably the extracted complex contains a smaller amount of CTA; the complex containing micelles cannot be extracted).[102] When shaking the system gallium-eriochrome cyanine R-CTA with chloroform, dichloromethane, or amyl alcohols, the ER-CTA associate passes to the organic phase, while the aqueous solution undergoes decolorization (the metal remaining in the aqueous phase). This means that after extraction of the excess of the reagent (ER-CTA) the ternary complex decomposes and eriochrome cyanine R passes from the ternary complex to the organic phase (as an associate with CTA).[104] Similar results were obtained in the case of the system indium-eriochrome cyanine R-CTA[105] and iron(III)-ER-CTA.[107]

In addition to chelating triphenylmethane reagents, other chromophore reagents have been used in the ternary metal systems involving CTA and CP. Gallein (and CTA or CP) has been used for the determination of aluminum,[118] REE,[119] and tungsten.[120] Pyrogallol red has been applied to the determination of tungsten,[121] and tin,[122] and disulfophenylfluorone — to the determination of titanium ($\epsilon = 1.2 \times 10^5$, $\Delta\lambda = 150$ nm).[123]

Among the long-chain quaternary bases (similar to CTA and CP) one should mention zephiramine (tetradecyldimethylbenzylammonium ion)



(41)

Chrome azurol S and zephiramine have been applied to the determination of Be, Sc, Fe(III), V(IV), Cu, and U. In the cases of beryllium and iron very high sensitivity has been attained (the molar absorptivities amount, respectively, to 1.09×10^5 and 1.47×10^5). The zephiramine has also been used in the determinations of Be with eriochrome cyanine R, Mo with gallein, Mo and W with bromopyrogallol red, Al with stilbazo, Zr with 5-dimethylamino-2-(2-thiazolylazo)phenol and Bi with 2-(2-thiazolylazo)-p-cresol (references to above determinations are given by Marczenko[47]). Recently zephiramine was applied in the determination of uranium(VI) and thorium with arsenaso III,[124,125] cobalt with TAR,[126] and iron with pyrogallol red.[127]

After discussing the spectrophotometric methods of the determination of metals, involving cationic surfactants and chromophore reagents, it should be mentioned that in a number of cases similar sensitivity has been obtained in methods using some nonionic surfactants, e.g., syntanol DS-10 and syntanol DT-7 (multihydroxyethylated ethers of higher alcohols), OP-7 and OP-10 (multihydroxyethylated ethers of alkylophenols) and OS-20 (multihydroxyethylated esters of higher fatty acids). These compounds do not dissociate into ions in aqueous solutions and their solubility in water is due to the presence in the molecule of a greater number of hydroxyl or ether groups of high affinity towards water.

With nonionic surfactants and chrome azurol S it is possible to determine beryllium[128] and aluminum[129-131] with high sensitivity. Manganese,[132] cobalt,[133] nickel,[134] and zinc,[135] were determined using various azo reagents.

Attempts to elucidate the mechanism of the above discussed color reactions have been made.[116,130,131] The nonionic surfactants, in the form of micelles, affect the protolytic equilibriums of the chromophore reagent, as well as the state of the metal ion. This results in the formation of compounds containing a greater number of dye molecules per metal ion. These compounds show new spectral properties. Hydrogen bonding also plays a role in the above color systems.[136]

4. *Other Systems*

Similarly methods involving basic dyes are the extraction-spectrophotometric methods in which complex anions (e.g., BF_4^-, ClO_4^-, $AuCl_4^-$, $SbCl_6^-$, $TlBr_4^-$, ReO_4^-) associate with color cationic complexes of iron(II) with 1,10-phenanthroline (ferroin) or 2,2'-bipyridyl, and copper(I) with cuproine or neocuproine.[3] With respect to sensitivity, these methods are inferior to those with basic dyes.

Trihydroxyfluorones (see Section III.B.3) form different-ligand complexes which make a basis of very sensitive spectrophotometric methods. For example, titanium is determined by means of its complexes with phenylfluorone and *N*-benzoyl-*N*-phenylhydroxylamine (BPHA),[137] and furoylphenylhydroxylamine;[138] propylfluorone and diantipyrylmethane (DAM) ($\epsilon = 1.28 \times 10^5$).[139] Tantalum can be determined with the aid of its different-ligand complex with oxalate, fluorone, and antipyrine ($\epsilon = 2.1 \times 10^5$).[140]

It has been suggested that the above-mentioned extractable complexes also contain halogenide ions.

Different-ligand complexes of morin and quercetin (flavonols) are also used in spectrophotometry.[141]

D. Inorganic Color Systems

The majority of metal complexes with inorganic ligands are not intensely colored and thus these complexes find limited application in trace analysis.

Thiocyanate methods for Fe(III), Mo, Nb, Re, Co, U, Ru, Os, and W, are of moderate sensitivity. The thiocyanate method for determining titanium can be considered sensitive. The determination of metals by thiocyanate is carried out in aqueous or aqueous-acetone media, or after extraction with oxygenated solvents. With organic bases such as pyridine, tri-*n*-butylamine or DAM, anionic thiocyanate complexes form ion pairs which can be extracted into chloroform and other inert solvents. Increased selectivity in the determination of metals by thiocyanate is obtained by the choice of acidity, thiocyanate concentration, masking agents, and metal oxidation state. The reducing medium precludes the color reaction of thiocyanate with iron.

Many sensitive methods involve metal complexes with thiocyanate, fluoride, chloride, bromide, and iodide, forming ion associates with basic dyes.

A group of elements (Si, Ge, P(V), As(V), V, Mo, W) forms yellow heteropolyacids which can be reduced to an intensely colored blue form. The reduced forms of heteropolyacids are put to good use in spectrophotometric methods for determining Si, Ge, P, and As. They can be extracted with oxygen-containing solvents.[142]

Peroxide complexes (Ti, V, U) are weakly colored.

E. Indirect and Amplification Methods

Indirect spectrophotometric methods involve a change, brought about by the determinand, in the color of another system. Most methods for fluoride are indirect. By forming stable colorless complexes with numerous metals, fluoride ions decompose certain colored complexes of these metals with organic reagents. Examples of these complexes are zirconium-eriochrome cyanine R, thorium-xylenol orange, and iron(III)-thiocyanate.

Sulfate can be determined indirectly, e.g., with barium complex of chlorophosphonazo III.[143] In the formation of $BaSO_4$ sulfate ions displace an equivalent amount of color reagent. There are numerous methods of this type for sulfate.

Indirect spectrophotometric methods include amplification methods. The amplification reactions underlying these methods can be defined as those in which the normal equivalence is altered in some way so that a more favorable measurement can be made. Thanks to their exceptionally high sensitivity, amplification methods are widely used for determining traces of some elements. Belcher[144] has given an exhaustive review of these methods.

Determination of iodide is a classical example of amplification methods.[145] The I^- ion is first oxidized to iodate which reacts with the added potassium iodide in an acid medium. ($IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$). The molar absorptivity (with respect to I^-) of the starch-iodine complex (after amplification via iodate) is 1.08×10^5 at 590 nm. Bismuth, antimony and palladium can be determined via amplification of iodide after conversion into complexes BiI_3, SbI_3, and PdI_2, and extractive separation.[3]

Mercuric iodate makes possible the determination, indirectly and with amplification, of many anions which form stable complexes with mercury(II) (e.g., Cl^-, Br^-, I^-, CN^-, SCN^-).[146]

Silicon, phosphorus, and arsenic are determined via amplification using appropriate heteropolyacids with molybdate. After quantitative extraction separation of these acids molybdenum is determined with thiocyanate,[147] with phenylfluorone,[148] with sulfonitrophenol S,[149] or with other reagents.

F. Methods Based on Other Reactions

There are numerous, often fairly sensitive, spectrophotometric methods in which the color is formed as a result of oxidizing some organic reagents by the determined elements in higher oxidation states. *o*-Tolidine (Cl_2, Br_2, I_2, O_3, Ce(IV), Fe(III), MnO_4^-), 3,3′-dimethylnaphthidine (O_2, Cr(VI), VO_3^-), variamine blue (I_2, Cu(II), Au(III), VO_3^-) belong to this type of organic reagent. Ferroin (1,10-phenanthroline complex of ferrous ion) can be also the object of oxidation. In this case a diminishing of the color is observed. Oxidation of manganese(II) to Mn(VII) and chromium(III) to Cr(VI) is the basis of a good but quite insensitive method for determining these metals.

Examples of reduction reactions are determinations of selenium, tellurium, and gold, as colored sols formed upon reduction of Se(IV), Te(IV) and Au(III) to their elemental forms.

There are some sensitive methods in which the color system is formed as a result of synthesis. Examples are the formation of methylene blue when determining sulfide, the pararosaniline method for sulfite, the benzidine-pyridine method for cyanide, or formation of indophenol in the method for ammonia.

Xylenols yield colored nitration products when heated with nitrate in sulfuric acid medium. The determination of bromine is based on bromination of some dyes, e.g., phenol red.

Methods for determining nitrite are based on reactions of nitrite with primary aromatic amines. The diazonium salt formed is then coupled with a suitable aromatic compound to yield an azo dye.

IV. SENSITIVE SPECTROPHOTOMETRIC METHODS FOR INDIVIDUAL ELEMENTS

A. Alkali and Alkaline Earth Metals

First of all it should be said that traces of Na, K, Rb, and Cs are not generally determined with the aid of spectrophotometric methods.

Lithium is determined by means of the sensitive reagent nitroanthranylazo; the reaction is carried out in alkaline aqueous-acetone solution ($\epsilon = 1.2 \times 10^4$; a = 1.7).[3] The thoron I method is one half as sensitive.[2,3]

Sodium can be determined directly with nitroanthranylazo or indirectly via precipitation of triple acetates.[3]

For determining potassium, rubidium, and caesium, there are indirect methods using dipicrylamine, dilituric acid, picric acid, or precipitation of cobaltinitrite.[2,3] Caesium is also determined indirectly as phosphomolybdenum blue.[3]

The long-time well-known methods for determining *beryllium* using triphenylmethane reagents, chrome azurol S, and eriochrome cyanine R,[3-5] have modified 3 to 4 times more sensitive owing to cationic surfactants (CTA, CP). Molar absorptivity in the method based on the ternary system Be-chrome azurol S-CTA equals 9.45×10^4 (a = 10.7) at 615 nm,[95] and in the system Be-eriochrome cyanine R-CTA — 8.65×10^4 at 590 nm.[102,103] Similar sensitivities are attained in the method with chromal blue G and CTA[110] and in the method based on the ternary system Be-chrome azurol S-polyoxyethylene-dodecylamine.[150] These methods are highly selective in the presence of EDTA. There also exists a sensitive extraction-spectrophotometric method for determining beryllium with the aid of benzoic acid and rhodamine B.[151]

There are two sensitive, old methods for *magnesium* using titan yellow (thiazol yellow) and eriochrome black T with $\epsilon = 3.6 \times 10^4$ (a = 1.52) at 545 nm, and $\epsilon = 2.3 \times 10^4$ at 525 nm.[2,3,152] The quality of the used titan yellow preparation is important for maximizing the ϵ value. In both cases, the determination of magnesium can be carried out in the presence of calcium. In the eriochrome black T method, an increase of sensitivity ($\epsilon = 5.5 \times 10^4$) is observed after extraction with a chloroform solution of tri-*n*-octylamine.[153] The methods of similar sensitivity, using chlorophosphonazo III,[154] chromotrope 2R,[155] or xylidyl blue II,[156] are worthy of mention.

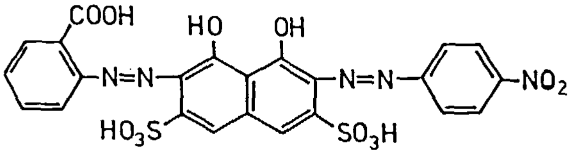
At present, the most recommendable method for *calcium* is the chlorophosphonazo III method,[154] particularly after preliminary separation of calcium by extraction with reagent azo-azoxy BN in CCl_4.[3,157] The coefficient $\epsilon = 5.4 \times 10^4$ (a = 1.3) in neutral medium and $\epsilon = 2.8 \times 10^4$ in slightly acidic solution. For determining traces of calcium, often the older method based on glyoxal bis(2-hydroxyanil) (GBHA) ($\epsilon = 1.8 \times 10^4$) is applied.[3-5,158,159] Recently, a valuable reagent for traces of calcium and other alkaline earth metals — hydroxynaphthol blue — has been proposed.[160]

The best reagents for determining microgram amounts of *strontium* and *barium* seem to be nitroorthanilic S (Sr) and sulfonazo III (orthanilic S) (Ba). Other methods make use of murexide, chlorophosphonazo III, arsenazo III, and metalophthalein (*o*-cresolphthalein complexone). Both metals can be determined indirectly using diphenylcarbazide.[3,5,161]

B. Scandium, REE, Thorium, and Uranium

Scandium is determined mainly by means of the xylenol orange method, which gives $\epsilon = 2.9 \times 10^4$ (a = 0.65).[3,5] Higher sensitivity can be attained using eriochrome brilliant violet B ($\epsilon = 6.4 \times 10^4$),[162] and TAR ($\epsilon = 5.1 \times 10^4$).[163] Recently there have been proposed some very sensitive methods based on ternary systems: Sc-chrome azurol S-CTA,[163a] Sc-eriochrome cyanine R-CTA ($\epsilon = 1.5 \times 10^5$),[106] and Sc-chromal blue G-CTA ($\epsilon = 1.65 \times 10^5$).[112]

REE (yttrium and lanthanides) in trace amounts are often determined with arsenazo III ($\epsilon = 5.6 \times 10^4$; a = 0.40).[3,164,165] A great increase in sensitivity can be obtained by carrying out the reaction in organo-aqueous media (ϵ about 1.5×10^5).[166] Also, chlorophosphonazo III is a good reagent for REE.[167,168] After the extraction of the diphenylguanidine ion pair into butanol, the value of the coefficient ϵ increases to 1.6×10^5. A very sensitive reagent for REE turned out to be carboxynitrazo (ϵ = 1.2 to 1.6×10^5).[169,170]



(42)

High sensitivity has been attained in ternary systems of REE with 1,10-phenanthroline and eosine (or erithrosine) (ϵ are 1.2×10^5 and 1.6×10^5, respectively) (toluene-butanol medium).[79] Considerable increases in the sensitivity of the reaction of REE with eriochrome azurol B and with xylenol orange have been obtained in the presence of cationic surfactants.[171,172]

Thorium is often determined with thoron I[2-5] but this method is not sufficiently sensitive for trace analysis ($\epsilon = 1.7 \times 10^4$). A much better method, as well, as better selectivity, is the arsenazo III method.[3,164,165,173,174] The molar absorptivity in 3*M* HCl equals 1.15×10^5 (a = 0.50) at 655 nm. In the presence of oxalic acid thorium can be determined in solutions containing Zr, Hf, Nb, or U(VI). Chlorophosphonazo III[175] and *p*-dimethylarsenazo III[176] react with thorium in a fashion similar to that of arsenazo III. In the determination of thorium with chrome azurol S in the presence of CTA[99] the greatest sensitivity was obtained ($\epsilon = 1.4 \times 10^5$).

The long-time, well-known and commonly used methods for determining *uranium*, thiocyanate, dibenzoylmethane, and arsenazo I, are insensitive.[2-5] The arsenazo III method is suitable for determining trace amounts of uranium.[3,164,165] For uranium(IV) in a 6 to 8 *M* HCl medium, the value of coefficient ϵ is 1.27×10^5 (a = 0.50). The sensitivity of the reaction with uranium(VI) is lower.[177-179] Arsenazo III methods for uranium are very selective. Chlorophosphonazo III is also recommended for uranium.[180,181] *Sensitivity and selectivity are similar to the case of arsenazo III. Extractive procedures* were also proposed.[179-181] Uranium can be determined with chrome azurol S in the presence of various cationic surfactants.[100,101] The value of coefficient ϵ in this method is about 1×10^5. The methods based on ion associates of anionic benzoate complex of uranium and of the basic dyes malachite green[182] and methylene blue[183] belong to the more sensitive methods for uranium.

C. Titanium, Zirconium, and Hafnium

Well-known hydrogen peroxide and chromotropic acid methods for *titanium* are insensitive and can not be applied in trace analysis. Many sensitive methods are based on thiocyanate. In extraction-spectrophotometric methods using thiocyanate ϵ is about 8×10^4 (a ~ 1.5).[184-187] Fluorones lead to more sensitive methods. In the system Ti-salicylfluorone-SCN^- ($CHCl_3$),[188] the molar absorptivity is 1.44×10^5, in Ti-propylfluorone-DAM ($CHCl_3 + C_2H_5OH$)[139] $\epsilon = 1.3 \times 10^5$, in Ti-disulfophenylfluorone-CP[114,123] $\epsilon = 1.2 \times 10^5$.

The best reagent for determining traces of *zirconium (hafnium)* is arsenazo III.[3,164,165,189,190] In a 9*M* HCl medium the value of coefficient ϵ is about 1.2×10^5 (a = 1.3) ($\Delta\lambda = 135$ nm). Only thorium and uranium(IV) interfere. In the extraction-spectrophotometric method with chlorophosphonazo III an ϵ value of about 2.1×10^5 was obtained.[191] In the often applied xylenol orange method and using gelatine a considerable increase in sensitivity ($\epsilon = 7.5 \times 10^4$) takes place.[192] 2′-Quinolylfluorone[39] is a very sensitive reagent for zirconium ($\epsilon = 1.65 \times 10^5$). The highest sensitivity has been obtained in the following procedure: the anionic picramine-epsilon complex of zirconium gives the ion associate with the basic dye ethylrhodamine B; the separated water-insoluble compound gives a color solution in acetone.[72]

D. Vanadium, Niobium, and Tantalum

The commonly used methods for determining *vanadium*, e.g., with oxine, BPHA, and hydroxamic acids, are not sensitive enough. Among the triphenylmethane reagents pyrocatechol violet is recommended ($\epsilon = 3.7 \times 10^4$).[193] Of the azo reagents the best seem to be: 3,5-Br-MEPADAP (pyridylazophenol) ($\epsilon = 5.4 \times 10^4$),[194] and sulfonitrophenol K (+ NH_2OH) ($\epsilon = 8.5 \times 10^4$).[195] Numerous methods, based on redox effects, generally have low sensitivity. In a recently published method vanadium(V) is reduced by the Jones reductor to V(II), which reduces iron(III) and the equivalent amount of iron(II) reacts with ferrozine (apparent $\epsilon = 5.5 \times 10^4$).[196] In a very sensitive method, anionic complex of vanadium with PAR is associated with crystal violet; the associate is soluble in benzene-MIBK ($\epsilon = 1.1 \times 10^5$).[197]

Niobium reacts with thiocyanate in about 3 *M* HCl to form an extractable yellow complex ($\epsilon = 3.5 \times 10^4$; a = 0.38). This method is most often utilized.[2-5,198,199] Among the recommended reagents are PAR ($\epsilon = 3.5 \times 10^4$),[3,5,200,201] bromopyrogallol red ($\epsilon = 4.8 \times 10^4$),[3,202] and sulfonitrophenol M ($\epsilon = 5.3 \times 10^4$).[203,204] Really sensitive reagents for niobium can be found among the trihydroxyfluorones.[38] Molar absorptivities attained with *o*-nitrophenylfluorone and other reagents are equal to 1.3 to 1.7×10^5. In the method, use of *o*-nitrophenylfluorone and DAM[204a] increases the sensitivity to 1.9×10^5.

Almost all sensitive methods for determining *tantalum* are based on extractable ion pairs: TaF_6^- and a basic dye. Worthy of mention are the following dyes: methyl violet and crystal violet (ϵ about 7.5×10^4; a = 0.42),[3,5,205] malachite green and crystal green,[4,205,206] methyl green and methylene blue,[207] Capri blue ($\epsilon = 1.07 \times 10^5$),[208] and nitrochrompyrazol.[209] The complex compound of tantalum with 9-(2′-hydroxyphenyl)-2,3,7-trihydroxy-6-fluorone and antipyrine is the basis of the very sensitive extractive method: $\epsilon = 2.5 \times 10^5$ at 505 nm.[140]

E. Chromium, Molybdenum, and Tungsten

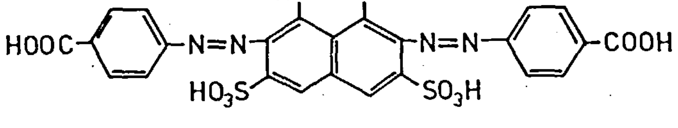
Undoubtedly the best method with respect to sensitivity and commonly used method for determining *chromium* is based on 1,5-diphenylcarbazide. In the reaction with chromium(VI) (in 0.02 to 0.2 *M* H_2SO_4) a violet complex is formed; $\epsilon = 4.3 \times 10^4$ (a = 0.81) at 542 nm. The quality of the reagent influences the sensitivity of the reaction. This method is highly selective. Preliminary oxidation of chromium(III) to Cr(VI) is performed by means of $KMnO_4$ or $(NH_4)_2S_2O_8$.[2-5,10,210-211a] Among other methods worth mentioning is the method based on ion pair formation: the anionic PAR complex of chromium(III) with zephiramine, extractable into $CHCl_3$ ($\epsilon = 4.7 \times 10^4$).[212]

Dithiol and thiocyanate methods are frequently used in determining traces of *molybdenum.*[2-5,213,214] The green molybdenum dithiolate is extracted by amyl acetate ($\epsilon = 2.1 \times 10^4$; a = 0.22). The orange-red thiocyanate complex is formed in the presence of reducing agents ($\epsilon = 2.0 \times 10^4$) and can be extracted with oxygen-containing solvents. It is extracted into chloroform in the presence of organic bases. A very sensitive flotation method is based on the ion associate of thiocyanate complex with crystal violet ($\epsilon = 2.3 \times 10^5$).[63] In the method using SCN^- and rhodamine B (without extraction)[215] the value of the coefficient ϵ is 1.1×10^5. In determining molybdenum with sulfonitrophenol K, $\epsilon = 5.0 \times 10^4$ ($\Delta\lambda$ = 100 nm).[216]

Determination of *tungsten* is often performed with the aid of two insensitive methods: dithiol ($\epsilon = 1.9 \times 10^4$; a = 0.10) and a thiocyanate method ($\epsilon = 1.6 \times 10^4$).[2-5,217,218] Considerably more sensitive are methods using cationic surfactants. In the method with gallein (+ CTA) $\epsilon = 6.0 \times 10^4$,[116,121] and in the method with pyrocatechol violet (+ CP or CTA)[114,219] $\epsilon = 8.0 \times 10^4$. The most sensitive is the flotation method based on the system W-SCN^--crystal violet ($\epsilon = 2.1 \times 10^5$).[71] In another method of this type, with 3,5-dinitropyrocatechol and brilliant green,[220] $\epsilon = 1.3 \times 10^5$.

F. Manganese and Rhenium

The classical permanganate method shows too low a sensitivity ($\epsilon = 2.4 \times 10^3$) for determining *manganese* in trace amounts. The not very sensitive ($\epsilon = 1.12 \times 10^4$) formaldoxime method is highly selective.[3-5,221-223] The PAN method is characterized by good sensitivity ($\epsilon = 5.8 \times 10^4$; a = 1.05) and selectivity.[3,5,132,224] Also worth recommending is the PAR method.[225,226] In the extractive dithizone method (in the presence of pyridine)[227] $\epsilon = 5.7 \times 10^4$ and in the presence of phen[227a] $\epsilon = 4.6 \times 10^4$. A highly sensitive and contrast reaction ($\epsilon = 1.5 \times 10^5$; $\Delta\lambda$ = 180 nm) uses carboxybenzene S



(43)

and has been used for direct determination of manganese in the extract after extracting manganese diethyldithiocarbamate into chloroform.[228]

Rhenium is often determined with two sparingly sensitive methods: thiocyanate ($\epsilon = 3.8 \times 10^4$) and the α-furildioxime method ($\epsilon = 4.1 \times 10^4$; a = 0.22).[2-5,229-231] The extractive methods based on ion associates of perrhenate ion with basic dyes are sensitive. In the case of brilliant green,[232] $\epsilon = 1.0 \times 10^5$. In addition, the Nile blue A,[233] methyl green,[234] and rhodamine B,[235] methods are worthwhile.

G. Iron, Cobalt, and Nickel

Among the great number of existing methods for *iron* the classical thiocyanate,[2-5] 1,10-phenanthroline (phen),[2-5,236] and bathophenanthroline,[2-5,237,238] methods are the most known and applied. Molar absorptivities of thiocyanate and bathophenanthroline methods are equal to about 2.4×10^4 (a = 0.43). The sensitivity of 1,10-phenanthroline method is two times lower. 2,4,6-Tri(2′-pyridyl)-symtriazine (TPTZ),[239] ferrozine,[240,241] and 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PPDT),[242,243] are reagents related to bathophenanthroline. Extraction of ferroin ($Fe(phen)_3^{2+}$) associated with methyl orange[82] or bromophenol blue[80] is the basis of the methods with $\epsilon = 4.8 \times 10^4$ and $\epsilon = 5.9 \times 10^4$. A great increase in sensitivity of determining iron was attained owing to cationic surfactants.[107,246] In the systems Fe(III)-eriochrome cyanine R (chrome azurol S), or in the presence of CTA or TDEA (tridodecylethylammonium ion), ϵ values are 1.3 to 1.7×10^5. It is also possible to extract the ion pairs of $FeCl_4^-$ or the Fe(III)-nitroso-2-chloro-4-phenol complex with basic dyes (rhodamine B, crystal violet) (ϵ values near 1×10^5).[247-249]

1-Nitroso-2-naphthol, 2-nitroso-1-naphthol, and nitroso-R salt are the reagents most often used for determining traces of *cobalt*.[2-5,250] These methods are very selective and sensitive enough (ϵ values 2.7 to 3.7×10^4; on the average a = 0.5). In the method using 2-nitroso-5-diethylaminophenol,[251,252] $\epsilon = 6.2 \times 10^4$. Some pyridine azo reagents are recommended, because their cobalt complexes exhibit very high ϵ values, namely: 4-(5-chloro-2-pyridylazo)-1,3-diaminobenzene (Cl-PADAB) ($\epsilon = 1.13 \times 10^5$),[253] Br-PADAB ($\epsilon = 1.23 \times 10^5$),[254] and 5-(3,5-dichloro-2-pyridylazo)-2,4-diaminotoluene (3,5-diCl-PADAT) ($\epsilon = 1.19 \times 10^5$).[255] There are also methods based on the extraction of some anionic cobalt complexes with basic dyes, e.g., malachite green,[256] and rhodamine 6G.[257]

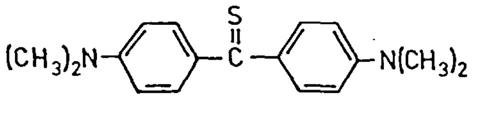
Important photometric reagents for determining *nickel* are dimethylglyoxime (plus oxidant) and α-furildioxime (with extraction.)[2-5] They are specific but not very sensitive: $\epsilon = 1.5 \times 10^4$ (a = 0.26) and $\epsilon = 2.0 \times 10^4$. Sensitivity of the formaldoxime method is similar.[221] The dimethylglyoxime-nickel(IV) complex can be extracted into organic solvents in the presence of diphenylguanidine.[258] More sensitive are the methods using the following reagents: pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) ($\epsilon = 6.7 \times 10^4$),[259] 2-(5-nitro-2-pyridylazo)-1-naphthol (plus nonionic surfactant Triton X-100) ($\epsilon = 7.4 \times 10^4$),[134] 2-[2-(5-bromopyridyl)azo]-5-dimethylaminophenol (br-PADAP) ($\epsilon = 1.28 \times 10^5$)[32] chloro-oxine plus rhodamine 6G ($\epsilon = 7.5 \times 10^4$),[260] and 4-chloro-2-nitroso-1-naphthol plus crystal violet ($\epsilon = 8.2 \times 10^4$).[260a] In a highly sensitive, indirect method (ϵ about 3×10^5) nickel is separated as a compound with dimethylglyoxime and diphenylboric acid. After mineralization, boron is determined by the curcumin method.[261]

H. Platinum Metals

p-Nitrosodiethylaniline is a fairly sensitive reagent for *platinum* ($\epsilon = 5.7 \times 10^4$) and palladium ($\epsilon = 8.6 \times 10^4$).[2-5] Reagents related to rhodanine and thiorhodanine allow platinum and palladium to be determined with good sensitivity (ϵ values about

1×10^5).[262,263] Ternary complexes with the acid dye, tetrabromofluorescein ethyl ester,[264] and with the basic dye, crystal violet,[67] are the basis of sensitive methods (ϵ values 8.4×10^4 and 2.1×10^5).

Among azo reagents relatively sensitive for *palladium* is sulfonitrophenol M ($\epsilon = 8.0 \times 10^4$).[265] More sensitive are *p*-nitrosodiethylaniline,[2-5] nitrosodibenzylaniline ($\epsilon = 1.1 \times 10^5$),[543] and thio-Michler's ketone [4,4'-bis(dimethylamino)thiobenzophenone] ($\epsilon = 1.6 \times 10^5$).[266,266a]


(44)

A sensitive method was developed ($\epsilon = 1.25 \times 10^5$) based on the extractable ternary complex formed by palladium with pyridine and the acid dye, Bengal rose.[74] In the flotation method using bromide and rhodamine 6G[65] $\epsilon = 3.0 \times 10^5$. The increase in sensitivity in the reactions with some triphenylmethane chelating reagents was obtained owing to cationic surfactants (CTA, CP).[108,109,111] The indirect amplification iodide method is also suitable for trace determination. Extraction of PdI_2 into benzene is the initial stage in this method (apparent $\epsilon = 2.2 \times 10^5$).[3]

Tin(II) chloride (or bromide) methods for *rhodium, iridium* (for platinum as well)[2-5] are insensitive and are not suitable for determination of traces. Extraction variants of determination of rhodium and iridium using some organic bases give considerably higher sensitivity.[267] Fairly sensitive (ϵ about 5×10^4) is the determination of rhodium(III) with eriochrome cyanine R in the presence of a cationic surfactant (CP).[268] In the flotation-spectrophotometric method for rhodium with malachite green[68] $\epsilon = 1.44 \times 10^5$.

There is a lack of sensitive methods suitable for determining *ruthenium* in trace amounts. Among the commonly used methods can be mentioned the following: 1,4-diphenylthiosemicarbazide ($\epsilon = 1.0 \times 10^4$),[269] and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) ($\epsilon = 2.1 \times 10^4$).[270]

There is a sensitive extractive method for determining *osmium* using 1,5-diphenylcarbazide.[271,272] Depending on the quality of the reagent, $\epsilon = 1.4$ to 2.2×10^5. The flotation-spectrophotometric method is based on the ion pair: anionic thiocyanate osmium complex and basic dye, methylene blue ($\epsilon = 2.2 \times 10^5$).[64]

I. Copper, Silver, and Gold

Among numerous methods for *copper*, the dithizone method is sensitive and highly selective ($\epsilon = 4.5 \times 10^4$; a = 0.71). The widely known cuproine (2,2'-diquinolyl), neocuproine, bathocuproine, DDTC and cuprizone methods are selective but insensitive ($\epsilon = 0.64$ to 1.6×10^4).[2-5,29] Worth mentioning, and proposed many years ago, is the very sensitive 1,5-diphenylcarbazide method ($\epsilon = 1.5 \times 10^5$).[273,274] A selective and fairly sensitive reagent for copper is quinoline-2-aldehyde-2-quinolylhydrazone.[275] The extractive methods, in which cationic complexes of copper(I) with cuproine (or neocuproine) or copper(II) with phen are associated with acid dyes (Bengal rose, bromophenol blue, bromocresol purple and others) belong to the class of sensitive methods (ϵ values 6 to 8×10^4).[73,83-85] In the method based on the ion pair formation of $Cu(CN)_2^-$ with methylene blue[275a] (extraction into 1,2-dichloroethane, $\epsilon = 9.8 \times 10^4$. Another good method is the one based on the ternary complex of copper with pyrocatechol violet and tridodecylethylammonium ion (TDEA) ($\epsilon = 7.9 \times 10^4$, extraction into benzene).[276] Quite recently a very sensitive method for copper was proposed ($\epsilon = 1.91 \times 10^5$) using cyclohexylfluorone.[276a]

Selective but not very sensitive are the old reagents for determining *silver*, namely dithizone ($\epsilon = 3.05 \times 10^4$, $a = 0.28$) and rhodanine (*p*-dimethylaminobenzylidenerhodanine) ($\epsilon = 2.0 \times 10^4$).[2-5,29] More sensitive are the methods using thio-Michler's ketone ($\epsilon = 9.4 \times 10^4$),[277] and thirhodine (derivative of rhodanine).[278,278a] The ternary complex of silver with 1,10-phenanthroline and bromopyrogallol red forms the basis of a selective method ($\epsilon = 5.1 \times 10^4$).[279] The same sensitivity was obtained in the ternary system with phen and eosine.[280] Molar absorptivities near 1×10^5 are obtained in the systems of silver-iodide (cyanide)-basic dye; e.g., Nile blue A, ethyl violet, and methylene blue.[281-283]

A sensitive method used for many years for determining *gold* is based on the ion associate of $AuCl_4^-$ with rhodamine B ($\epsilon = 9.7 \times 10^4$; $a = 0.49$).[2-5,284] Also interesting are the methods using other basic dyes, e.g., methyl violet ($\epsilon = 1.15 \times 10^5$) and crystal violet,[284,285] brilliant green,[232,286] and chrompyrazol I (antipyrine dye).[287] Thio-Michler's ketone is a reagent recommended for determining gold traces ($\epsilon = 1.2 \times 10^5$ at 540 nm).[288,289] Worth mentioning are also the methods using rhodanine[290,291] and sulfochlorophenolazorhodanine.[292]

J. Zinc, Cadmium, and Mercury

Undoubtedly the best method for determining traces of *zinc* is the dithizone method[2-5,29] ($\epsilon = 9.26 \times 10^4$; $a = 1.4$), which is close to specific in the presence of thiosulfate or if necessary of other masking agents. PAR ($\epsilon = 8.7 \times 10^4$) and PAN ($\epsilon = 6.2 \times 10^4$) and its derivatives are also recommended for determining zinc.[293-295] The 2-[2-(5-bromopyridl)azo]-5-dimethyl-aminophenol (Br-PADAP) method ($\epsilon = 1.33 \times 10^5$) is very sensitive.[32] The zinc-PAR complex can be extracted in the presence of cetyldimethylbenzylammonium ion ($\epsilon = 9.14 \times 10^4$).[296] In the method based on the ternary complex of $Zn(phen)_2^{2+}$ with the acid dye, eosine, high sensitivity ($\epsilon = 1.2 \times 10^5$, extraction into $CHCl_3$) was attained.[78] A method with 8-(8-quinolylazo)-4,5-diphenylimidazole and nonionic surfactant Triton X-100 ($\epsilon = 8.3 \times 10^4$) has recently been proposed.[135]

The widely known dithizone method of *cadmium* determination is selective as well as sensitive ($\epsilon = 8.8 \times 10^4$; $a = 0.78$).[2-5,29] A new, very sensitive reagent for cadmium is 2-[2-(5-bromopyridyl)azo]-5-dimethylaminophenol (Br-PADAP) ($\epsilon = 1.4 \times 10^5$).[33] Also enumerated are the methods based on ternary systems of halogenide complexes of cadmium with basic dyes: crystal violet ($\epsilon = 1.3 \times 10^5$),[57] malachite green, Victoria blue 4R, and rhodamine B.[297,297a]

The dithizone method for *mercury* shows quite good selectivity and sensitivity ($\epsilon = 7.1 \times 10^4$; $a = 0.35$).[2-5,29] Mercury(II) forms anionic complexes with I^-, Br^-, and Cl^-, which give extractable ion pairs with basic dyes. The following dyes are used in these sensitive methods: Bindschedler's green ($\epsilon = 1.7 \times 10^5$),[298] methyl green ($\epsilon = 1.3 \times 10^5$),[299] malachite green, methyl violet,[299a] crystal violet,[285,300,301] brilliant green rhodamine B, and others.[301] Thio-Michler's ketone ($\epsilon = 1.5 \times 10^5$)[266,302] and 2-(quinolylazo)-4,5-diphenylimidazole ($\epsilon = 8 \times 10^4$)[303] can be recommended as good reagents for mercury as well.

K. Aluminum, Gallium, Indium, and Thallium

The 8-hydroxyquinoline method for *aluminum* is commonly known, highly selective (in the presence of appropriate masking agents) but comparatively insensitive ($\epsilon = 7.3 \times 10^3$; $a = 0.27$).[2-5] Triphenylmethane reagents (mostly chrome azurol S and eriochrome cyanine R) are good reagents for determining aluminum (ϵ values 5 to 7×10^4).[3-5,304,305] The sensitivity of the chrome azurol S method increases significantly in the presence of CTA ($\epsilon = 1.3 \times 10^5$),[96,97] and similarly in the presence of nonionic surfactants.[129,130] A little lower sensitivity is the case of sulfochrome and cationic surfactants.[114,117] Of other fairly sensitive reagents 9-(5-bromohydroxyphenyl)fluorone ($\epsilon = 7.5 \times 10^4$) can be mentioned.[306]

A classical method for *gallium* is that of rhodamine B (ϵ about 1×10^5; a = 1.4).[2-5,307] Many other basic dyes[308] were proposed for determining gallium, e.g., brilliant green ($\epsilon = 9.2 \times 10^4$),[309] methylene blue,[310] methyl green,[311] and Victoria blue 4R.[312] More sensitive (ϵ = 1.1 to 1.4×10^5) are the methods with CTA and chrome azurol S,[98] eriochrome cyanine R,[104] and pontachrome azure blue B.[313] In the extractive method, making use of pyrocatechol violet and diphenylguanidine[314] gives an ϵ value of 1.08×10^5. The method with PAR and tetraphenylarsonium ions ($\epsilon = 8.2 \times 10^4$) is worthy of notice.[315]

Sensitive methods for determining *indium* are based on extractable ion pairs of $InBr_4^-$ (InI_4^-) with basic dyes: brilliant green ($\epsilon = 9.3 \times 10^4$; a = 0.81),[309,316]malachite green,[317] rhodamine B, and butylrhodamine B ($\epsilon = 1.1 \times 10^5$).[318] In the methods using chrome azurol S,[98] or eriochrome cyanine R[105] and CTA, the ϵ values are 1.0 to 1.2×10^5. The dithizone method ($\epsilon = 7 \times 10^4$)[4,5,29] can also be numbered in the methods suitable for determining trace amounts of indium.

The only appropriate methods for determining *thallium* in trace amounts are the extractive methods based on the ion associates of $TlCl_4^-$ ($TlBr_4^-$) with basic dyes. The most often applied dyes are: rhodamine B ($\epsilon = 9.7 \times 10^4$; a = 0.40),[2-5] and brilliant green.[3,309,319] Crystal violet,[51,285] Victoria blue 4R,[320] and various thiazine dyes[321] are also used.

L. Germanium, Tin, and Lead

The phenylfluorone method is sensitive and commonly used for determining trace amounts of *germanium* ($\epsilon = 5.3 \times 10^4$; a = 0.73; at 510 nm).[2-5] The extractive method with phenylfluorone (or salicylfluorone) in the presence of antipyrine is twice as sensitive.[322] High sensitivity characterizes the methods based on the formation of sparingly water-soluble compounds with basic dyes. The flotation methods make use of brilliant green ($\epsilon = 1.9 \times 10^5$) and rhodamine 6G ($\epsilon = 2.9 \times 10^5$),[61,62] and the extractive methods of brilliant green, malachite green, and Nile blue A (ϵ = 1.3 to 1.4×10^5).[323,324] Pyrocatechol violet-CTA method (ϵ about 5×10^4) should also be mentioned.[92]

The most known method for *tin* is the phenylfluorone method ($\epsilon = 7.7 \times 10^4$; a = 0.65).[2-5,325,325a] A more sensitive reagent is 3-pyridylfluorone (ϵ about 1.1×10^5).[37] The sensitivity ($\epsilon = 6.8 \times 10^4$) of the pyrocatechol violet method[3-5,326] increases in the presence of CTA or CP ($\epsilon = 9.5 \times 10^4$).[87,93,94] An extractive dihydroxyfluorescein method was recommended ($\epsilon = 1.08 \times 10^5$).[327] In sensitive extractive methods with 3,5-dinitropyrocatechol and brilliant green or Nile blue A,[328] the ϵ values are 1.75×10^5 and 1.3×10^5, respectively. Less sensitive are methods based on malachite green,[55] crystal violet,[329] and rhodamine 6G.[330]

The well-known dithizone method is a good extractive method for determining traces of *lead* ($\epsilon = 6.86 \times 10^4$; a = 0.33). In the presence of cyanide, the dithizone method is highly selective.[2-5,29] The diphenylcarbazone method shows similar sensitivity[331] while PAR method is one half as sensitive.[3,4,332,333] In the 2-(5-bromopyridylazo)-5-diethylaminophenol (5-Br-PAAP) method[334] $\epsilon = 4.9 \times 10^4$. The ion associate of $Pb(phen)_2^{2+}$ and eosin is the basis of a more sensitive method.[76]

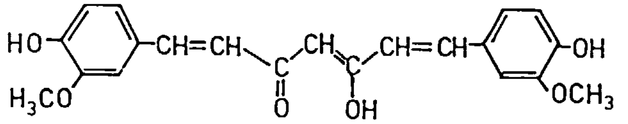
M. Antimony and Bismuth

The classical method for *antimony*, rhodamine B, is selective and sensitive ($\epsilon = 9.7 \times 10^4$; a = 0.80; at 552 nm).[2-5,335] Other basic dyes associated with $SbCl_6^-$ in extractive methods can be recommended: brilliant green ($\epsilon = 1.03 \times 10^5$),[309,336-338] malachite green, crystal violet, methyl green, butylrhodamine B, and rhodamine 6G.[338-340] The determination of antimony with fluorones (salicylfluorone, dibromophenylfluorone) is carried out with good sensitivity (ϵ about 9×10^4).[341,342] In the starch-iodine amplification method for determining antimony[3] (the first stage is extraction of SbI_3 into benzene) the apparent ϵ value equals about 3×10^5.

Suitable methods for traces of *bismuth* are based on extractable ion associates of BiI_4^- with the following basic dyes: rhodamine B, butylrhodamine B, rhodamine 6G ($\epsilon = 1.1$ to 1.3×10^5),[343] and basic azo dye ($\epsilon = 9.2 \times 10^4$).[344] In the flotation version[60] with rhodamine 6G, the ϵ value attains 1.5×10^5. Among fluorones, the best reagent is 3-nitrophenylfluorone ($\epsilon = 5.0 \times 10^4$).[345] Dithizone has been used for many years; the method is highly selective ($\epsilon = 7.9 \times 10^4$; a = 0.38).[2-5,29] Attention should also be paid to a very sensitive starch-iodine amplification method (ϵ about 3×10^5).[3]

N. Boron, Carbon, and Silicon

The curcumin method[3-6] is both the most sensitive method for determining *boron* and the most sensitive of all known direct spectrophotometric methods; $\epsilon = 1.8 \times 10^5$ and a = 16.6!



(45)

The sensitivity of the method depends on the quality of the curcumin preparation. The modification of this method (with oxalic acid) is only about half as sensitive. Other methods for boron, with carminic acid ($\epsilon = 5.5 \times 10^3$; a = 0.51), with 1,1′-dianthrimide ($\epsilon = 1.9 \times 10^4$), and with quinalizarine, are much less sensitive. The ion BF_4^- forms extractable ion associates with basic dyes which constitute a basis for suitable methods. The following dyes are used: methylene blue ($\epsilon = 6.5 \times 10^4$),[4-6] brilliant green,[347] Nile blue A,[348] crystal violet, Capri blue, and others.[349]

Cyanide can be determined by means of the methods based on the formation of polymethine dyes.[3,5,6,350-352] They are highly sensitive and almost specific. In the benzidine-pyridine method, $\epsilon = 6.0 \times 10^4$ (a = 2.3). Other variations utilize *p*-phenylenediamine, barbituric acid, and pyrazolone. In indirect methods, the cyanide prevents the formation of the strongly absorbing ternary complexes between silver, 1,10-phenanthroline, and bromopyrogallol red[353] or eosin.[354]

Among methods for determining trace amounts of *thiocyanate* the following can be mentioned: the methods based on the extraction of the ion-pairs: SCN^--rhodamine B[355] or SCN^--methylene blue,[356] and an indirect method using dithizone and mercury(II).[357]

There exist numerous methods for the determination of other carbon compounds as, e.g., free carbon, carbon monoxide, and carbon dioxide.[3,5,6]

Silicon in small and trace amounts is mainly determined as silicomolybdenum blue, the product of reduction of molybdosilicic acid ($\epsilon = 1.7 \times 10^4$; a = 0.60).[3-6,358,359] Very sensitive methods are based on ion associates of molybdosilicate with basic dyes, e.g., safranine T ($\epsilon = 1.5 \times 10^5$; extraction),[360] rhodamine B ($\epsilon = 5.0 \times 10^5$; flotation),[69] crystal violet ($\epsilon = 4.3 \times 10^5$, centrifugation).[58] Also sensitive are indirect amplification methods in which molybdosilicic acid is separated by extraction, and the molybdenum is determined by means of phenylfluorone ($\epsilon = 1.1 \times 10^5$),[148] or of 2-amino-4-chlorobenzenethiol ($\epsilon = 1.6 \times 10^5$).[361]

O. Nitrogen, Phosphorus, and Arsenic

Traces of *ammonia* can be determined with the classical Nessler method[3,5,6,362] or with the newer (of similar sensitivity) indophenol method ($\epsilon = 4.5 \times 10^3$; a = 0.32).[3,5,6,363-365]

Nitrite is determined frequently with methods which are based upon the formation of azo dyes, i.e., with the Griess method and related ones.[3,5,6,366-368a] The Griess method is highly sensitive ($\epsilon = 4.0 \times 10^4$, a = 2.8) and specific.

A well-known method for *nitrate* is the phenoldisulfonic acid method ($\epsilon = 9.4 \times 10^3$; a = 0.67).[3,5,6] This specific method (and similar ones using phenol[369] and 2,4- or 2,6-xylenols[3,370,371]) is based on the color of the nitration product. Much more sensitive are the extractive methods using ion associates between NO_3^- and basic dyes, methylene blue[372] or crystal violet.[373]

There are sensitive spectrophotometric methods for determining other nitrogen compounds, as hydrazine, hydroxylamine, nitrogen oxides, azide, and hyponitrite.[3,5,6]

The most often used method for determining traces of *phosphorus(V)* is the phosphomolybdenum blue method ($\epsilon = 2.5 \times 10^4$; a = 0.81).[3-6,374] High sensitivity is shown by the methods based on the ion pairs of molybdophosphate and basic dyes, e.g., crystal violet ($\epsilon = 2.7 \times 10^5$, flotation),[66] methylene blue (extraction),[375] and malachite green (color sol).[376] Traces of phosphorus(V) can be determined indirectly: in the separated (by extraction) molybdophosphoric acid (Mo:P = 12:1) molybdenum is determined with thiocyanate,[147] 2-amino-4-chlorobenzenethiol ($\epsilon = 9.7 \times 10^4$),[377] phenylfluorone ($\epsilon = 1.1 \times 10^5$),[148] dithiol ($\epsilon = 1.7 \times 10^5$) or sulfonitrophenol S ($\epsilon = 4.6 \times 10^5$).[149]

The well-known methods for determining *arsenic* are: the arsenomolybdenum blue method ($\epsilon = 3.0 \times 10^4$; a = 0.40),[2-5,378] and the less sensitive silver diethyldithiocarbamate (Ag-DDTC) method ($\epsilon = 1.4 \times 10^4$).[3-5,379-382] The old Gutzeit method[3,5] is less popular. Indirect methods via separated molybdoarsenic acid allow very high sensitivity. Molybdenum is determined by means of dithiol ($\epsilon = 2.0 \times 10^5$) or by sulfonitrophenol S ($\epsilon = 4.5 \times 10^5$).[149] In the flotation-spectrophotometric method[59] with the associate between molybdoarsenate and crystal violet has an ϵ value of 3.1×10^5. Recently, the ion associate of the reduced form of Mo-As acid with crystal violet has been extracted with a mixture of toluene and acetone (10:1) (sensitivity as above).[382a]

P. Sulfur, Selenium, and Tellurium

There are two sensitive methods for determining *sulfur:* the methylene blue method,[3-6,383,384] in which sulfur is first converted into H_2S, and the pararosaniline method,[3-6,385,386] in which SO_2 is the reacting species. Both methods are specific. ϵ values are 3.5×10^4 (a = 1.1) in the first case, and 3.0×10^4 in the second. Sulfate can be determined indirectly using complexes of barium with nitro-orthanilic S,[387] chlorophosphonazo III,[143] or dimethylsulfonazo III.[388] In the amplification starch-iodine method sulfate displaces IO_3^- from the sparingly soluble $Ba(IO_3)_2$.[389]

The often used 3,3'-diaminobenzidine (DAB) method for determining *selenium* is, unfortunately, not very sensitive ($\epsilon = 1.02 \times 10^4$; a = 0.13; at 420 nm in toluene).[3-6] More sensitive is the related *o*-phenylenediamine method.[3,390] Dithizone has been proposed to determine selenium ($\epsilon = 7.0 \times 10^4$).[391,392] In the indirect method, with formation of azo dye,[393] ϵ value = 1.9×10^5.

The well-known bismuthiol II method for *tellurium* is highly selective and fairly sensitive ($\epsilon = 3.6 \times 10^4$; a = 0.31; at 330 nm).[3,4,6,394] The 5,5-Methylene-*bis*-salicylfluorone method exhibits similar sensitivity.[395] Salicylfluorone[395a] gives $\epsilon = 5.5 \times 10^4$, and in the presence of CTA the value of ϵ increases to 1.07×10^5. In the bromopyrogallol red (plus diphenylquanidine) method[396] $\epsilon = 5.7 \times 10^4$. The ion $TeBr_6^{2-}$ associates with rhodamine 6G ($\epsilon = 1.7 \times 10^5$; flotation)[70] and with Victoria blue 4R ($\epsilon = 8.0 \times 10^4$; extraction).[397] Recently an extractive method has been proposed based on the associate of tellurium iodide complex and CTA ($\epsilon = 4.9 \times 10^4$).[398]

Q. Halogens, Oxygen

The most important method for determining *fluoride* is the new direct La(Ce) alizarin complexone (AC) method ($\epsilon = 1.4 \times 10^4$; a = 0.74).[3,5,6,399,400] In the extraction version with amines the sensitivity is a little higher.[401,402] The flotation variant of the AC method was also published.[403] There were proposed related reagents.[404-406] In the direct method with Zr-sulfochlorophenol S[407] the ϵ value is 3×10^4. There are numerous indirect sensitive methods based on the fact that fluoride forms stable compounds with multivalent metals, bound initially with chromophore reagents (e.g., Zr-eriochrome cyanine R, Th-xylenol orange).[3,5,6] Recently the above systems modified by involving the cationic surfactant CTA were proposed.[408]

Chlorine (and chloride after oxidation to Cl_2) can be determined by redox reactions leading to disappearance or appearance of color. Methyl orange is used ($\epsilon = 4.02 \times 10^4$; a = 1.1),[6,409,410] methyl red ($\epsilon = 1.17 \times 10^4$).[3,6] and *o*-tolidine ($\epsilon = 3.4 \times 10^4$).[5,6,411] In the indirect thiocyanate method chloride displaces SCN^- from stable $Hg(SCN)_2$, which reacts with added iron(III).[412,413] There are numerous other good indirect methods for traces of chloride.[3,6] Perchlorate is determined with good sensitivity by formation of extractable ion pairs with crystal violet,[414] neutral red,[415] or brilliant green ($\epsilon = 9.4 \times 10^4$).[416]

Bromine (and bromide after oxidation to Br_2) is often determined by bromination of phenol red ($\epsilon = 1.14 \times 10^4$; a = 0.14)[3,6] and by reactions with methyl orange[6,409,417] or *o*-tolidine.[411] High sensitivity is obtained in the extractive method with Nile blue A.[418] A method was proposed for determining perbromate based on the extractable ion associate with crystal violet.[419]

The amplification starch-iodine method for determining *iodide* (iodine) is highly selective and sensitive ($\epsilon = 1.08 \times 10^5$; a = 0.85).[3,145] Iodide forms extractable ion pairs with: neutral red,[415] Nile blue A,[418] crystal violet,[420] and with ferroin[421] or the bis(neocuproine)Cu(I) complex.[422] Worth mentioning is the indirect dithizone method (with Hg(II))[423] and 2-nitroso-5-diethylaminophenol (with Pd(II)).[423a]

Oxidizing properties of *oxygen* are exploited in the determination of traces of oxygen in water and in various gases. Utilized reagents are antraquinone-2-sulfonate,[3] 3,3′-dimethylnaphthidine,[424] (4,7-dihydroxy-phen)$_3$Fe(II),[425] leuco-indigo carmine,[6] leuco-berbelin blue,[426] and leuco-methylene blue.[427,427a]

Since *ozone* is a stronger oxidant than oxygen, it is determined on the basis of the color redox reactions with reagents which are not oxidized by oxygen. The following reagents can be recommended: diphenylaminesulfonate,[6] *o*-tolidine,[6,428] eugenol (4-allyl-2-methoxyphenol),[429] and 1,1-diphenylethylene.[430]

The methods for determining *hydrogen peroxide,* based on its capacity to form peroxide complexes, show little sensitivity. Among methods in which oxidizing properties of H_2O_2 are utilized can be mentioned: the iodide method, the iron-thiocyanate and iron-phen methods, and the leuco-phenolphthaleine method.[3,6]

As follows from the above, sensitive spectrophotometric methods are available nowadays for a great number of elements (particularly if the new methods recently published are taken into account). The most sensitive direct spectrophotometric methods are the curcumin method for boron ($\epsilon = 1.8 \times 10^5$; a = 16.6) and methods using triphenylmethane dyes and surfactants for beryllium. Similar sensitivities are attained in the indirect methods for the determination of silicon and phosphorus.

The group of elements for which very sensitive spectrophotometric methods are available (a values > 1.5) comprises: Al, Sc, Ge, N (as NO_2^- or NO_3^-), Ti, Mo, Mn, Fe, Co, V, Cu, Pd, As, Sb, Zn, Ca, C (as CN^-), Ni, and Nb.

There are, however, elements for which no sensitive methods are known. These are metals: Th, U, Ir, Tl, Pb, Au, and Re. The values of the coefficient a for these metals are less than 0.6. Part of the difference is because the above-mentioned metals exhibit high atomic weight. It should be emphasized and apparent that lighter elements can be determined spectrophotometrically with a higher sensitivity than the heavier ones. Table 6, with sensitive spectrophotometric methods recommended for most elements, gives a recapitulation of the material discussed in this section.

V. DETERMINATION OF TRACE ELEMENTS IN VARIOUS MATERIALS

In this Section papers devoted to trace analysis of various materials are discussed. In principle, the papers referred to here have been published approximately in the last decade. When there were several new papers concerned with the determination of a given element in any material, only some of them were chosen, in order to avoid an unwieldy extension of "References". References to older papers can be found in comprehensive monographs.[2-6] The order of referred elements in this Section is the same as in Section IV.

A. Environment Trace Analysis (Water and Air)

This review begins with water, since this material is very simple and most often analyzed for trace elements. In Table 7 about 40 elements (ions) are listed. In many cases the preconcentration of trace elements is performed by means of anion-exchangers.[434,435,441,443,448,452,456-458] The examples of extraction preconcentration can be found in many papers,[174,431,450,471] and froth flotation.[437] Traces of arsenic are evolved as arsine.[478] In analysis of high-purity water, trace amounts of chloride were coprecipitated as $PbCl_2$ with lead phosphate.[412] In work[466] traces of silicon were coprecipitated with niobic acid as collector. The following silicon contents were found: in normal distilled water, 21 ppb; after bidistillation in glass apparatus, 12 ppb; in quartz, 6 ppb; in palladium, 2 ppb ($= 2 \times 10^{-7}\%$). In many cases trace elements (Ca, Mg, Mn, Zn, B, HCN, P, H_2S) in waters were determined automatically.[432,445,455,462,464,475,480]

Spectrophotometric methods used in trace analysis of air are presented in Table 8. In Reilly's paper[495] an automatic determination of hydrogen cyanide in air is described. In the work of Pacz and Guagnini[502] traces of hydrogen sulfide are absorbed by anion-exchanger Amberlite IRA-400.

B. Biological Materials, Plants, Foods

A good introduction to general problems of trace analysis of biological materials (e.g., decomposition of organic matter, use of microanalytical techniques) is given in several papers.[508-510]

The paper by Morsches and Tölg[508] is devoted to microspectrophotometric determination of As, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Sb, Sn, and V in human skin and nails. The enumerated elements are determined from one 100 mg sample. A scheme of separation (mainly by extraction) of these trace elements is given. The technique of this microspectrophotometric analysis is also described. Heating is performed electrically by means of a block made of pure aluminum. All evaporations are carried out at a temperature below the boiling point. Techniques of pressure decomposition of biological and food samples are described in several papers.[509,510]

Table 9 lists collected papers concerning the trace spectrophotometric analysis of biological samples. The article by Jacobs[529] gives a general survey on the determination of nitrogen in biological samples. In Pollak and Kubaň's paper[522] the comparison of four well-known methods for determining zinc (PAN, PAR, dithizone, zincon) was reported.

Table 6
SENSITIVE SPECTROPHOTOMETRIC METHODS RECOMMENDED FOR DETERMINATION OF TRACE ELEMENTS

Element, ion determined	Method, reagent (medium)	Absorptivity	
		Molar	Specific
		$\epsilon \times 10^{-4}$	$a = \frac{\epsilon}{\text{at. wt} \times 1000}$
Al	Chrome azurol S (pH 6)	4.9	1.8
	Chrome azurol S plus CTA (pH 5.8)	13.1	4.9
	9-(5-Bromohydroxyphenyl)fluorone (pH 3—4)	7.5	2.8
Ag	Dithizone (CCl_4)	3.1	0.28
	Thio-Michler's ketone (pH 3, H_2O-ethanol)	9.4	0.87
	Methylene blue (CN^-) (1,2-dichloroethane)	9.9	0.92
As	Arsenomolybdenum blue (butanol)	3.0	0.40
	Crystal violet (with Mo-As acid) (flotation)	31.0	4.1
	Dithiol (indirectly) (determ. Mo in Mo-As acid)	20.0	2.7
Au	Rhodamine B (with $AuCl_4^-$) (di-isopropyl ether)	9.7	0.49
	Thio-Michler's ketone (toluene-butanol)	12.0	0.61
B	Curcumin (H_2SO_4-CH_3COOH) (H_2O-ethanol)	18.0	16.6
	1,1'-Dianthrimide (conc. H_2SO_4)	1.9	1.8
	Methylene blue (with BF_4^-) (1,2-dichloroethane)	6.5	6.0
Be	Chrome azurol S (pH 5.0)	2.4	2.7
	Eriochrome cyanine R plus CTA (EDTA, pH 7.0)	8.7	9.6
Bi	Dithizone (CCl_4)	7.9	0.38
	Rhodamine 6G (Br^-) (flotation)	15.0	0.70
	Iodide amplification method	30.0	1.4
Ca	Chlorophosphonazo III (pH 7)	5.4	1.3
	Glyoxal bis(2-hydroxyanil) (alkal. H_2O-methanol)	1.8	0.45
Cd	Dithizone (CCl_4)	8.8	0.78
	Br-PADAP (3-methyl-1-butanol)	14.1	1.2
	Crystal violet (I^-) (flotation)	13.0	1.1
Cl	*o*-Tolidine (oxid. by Cl_2)	3.4	0.96
	Methyl orange (oxid. by Cl_2)	4.0	1.1
CN^-	Benzidine-pyridine method (H_2O-ethanol)	6.0	2.3
Co	2-Nitroso-1-naphthol (chloroform)	3.7	0.63
	2-Nitroso-5-diethylaminophenol (1,2-dichloroethane)	6.2	1.1
	Br-PADAP (pH 2 to 6)	12.3	2.1
	Malachite green (SCN^-)(CCl_4-cyclohexanone)	8.6	1.5
Cr	1,5-Diphenylcarbazide (0.02 to 0.2 M H_2SO_4)	4.3	0.81
	PAR plus zephiramine (chloroform)	4.7	0.88
Cu	Dithizone (CCl_4)	4.5	0.71
	1,5-Diphenylcarbazide (pH 9)	15.0	2.4
	Pyrocatechol violet plus tridodecylethylammonium ion (benzene)	7.9	1.2
	Cyclohexylfluorone (pH 5)	19.1	3.0
F	La-alizarin complexone (H_2O-acetone, pH 4.0)	1.4	0.74
	Zr-sulfochlorophenol S (pH 2.8)	3.0	1.6
Fe	Thiocyanate (MIBK)	2.4	0.43
	Bathophenanthroline (chloroform-ethanol)	2.2	0.40
	Rhodamine B (with $FeCl_4^-$) (benzene)	9.0	1.6
	Eriochrome cyanine R plus tridodecylethylammonium (xylene)	17.0	3.0
Ga	Rhodamine B (with $GaCl_4^-$) (CCl_4-chlorobenzene)	10.0	1.4
	Eriochrome cyanine R plus CTA (pH 5.3)	12.0	1.7
	Pyrocatechol blue plus diphenylguanidine (*n*-butanol-chloroform)	10.8	1.5

Table 6 (continued)
SENSITIVE SPECTROPHOTOMETRIC METHODS RECOMMENDED FOR DETERMINATION OF TRACE ELEMENTS

		Absorptivity	
		Molar	Specific
Element, ion determined	Method, reagent (medium)	$\epsilon \times 10^{-4}$	$a = \frac{\epsilon}{\text{at. wt} \times 1000}$
Ge	Phenylfluorone (pH 5)	5.3	0.73
	Brilliant green (with Mo-Ge acid) (flotation)	13.0	1.8
	Rhodamine 6G (alizarin complexone) (flotation)	29.0	4.0
Hg	Dithizone (CCl_4)	7.1	0.35
	Malachite green (I^-) (benzene)	8.7	0.43
	Thio-Michler's ketone (pH 5.8, 30% *n*-propanol)	15.1	0.71
I	Amplification starch-iodine method	10.0	0.85
	Nile blue A (with I^-) (chloroform)	3.6	0.28
In	Brilliant green (with $InBr_4^-$) (butanol-chloroform)	9.3	0.81
	Butylrhodamine B (with $InBr_4^-$) (*di*-isopropyl ether-benzene)	11.2	0.97
	Eriochrome cyanine R plus CTA (pH 5.2)	10.1	0.90
Li	Nitroanthranylazo (alkal. H_2O-acetone)	1.2	1.7
Mg	Eriochrome black T (pH 10.4)	2.3	0.95
	Titan yellow (alkal. solution)	3.6	1.5
Mn	PAN (pH 9.2) (chloroform)	5.8	1.1
	Carboxybenzene S (chloroform)	15.0	2.7
Mo	Dithiol (amyl acetate)	2.1	0.22
	Thiocyanate ($SnCl_2$) (isoamylol)	2.0	0.21
	Sulfonitrophenol K (pH 3 to 4)	5.0	0.52
	Crystal violet (SCN^-) (flotation)	23.0	2.3
Nb	Thiocyanate (3 *M* HCl) (diethyl ether)	3.5	0.38
	Sulfonitrophenol M (0.5 *M* H_2SO_4)	5.3	0.56
	o-Nitrophenylfluorone (1 *M* HCl) (chloroform)	17.0	1.8
Ni	α-Furildioxime (chloroform)	2.0	0.34
	Pyridine-2-aldehyde-2-quinolylhydrazone (benzene)	6.7	1.1
	Br-PADAP (pH 5 to 9)	12.8	2.2
	Crystal violet (chloroform)	8.2	1.4
NH_3	Indophenol method (alkaline solution)	0.45	0.32
NO_2^-	Griess method (pH 2 to 2.5)	4.0	2.8
NO_3^-	Phenoldisulfonic acid method (ammoniacal solution)	0.94	0.67
Os	1,5-Diphenylcarbazide (chloroform)	21.5	1.1
	Methylene blue (SCN^-) (flotation)	22.0	1.2
P	Phosphomolybdenum blue (butanol)	2.5	0.81
	Crystal violet (with Mo-P acid) (flotation)	27.0	8.8
	Dithiol (indirectly) (determ. Mo in Mo-P acid)	17.0	5.5
Pb	Dithizone (CCl_4)	6.9	0.33
	Eosin plus phen (chloroform)	11.0	0.53
Pd	*p*-Nitrosodiethylaniline (pH 2 to 3)	8.6	0.81
	Thio-Michler's ketone (isoamylol)	16.0	1.5
	Rhodamine 6G (Br^-) (flotation)	30.0	2.8
	Iodide-amplification method	22.0	2.1
Pt	*p*-Nitrosodiethylaniline (pH 2 to 3)	5.7	0.29
	Crystal violet ($SnCl_2$) (flotation)	21.0	1.1
Re	Thiocyanate ($SnCl_2$) (isoamylol)	3.8	0.21
	α-Furildioxime (chloroform)	4.1	0.22
	Brilliant green (with ReO_4^-) (benzene)	10.0	0.54
REE	Arsenazo III (pH 2.5)	5.6	0.40
	Chlorophosphonazo III plus diphenylguanidine (butanol)	16.0	1.2
	Erithrosine plus phen (toluene-butanol)	16.0	1.2
Rh	Eriochrome cyanine R plus CP (pH 3.4)	5.0	0.48
	Malachite green ($SnCl_2$) (flotation)	14.4	1.4

Table 6 (continued)
SENSITIVE SPECTROPHOTOMETRIC METHODS RECOMMENDED FOR DETERMINATION OF TRACE ELEMENTS

		Absorptivity	
		Molar	Specific
Element, ion determined	Method, reagent (medium)	$\epsilon \times 10^{-4}$	$a = \frac{\epsilon}{\text{at. wt} \times 1000}$
S	Methylene blue method (ClO_4^-) (chloroform)	3.5	1.1
	Pararosaniline method (acidic solution)	3.0	0.94
Sb	Rhodamine B (with $SbCl_6^-$) (*di*-isopropyl ether)	9.7	0.80
	Brilliant green (with $SbCl_6^-$) (toluene)	10.3	0.85
	Iodide-amplification method	30.0	2.5
Sc	Xylenol orange (pH 2)	2.9	0.65
	Chromal blue G plus CTA (pH 5.5)	16.5	3.7
Se	Indirect method via formation of azo dye	19.3	2.4
	Dithizone (CCl_4)	7.0	0.88
Sn	Phenylfluorone (pH 1 to 1.2)	7.7	0.65
	Pyrocatechol violet plus CTA (pH 2.2)	9.6	0.81
	Brilliant green (dinitropyrocatechol) (CCl_4-benzene)	17.5	1.5
Si	Silicomolybdenum blue (isoamylol)	1.7	0.60
	Safranine T (with Mo-Si acid) (acetylacetone-ethyl acetate)	15.0	5.4
	Rhodamine B (with Mo-Si acid) (flotation)	50.0	17.8
Ta	Methyl violet (with TaF_6^-) (benzene)	7.5	0.42
	Capri blue (with TaF_6^-) (chloroform)	10.6	0.60
	9-(2′-Hydroxyphenyl)-2,3,7-trihydroxy-6-fluorone plus antipyr. ($CHCl_3$)	21.0	1.2
Te	Bismuthiol II (chloroform)	3.6	0.31
	Iodide plus CTA (chloroform)	4.9	0.38
	Salicylfluorone plus CTA (pH 4)	10.7	0.83
	Rhodamine 6G (with $TeBr_6^{2-}$) (flotation)	17.0	1.3
Th	Arsenazo III (3 M HCl)	11.5	0.50
	Chlorophosphonazo III (3-methyl-1-butanol)	12.2	0.53
	Chrome azurol S plus CTA (pH 4.5)	14.6	0.63
Ti	Thiocyanate plus organ. base (1,2-dichloroethane)	8.0	1.6
	Salicylfluorone plus thiocyanate (chloroform)	14.4	3.0
	Propylfluorone plus DAM (chloroform-ethanol)	12.8	2.6
Tl	Rhodamine B (with $TlCl_4^-$) (benzene-CCl_4)	9.7	0.47
	Brilliant green (with $TlCl_4^-$) (*di*-isopropyl ether)	10.6	0.50
U	Arsenazo III (6 M HCl)	12.7	0.50
	Chlorophosphonazo III (3-methyl-1-butanol)	12.1	0.47
	Chrome azurol S plus CP (pH 4.8)	9.9	0.40
	Malachite green (benzoate) (chlorobenzene)	8.3	0.31
V	Pyrocatechol violet (pH 6.2)	3.7	0.72
	Sulfonitrophenol K plus NH_2OH (pH 1 to 4)	5.5	1.1
	Crystal violet (PAR) (benzene-MIBK)	11.0	2.2
W	Pyrocatechol violet plus CTA (pH 1)	8.0	0.43
	Crystal violet (SCN^-) (flotation)	21.0	1.1
Zn	Dithizone (CCl_4)	9.3	1.4
	PAN (chloroform)	5.2	0.79
	Br-PADAP (pH 7 to 9)	13.3	2.0
	Eosin plus phen (chloroform)	12.0	1.9
Zr	Arsenazo III (9 M HCl)	12.0	1.3
	Chlorophosphonazo III (3-methyl-1-butanol)	21.0	2.3
	2′-Quinolylfluorone (acid solution)	16.5	1.8
	Ethylrhodamine B (flotation)	32.0	3.5

Note: See Section IV for references.

Table 7
DETERMINATION OF TRACE ELEMENTS IN WATERS

Element (ion)	Determined in	Reagent (method)	Ref.
Be	Natural	Beryllon II	431
Mg, Ca	Drinking	Eriochrome black T	432
REE	Natural	Arsenazo III	433
Th	Natural	Arsenazo III	174, 435
U	Sea	Arsenazo III	435—438
Ti	Natural	Tichromin	439
V	Sea	PAR plus zephiramine	440
Cr	River, waste	1,5-Diphenylcarbazide	211a, 441, 441a
Mo	Natural	Pyrogallol red	442
	Sea	Dithiol	443
		5-Chloro-7-iodo-8-quinolinol	443a
W	Sea	Dithiol	443
Mn	Natural	Formaldoxime	223, 443b
	Spring	Dithizone plus phen	227a
		o-Tolidine	444
	River	Zincon	445
Fe	Sea	TPTZ	239, 446
	Domestic, lake	TPTZ	446a
	Underground	1,10-Phenanthroline	447
		2-Nitroso-5-dimethylaminophenol	244
Co	Sea	PAR	448
	River, lake	2-Pyridyl-2-thienyl-β-ketoxime	449
	Sea	2-Nitroso-5-diethylaminophenol	251
Ni	Sea	Pyridine-2-aldehyde-2-quinolylhydrazone	259
		α-Benzildioxime	450
Cu	Sea	Neocuproine	446
		Quinoline-2-aldehyde-2-quinolylhydrazone	451
Au	Sea	Rhodanine	452
Zn	Potable	TAR	453
	Lake	PAN plus nonionic surfactant	454
		PAR	455
		Zincon	456
Cd	Potable	Dithizone	457
Al	River	Pyrocatechol violet	304
		Pyrocatechol violet plus zephiramine	457a
Pb	Potable	Dithizone	458
Sb	Sea	Rhodamine B	459
Bi	Natural	Iodide	460
B	River, Sea	Salicylate-ferroin	461
	Sea	Curcumin	462, 462a
	Natural	Azomethine H	463
HCN	Waste	Pyrazolone-pyridine	464
		Benzidine-pyridine	465
Si	Natural	Si-Mo blue	466—468
NH_3	Sea	Oxid. to NO_2^- and azo dye	469
		Indophenol method	470
NO_2^-	Sea, river	Formation azo dye	366, 368, 471—472a
NO_3^-	Fresh, river	Azo dye after red. to NO_2^-	472a, 473
P	Natural, river	P-Mo blue	475—476
As	River	As-Mo blue	476—478
		Ag-DDTC	479
H_2S	Natural	Methylene blue method	480, 502
S^{2-}, SO_3^{2-}	Waste	Cu(I)-neocuproine	481
SO_4^{2-}	Natural	Barium violurate	482
	River	Ba-dimethylsulfonazo III	388

Table 7 (continued)
DETERMINATION OF TRACE ELEMENTS IN WATERS

Element (ion)	Determined in	Reagent (method)	Ref.
F^-	Potable	La-alizarin complexone	483, 484
Cl^-	High purity	Iron(III) plus $Hg(SCN)_2$	412
Cl_2	Potable	Phenolphthalein plus $Fe(CN)_6^{4-}$	485
Br^-	Sea	Phenol red method	486, 487
I^-	Sea	Amplif. starch-iodine method	488
O_2	Surface	3,3′-Dimethylnaphthidine	424
		Leuco-berbelin blue	426
	Power station	Leuco-methylene blue	427a
O_3	Polluted	*o*-Tolidine	428

Table 8
DETERMINATION OF TRACE ELEMENTS IN AIR

Element (compound) determined (in)	Reagent (method)	Ref.
Be	Chrome azurol S plus CP	489
Cr	1,5-Diphenylcarbazide	490
ZnO (fume)	TAR	491
Cd	Dithizone	492
Pb	Dithizone	493
	Eosine plus phen	76
SbH_3	$SbCl_6^-$ with crystal violet	494
HCN		
Combustion gases	Sodium picrate	495, 528
Tobacco smoke	Hemoglobin	528
CO	Ag-*p*-sulfamoylbenzoate	496, 497
NH_3	Indophenol method	498
NO, NO_2	Formation of azo dye	499
NO_2		
Combustion gases	Formation of azo dye	500
H_2S	Methylene blue method	501, 502
SO_2	Pararosaniline method	503
Te	Butylrhodamine B	504
HF	La-alizarin complexone	505, 506
	Quinalizarin complexone	404
Cl_2	Methyl orange method	410
	Crystal violet (indirect)	420
	4-Nitroaniline (alkal.)	507
O_3 (gases)	*o*-Tolidine	428
	Eugenol	429
	1,1-Diphenylethylene	430

In other reports[534,536] automated methods are presented for determining sulfur in animal feces and leaf samples, and fluoride in urine.

Table 10 contains papers devoted to determination of trace elements in plant material. Of metals retained on the cation-exchanger Dowex 50, Na, K, Mg, and Ca were eluted one after the other.[538] In additional papers[540,548,549] flow injection analyses are presented concerning the determination of molybdenum, total nitrogen and phosphorus in plant material. An automated procedure for the determination of boron is described by Basson et al.[547]

Table 9
DETERMINATION OF TRACE ELEMENTS IN BIOLOGICAL MATERIALS

Element	Determined in	Reagent (method)	Ref.
Mg	Serum	Azovan blue	511
Ca	Serum	Chlorophosphonazo III	512
Th	Bone	Arsenazo III	513
	Urine	Arsenazo III	434
Cr	Serum, skin	1,5-Diphenylcarbazide	10, 508, 514
V		*N*-benzylbenzohydroxamic acid	515
	Skin, nails	PAN ($CHCl_3$)	508
Mo	Liver	Dithiol ($CHCl_3$)	508, 516, 517
Mn	Beef liver	Morpholine-N-DTC	518
Fe	Skin, nails	Thiocyanate	508
	Serum	Ferrozine	241
	Blood	2,4-Bis(5,6-diphenyl-1,2,4-triazin-3-yl)pyridine tetrasulfonic acid	519
Co	Skin, nails	1-Nitroso-2-naphthol	508
		Nitroso-R salt	520
Cu	Skin, nails	1,5-Diphenylcarbazide	508
	Blood	2,4-Bis(5,6-diphenyl-1,2,4-triazin-3-yl)pyridine tetrasulfonic acid	519
		Na-DDTC	521
Zn	Serum, urine	PAR, PAN, H_2Dz, zincon	522
Hg	Skin, nails	Dithizone	508
Tl	Tissues, fluids	Dithizone	523
	Tissue, hair	Crystal violet	524
Sn	Skin, nails	Dithizone	508, 525
B	Tissue	Curcumin	526
	Tissue	1,1′-Dianthrimide	527
HCN		Hemoglobin	528
NH_3		Nessler m., indophenol m.	529
NO_2^-	Blood	Formation of azo dye	530
P		Crystal violet	531
	Blood, bone	P-Mo blue	532
	Blood, urine	Det. U in UO_2Mg phosphate	474
As	Skin, nails, hair	As-Mo blue	508, 533
S	Feces	Bismuth sulfide susp.	534
Se	Tissue	3,3′-Diaminobenzidine	535
F^-	Urine.	La-alizarin complexone	536
ClO_4^-	Biol. fluids	Cu(I) (neocuproine)$_2$	537

In Table 11 papers concerning trace determination in foods are presented. Not long ago Crosby[550] published an excellent comprehensive review on this theme. He discusses the role of particular trace elements in biological processes. At present, the following elements are believed to be essential for animal life: Co, Cr, Cu, F, Fe, I, Mg, Mn, Mo, Ni, Se, Si, Sn, V, and Zn. Some metals exist as chelate complexes, e.g., magnesium in the chlorophylls, iron in the porphyrins, and cobalt in vitamin B_{12}. Arsenic, antimony, lead, cadmium, and mercury are important because they are known to be toxic at very low levels. Toxic elements are present in foods as contaminants as a result of increasing industrialization and associated pollution of the biosphere. Reference 550 discusses in detail the principal stages in the analysis of a foodstuff for trace element content: obtaining a representative sample, destruction of organic matter, separation and

Table 10
DETERMINATION OF TRACE ELEMENTS IN PLANTS

Element	Determined in	Reagent (method)	Ref.
Mg	Tobacco	Eriochrome black B	538
V	Rye, straw	PAR-crystal violet	197
Mo	Leaves	Dithiol	539
		SCN^--rhodamine B	215
	Extracts	Thiocyanate	540
Co		2-Nitroso-1-naphthol	541
Fe	Tobacco	Bathophenanthroline	542
Pd		Nitrosodibenzylaniline	543
Cu		Cuprizone	544
Pb		Dithizone	545
Al	Digests	Eriochrome cyanine R	546
B		Azomethine H	547
N(as NH_3)		Indophenol method	548, 549
N(as NO_3^-)		Nitration of phenol	369
P	Digests	P-Mo blue	549
As		As-Mo blue	477
S(reducted to H_2S)		Bismuth sulfide suspension	534

Table 11
DETERMINATION OF TRACE ELEMENTS IN FOODS

Element	Determined in	Reagent (method)	Ref.
Zr	Table salt	2'-Quinolylfluorone	39
Mo	Milk	Dithiol	551
	Rye, fish	Dithiol	516
Fe	Sugar	2-Nitroso-5-dimethylaminophenol	245
Ni	Margarine	Dimethylglyoxime plus oxid.	552
Cu	Sugar, cocoa	Pyridine-2-aldehyde-2'-pyridylhydrazone	553
	Fish, milk	Dithizone	550, 554
		Na-DDTC	521
Cd	Meat	Dithizone	550, 555, 555a
Hg	Fish, milk	$Pb(DDTC)_2$	554
	Meat	Dithizone	555, 555a
	Fish	Dithizone	550, 556
Sn		Quercetin	550, 557, 558
Pb	Meat	Dithizone	550, 555, 555a
B	Milk	1,1'-Dianthrimide	559
NH_3		Indophenol method	560
NO_3^-	Meal	Red. to NH_3, indophenol	561
P	Flour	Det. U in UO_2Mg phosphate	474
		P-Mo blue	562
	Fish	As Mo-V-P-acid	563
As	Meat	As-Mo blue	550, 555
		Ag-DDTC	550
SO_2	Wine	Pararosaniline method	564
Br^-	Rice, barley	Phenol red method	565
I^-	Milk	Tetrabase plus chloramine T	566

concentration, and determination of trace elements. According to the author of the survey,[550] despite the growth of other instrumental methods, especially of atomic absorption, spectrophotometric procedures in food analysis are still widely used and are of interest as they require relatively simple and cheap equipment and are attractive to small laboratories.

Nitrogen content in grain-meal samples was determined with an autoanalyzer.[561] Also sulfurous acid was automatically determined in wine.[564] In the analysis of meat samples for traces of Cd, Hg, Pb, and As content, pressure digestion method with oxygen was applied.[555,555a]

C. Geological Samples

Elements found in rocks and minerals in quantities smaller than 0.01% are called microelements. According to Zolotov and Blyum[567] trace analysis of geological samples was successful in determining 34 elements. Discussing different instrumental methods for this purpose, the authors[567] consider that in the case of determining many trace elements (As, Au, B, Bi, Co, Cu, F, Ge, Hg, Mo, Nb, Ni, Sb, Se, Ta, Te, Tl, W, Zn) the role of spectrophotometric methods is all-important. Since geological samples are very complex, separation and preconcentration methods are of paramount importance. Extraction, coprecipitation, distillation of the microcomponents or of the accompanying elements are frequently used. According to Zolotov and Blyum the prospect of determining all or most microelements in geological materials by instrumental methods alone will apparently not be realized in the near future. Chemical separation and concentration remains an important stage of geological sample analysis.

Table 12 presents the papers devoted to trace analysis of geological samples. In determining some microelements, ion-exchangers are applied.[572-575,583,586,592] An automated spectrophotometric determination of phosphorus in silicate rocks in the presence of silicon was proposed.[602]

D. Metals and Alloys

These materials are discussed in the following order: steels and cast iron (Table 13), light (Al, Ti) (Table 14), heavy (Cu, Ni, Co, Zn, Cd, Pb, U) (Table 15), refractory (Zr, Mo, W, Nb, W) (Table 16), and noble metals (Ag, Au, Pt) (Table 17).

In trace analysis of metals and their alloys, all chemical methods of separation and enrichment of traces are used. In order to indicate methods in use, some examples will be discussed.

Extraction methods are widely applied. Traces of arsenic,[637,694] tin,[627,628] and antimony,[652] are extracted from iodide medium. Indium[670] and thallium[672] are extracted as bromides, and gallium,[642] and zinc (using tri-*n*-octylamine in CCl_4)[641] as chloride complexes. Traces of tantalum were separated from a niobium matrix in the form of fluoride complex.[697] Traces of bismuth were separated using DDTC and xanthate extraction,[654] traces of thallium — as DDTC complex,[692] traces of zirconium — as TTA complex,[660] and traces of titanium — as cupferron complex.[687] Traces of Ag, Hg, and Cu were extracted as dithizonates.[674] Examples of extractive removal of the matrix are: extraction of iron[632] and gold[701,703] from HCl medium, and extraction of Nb, Ta, Mo, and W as cupferronates.[689]

Traces of tin were separated by flotation with iron(III) hydroxide and paraffin,[673] and zirconium was separated by froth flotation.[661]

The cation-exchanger Amberlite IR-120 was used for separating trace amounts of Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in the analysis of a platinum-rhodium(10) alloy.[702] Traces of calcium were retained on cation-exchangers in the analysis of steel,[610] aluminum alloy,[639] cobalt,[665] and molybdenum.[683] Traces of manganese were separated on Dowex 50 from an uranium matrix using the medium MIBK-acetone-HNO_3.[678] The

Table 12
DETERMINATION OF TRACE ELEMENTS IN GEOLOGICAL SAMPLES[a]

Element	Determined in	Reagent (method)	Ref.
Be		Beryllon II	567
Sc		Sulfonitrazo R	568
REE		Arsenazo III	569, 570
Th	Yellow cake	Arsenazo III, thoron I	571—573
	Mn-nodule	Arsenazo III	574
U		Arsenazo III	573, 575
Ti	Chromite	Tiron	576
Zr		Arsenazo III	573
	Ilmenite, phosphorite	Arsenazo III	577, 578
		Xylenol orange	579
V		BPHA	580
		3,5-Br-MEPADAP	194
Nb	Ilmenite	Sulfochlorophenol S	577
		Sulfonitrophenol M	204
		o-nitrophenylfluorone	581
		PAR	582
Ta		TaF_6^- with basic dyes	567
Mo		Thiocyanate	583
	Cu-Pb ores	Dithiol	516, 584
W		Dithiol	584
		Thiocyanate	585
Re	Cu-concentrate	α-Furildioxime, SCN^-	230
		Ethylrhodamine B	567
Co	Meteorites	5-Br-PADAB	254
	U-minerals	Nitroso-R salt	586, 587
Ni	Basaltic rocks	α-Furildioxime, H_2Dm	587, 588
Pd		Palladiazo	589
Pt	Ores	$SnCl_2$ method	589a
Cu		Cuproine, DDTC	567
		Dithizone	587
Au	Ores	$AuCl_4^-$ with basic dyes	567, 590
Zn	Fe-ores	PAN, dithizone	567, 587, 591
Cd	U-minerals	Dithizone	592
Hg	Sulfide minerals	Dithizone	593
Ga	Ores	Rhodamine B	567, 594
Ge	Zn-concentrate	Salicylfluorone	322
		Phenylfluorone	567
		Assoc. with basic dyes	323, 595
Sn		Phenylfluorone	596
	Ores	Pyrocatechol violet	597
		Assoc. with brilliant green	598
Pb		Dithizone	567
Sb		Rhodamine B	335
B	Shale	Azomethine H	463
	Magnesite	Carmine	599, 600
		Crystal violet	567
P		P-Mo blue	601, 602
As		As-Mo blue	567, 603
Se		3,3'-Diaminobenzidine	567
	Ores	Dithizone	392
	Ores	*o*-Phenylenediamine	390
Te	Ores	Naphthylbismuthiol	604
F^-	Felsite	La-alizarin complexone	605, 606
		Zr-eriochrome cyanine R	607
Cl^-		Iron(III) plus $Hg(SCN)_2$	607
I^-		Amplif. starch-iodine m.	608
		Butylrhodamine B	609

[a] Silicate rocks and minerals.

Table 13
DETERMINATION OF TRACE ELEMENTS IN STEELS AND CAST IRON

Element determined	Reagent (method)	Ref.
Ca	Chlorophosphonazo III	610
Sc (iron)	Xylenol orange	611
REE	Carboxynitrazo	170
	Arsenazo III	612
Ti	DAM plus $SnCl_2$	613
	N-furoylphenylhydroxylamine plus phenylfluorone	138
Zr	Catechol violet	614
	Arsenazo III	615, 616
V	BPHA	580
	Sulfonitrazo	617
Nb	PAR	618
	Thiocyanate	619
	Sulfochlorophenol S	620
Ta	TaF_6^- with nitrochrompirazol	209
Pd	Dithiopyrylmethane	621
Ag (iron)	$AgBr_2^-$ with ethyl violet	282
Cu	Neocuproine	622
Cd	Dithizone	622
Al (iron)	Pyrocatechol violet	623
	Eriochrome cyanine R	624
	Chrome azurol KS	625
Ga	Rhodamine B	626
In	Dithizone	622
Sn	Phenylfluorone	622
	3′-Pyridylfluorone	627
	Pyrocatechol violet plus CTA	628
Pb	Dithizone	622
Sb	Ag-DDTC	629
	Safranine T	630
	Methylfluorone	631
Bi	Iodide	632
B (iron)	Curcumin	633
	BF_4^- with methylene blue	634
	BF_4^- with Nile blue A	618
P	As Mo-V-P acid	635
As (iron)	Ag-DDTC	629, 636
	As-Mo blue	637
Te	As tellurium sol	638
	$TeBr_6^{2-}$ with rhodamine 6G	70

anion-exchanger Amberlite IRA-400 was used in separating traces of lead from a cobalt matrix.[667] Traces of silver were retained on the anion-exchanger (Cl^-) and washed out with ammonia (in analysis of copper).[650]

Examples of separation of traces by coprecipitation follow. Silver cyanide is a suitable collector for highly selective enrichment of traces of palladium.[649] Traces of mercury were coprecipitated with silver iodide,[704] and traces of copper (as cuprizone complex) with silver bromide,[663] traces of silver with thallium(I) bromide.[650] Traces of antimony (in analysis of steel) were separated with MnO_2aq.[631] Traces of selenium (from lead and copper matrix) were coprecipitated (as SeO_4^{2-}) with $PbSO_4$.[657] Traces of Tl(III), Ga, In, Bi, and Al (in analysis of cadmium) were separated at pH 4.6 with $Fe(OH)_3$ as the collector.[674]

Table 14
DETERMINATION OF TRACE ELEMENTS IN LIGHT METALS

Element determined	Reagent (method)	Ref.
	Aluminum and its alloys	
Ca (alloys)	Chlorophosphonazo III	639
Ti	DAM plus $SnCl_2$	613
	N-furoylphenylhydroxylamine plus phenylfluorone	138
Zr, Hf (alloys)	Arsenazo III	640
V (alloys)	BPHA	580
Ag	$AgBr_2^-$ with ethyl violet	282
Zn	Dithizone	641
Ga	Hematein	642
P (Si alloys)	P-Mo blue	643
	As Mo-V-P acid	644
	Titanium	
Nb	PAR	645
	o-Nitrophenylfluorone	38
Al	Chrome azurol S plus CTA	97
N (as NH_3)	Indophenol method	646
S	Methylene blue method	647

The method of preconcentration of the trace elements by the partial dissolution of the matrix metal deserves mention here. In the analysis of high-purity zinc, using this method, a trace concentrate was obtained, containing Ag, Au, Bi, Cd, Co, Ni, Pb, Pd, Sn, and Tl.[669]

Before determining traces of As, P, and Si, the gold or platinum matrix can be electrolytically removed.[707]

Before its determination, arsenic (in analysis of iron and steel) was evolved as AsH_3.[636] Traces of sulfur from boron, tungsten, and copper, were evolved as sulfur dioxide and determined with pararosaniline method.[695,696]

E. Semiconductor Materials

Table 18 contains recently published works on trace determinations in simple semiconductor materials: metals (gallium, indium, antimony, bismuth) and nonmetals (silicon, arsenic, selenium, tellurium). In addition, there are the trace analyses of some semiconductor compounds: determination of traces of silver, with dithizone in cadmium-mercury telluride,[723] and in lead-, tin-, germanium tellurides;[724] traces of chloride and bromide were determined indirectly with dithizone in lead- and bismuth tellurides.[725]

F. Trace Analysis of Reagents

The reagents used in trace analysis have to be more pure than the materials analyzed. Some procedures devoted to the control of purity of these reagents have been published.

High-purity nitric and hydrofluoric acids were analyzed (according to the scheme of separation given in Reference 3 (page 82) for 18 trace metals (Ag, Hg, Cu, Ca, Mg, Ga, Al, In, Bi, Ti, Fe, Tl, Pb, Mn, Cd, Zn, Co, Ni) (contents not greater than about $10^{-6}\%$).[726] Traces of Si, B, As, and P were determined in various mineral acids.[466,727,728] Iron was

Table 15
DETERMINATION OF TRACE ELEMENTS IN HEAVY METALS

Element determined	Reagent (method)	Ref.
	Copper and its alloys	
Pd (Ni alloy)	4-Heptanone oxime	648
	Iodide	649
Ag	Bromopyrogallol red	650
	$AgBr_2^-$ with ethyl violet	282
Au	$AuCl_4^-$ with chrompyrazol I	287
	Thio-Michler's ketone	288
Al	Chrome azurol KS	625
(alloy)	Chrome azurol S plus surfactant	651
Sb	Pyrocatechol violet	652
Bi (brass)	Iodide	653, 654
B (alloys)	Curcumin	655
P	As Mo-V-P acid	644
S	Pararosaniline method	656
Se	*o*-Phenylenediamine	390
	3,3′-Diaminobenzidine	657, 658
Te (brass)	$TeBr_6^{2-}$ with DAM	659
	Nickel and its alloys	
Zr (alloys)	Arsenazo III	660, 661
Co	PAN	662
Pd	Iodide	652
Cu	Bathocuproine	663
Sn	Phenylfluorone	664
B (alloys)	Curcumin	655
P (alloys)	As Mo-V-P acid	644
	Cobalt	
Ca	Chlorophosphonazo III	665
Fe	Bathophenanthroline	666
Zn	Dithizone	666
Pb	Dithizone	667
S	Methylene blue method	668
	Zinc	
Zr, Hf	Arsenazo III	640
Ni	Dimethylglyoxime	669
Pd	Iodide	669
Cu	Na-DDTC	669
Ag	$AgBr_2^-$ with ethyl violet	282
Au	Rhodamine B	669
Cd	Basic azo dye	50
In (alloys)	Bromopyrogallol red	670
Tl (alloys)	Crystal violet	671
	Iodide	672
Sn	Phenylfluorone	673
Bi	Na-DDTC	669

Table 15 (Continued)
DETERMINATION OF TRACE ELEMENTS IN HEAVY METALS

Element determined	Reagent (method)	Ref.
	Cadmium	
Cu, Zn, Hg, Ag, Pb, Bi	Dithizone	674
Mn	PAN	674
Co	1-Nitroso-2-naphthol	674
Ni	α-Furildioxime	674
Al	Chrome azurol S	674
Ga	Rhodamine B	674
In	PAR	674
Tl	Brilliant green, iodide	674, 672
	Lead and its alloys	
Co (alloys)	Thiocyanate	675
Ni	Dimethylglyoxime plus Br_2	676
Cu	Bathocuproine	663
Au	Thio-Michler's ketone	288
Tl	Crystal violet	51
	Iodide	672
Sb (alloys)	Pyrocatechol violet	652
Bi (alloys)	Iodide	654
P (alloys)	Mo-V-P acid	644
Se	3,3'-Diaminobenzidine	657
	Uranium, its alloys and oxides	
Zr	Arsenazo III	677
Nb	PAR	677
Ta (alloys)	Malachite Green	206
Mn (oxide)	Formaldoxime	678
Co	2-Nitroso-5-dimethyl-amino-phenol	679
Si (oxide)	Si-Mo blue	680
F^- (oxide)	Zr-xylenol orange	681

determined in numerous acids with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine[729] and as an ternary complex of Fe(II) with 4-chloro-2-nitrosophenol and rhodamine B.[730]

In high-purity alkali hydroxides, traces of the following were determined: Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Si, Ti, and Zn[731] as well as individual trace elements: Fe (2,2'-bipyridyl ketoxime),[732] Cu (2,9-dimethyl-4,7-dihydroxy-1,10-phenanthroline),[733] W (brilliant green),[220] P and As (P-Mo blue and Ag-DDTC).[728] Traces of Ca were determined in ammonia (chlorophosphonazo III).[157]

Magnesium (10^{-4} -5×10^{-6}%) was determined in sodium chloride (eriochrome black T),[152] traces of Ti in lithium chloride and natrium carbonate (salicylfluorone),[188] Al in alkali metals halogenides (bromo-oxine plus 5-bromosalicylfluorone),[734] Fe in various salts,[730] Cd in sulfur,[297a] Au in nickel chloride and in aluminum nitrate (thio-oxine),[708] W in rhenium salts (gallein plus CTA),[120] and Sn in H_2O_2 solutions (3'-pyridylfluorone).[735]

Traces of boron were determined in phosphorus- and arsenic chlorides,[727] Si in calcium carbonate and sodium phosphate (Si-Mo blue),[466] P and As in silver nitrate and

Table 16
DETERMINATION OF TRACE ELEMENTS IN REFRACTORY METALS

Element determined	Reagent (method)	Ref.
	Zirconium and its alloys	
Ca	Murexide	682
(Mo alloy)	Chlorophosphonazo III	683
Ti (alloys)	DAM	684
Ta	Malachite green	206
Cd (zircaloy)	Dithizone	685
P	As Mo-V-P acid	686
S	Methylene blue method	668
	Molybdenum	
Ti	DAM	687
W	Thiocyanate	688
Mn	PAN	689
N	Indophenol method	690
	Tungsten and its trioxide	
Ti	DAM plus $SnCl_2$	613, 687
Mo (trioxide)	PAR plus NH_2OH	691
Mn	PAN	689
Tl	Methyl violet	692
N	Indophenol method	690
Si (trioxide)	Si-W-Mo blue	693
P (trioxide)	P-W-Mo blue	693
	As P-V-Mo acid	686
As	As-Mo blue	694
S	Cr-diphenylcarbazide (indirect)	695
	Niobium and tantalum	
Ti	Salicylfluorone plus antipyrine	696
	DAM plus $SnCl_2$	613, 684
Ta	Malachite green	697
Mo, W	Dithiol	698
Mn	PAN	689
Cu	Dibenzyl-DTC	699
N (alloys)	Indophenol method	690, 700
P	As P-V-Mo acid	686

ammonium molybdate,[728] perchlorate in potassium chlorate (brilliant green),[416] bromide in alkali metals chlorides,[736] and iodide in alkali metals iodates and chlorides,[737] fluoride traces in sodium phosphate and aluminum sulfate,[402] and in silica gel, sodium silicate, and calcium phosphate.[738]

In the papers referenced in this review dating from the last decade, 52 trace elements were determined spectrophotometrically in various materials (REE are treated as one, as are various forms of nitrogen, of sulfur, and of other elements).

The two elements P and Cu are most often determined; often determined are: Fe, As, S, Ti, Al, Co, Ag, B, Zn, Cd, Pb, N, Mn, Ni, Bi; determined on the average: Si, Cl, Ca, Zr,

Table 17
DETERMINATION OF TRACE ELEMENTS IN NOBLE METALS AND ITS ALLOYS

Element determined	Reagent (method)	Ref.
Ag, Cu, Bi, Zn, Cd, Pb (gold, platinum)	Dithizone	701—703
Zr, Hf (silver)	Arsenazo III	640
Pd (silver)	Sulfonitrophenol M	265
	Iodide	649
Ag (platinum)	Dithizone	703a
Au (silver)	Thio-Michler's ketone	288
Hg (silver)	Dithizone	704
Pd (gold)	α-Furildioxime	703, 705
Pt (gold)	$SnCl_2$ plus TOA	703
(gold)	*p*-Nitrosodiethylaniline	705
Os (platinum—ruthenium)	1,5-Diphenylcarbazide	706
Fe (gold)	Bathophenanthroline	701, 703
(platinum)	Thiocyanate (MIBK)	702
Co (gold, platinum)	2-nitroso-1-naphthol	701, 702
Ni (gold, platinum)	α-Furildioxime	701, 702
Mn (gold, platinum)	PAN	701, 702
Al (gold, platinum)	Eriochrome cyanine R	701, 702
Ga (gold)	Rhodamine B	703
Si, P, As (gold, platinum)	Si(P, As)-Mo blues	707

Sn, Tl, Pd, F, V, Mo, Hg, Ga, In, Sb, Au, Se, Te, Mg, W; rarely determined: Nb, Ta, Br, I, C (as CN^-), Cr, Be, Th, U, REE, Sc, Ge, Pt, O (as O_2 or O_3), Re, Os.

VI. CONCLUSION

Great progress in the field of sensitive spectrophotometric methods for trace analysis has been recently made with the advent of new, sensitive organic reagents, increasing use of ternary systems (with basic dyes and surfactants), and amplification methods. As it has been pointed out in Section IV, sensitive or even very sensitive methods are now available for most elements. Only a few elements are not covered by methods with an a value greater than 0.6. Spectrophotometry can, therefore, successfully compete with other sensitive techniques of trace analysis.

New sensitive spectrophotometric methods and new sensitive reagents are, however, introduced into the practice of trace analysis all too slowly. Comparing the data of Sections IV and V one may see that availability of sensitive methods did not force out the old, less sensitive, ones which are still often used in many laboratories for the determination of traces.

As evidenced by the literature cited in this article, spectrophotometry still plays an important role in the determination of trace elements in various fields. In the latest few years, a decrease in the number of published works dealing with spectrophotometry has been observed. This, however, does not change the fact that in many laboratories, particularly in the small ones, a vast number of routine trace determinations are carried out with the aid of spectrophotometric methods, which can be easily automated and therefore are attractive for routine determinations. It should be stressed that, in general, the spectrophotometric methods in trace analysis are closely connected with preconcentration and separation methods (solvent extraction, ion exchange, coprecipitation, volatilization, electrodeposition).

Table 18
DETERMINATION OF TRACE ELEMENTS IN SEMICONDUCTOR MATERIALS

Element	Determined in	Reagent (method)	Ref.
		Metals	
Ni	Indium	Rhodamine 6G	260
	Antimony	Dimethylglyoxime plus Br_2	676
Au	Indium	Thio-oxine	708
In	Gallium	Malachite green	317
Tl	Indium	Brilliant green	319
		Iodide	672
P	Gallium	P-Mo blue	709
As	Antimony	As-Mo blue	710, 711
Cl^-	Gallium, bismuth	*o*-Tolidine	411
		Nonmetals	
Ti	Silicon	Thiocyanate	712
V	Silicon	*N*-phenylhydroxamic acid	712
Fe	Silicon	Bathophenanthroline	712, 713
	Selenium	Methyl orange plus phen	714
Al	Silicon	Pyrocatechol violet	712
		Eriochrome cyanine R	713
Ag	Tellurium	Pyrogallol red plus phen	715
Cu	Tellurium	Bengal rose plus phen	716
Au	Tellurium	Rhodamine B	717
Zn	Tellurium	Dithizone	717
Ge	Arsenic	Brilliant green	718
B	Silicon	Curcumin	719
		BF_4^- with methylene blue	720
Si	Tellurium	Si-Mo blue	715
P	Silicon	Indir. Mo-SCN^-	721
S	Arsenic	Methylene blue method	722
Se	Tellurium	*o*-Phenylenediamine	390
		Dithizone	716
Cl^-	Selenium, tellurium	*o*-Tolidine	411

For some trace elements, particularly nonmetals, precision and sensitivity of the spectrophotometric methods are higher than those of some other instrumental methods. Elements of this group (B, P, As, Cl, F, I, S, N, Si, Fe, Ti, Cu, Al, Zn, Co) are, of course, determined spectrophotometrically more often than other ones.

In journals dealing with analytical chemistry there are numerous reports on new spectrophotometric methods (and reagents) which are often revealed as inferior to the majority of those in present use. Although the research significance of these papers can by no means be denied, they are of no value for trace and even classical analysis. On the other hand, publication of papers concerned with comparing and evaluating the methods for determining particular elements is strongly encouraged. Research on optimization of the known methods should be also given more attention.

SYMBOLS AND ABBREVIATIONS

a — Specific absorptivity
BPHA — *N*-benzoyl-*N*-phenylhydroxylamine
CP — Cetylpyridinium ion
CTA — Cetyltrimethylammonium ion
DAM — Diantipyrylmethane
DDTC — Diethyldithiocarbamate
DTC — Dithiocarbamate
ϵ — Molar absorptivity
EDTA — Ethylenediaminetetraacetic acid (or its disodium salt)
H_2Dz — Dithizone
MIBK — Methyl isobutyl ketone, hexone
oxine — 8-Hydroxyquinoline, 8-quinolinol
PAN — 1-(2-Pyridylazo)-2-naphthol
PAR — 4-(2-Pyridylazo) resorcinol
phen — 1,10-Phenanthroline
REE — Rare earth elements
TAR — 4-(2-Thiazolylazo) resorcinol
TBP — Tri-*n*-butyl phosphate
TOPO — Tri-*n*-octylphosphine oxide
TPTZ — 2,4,6-Tri(2′-pyridyl)-*s*-triazine
TTA — Thenoyltrifluoroacetone

REFERENCES

1. **Sandell, E. B. and Onishi, H.**, *Photometric Determination of Traces of Metals. General Aspects*, 4th ed., John Wiley & Sons, New York, 1978.
2. **Sandell, E. B.**, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959.
3. **Marczenko, Z.**, *Spectrophotometric Determination of Elements*, Horwood-Wiley, Chichester, England, 1976.
4. **Koch, O. G. and Koch-Dedic, G. A.**, *Handbuch der Spurenanalyse*, 2nd ed., Springer-Verlag, Berlin, 1974.
5. **Charlot, G.**, *Dosages Absorptiométriques des Éléments Minéraux*, 3rd ed., Masson, Paris, 1978.
6. **Boltz, D. F. and Howell, J. (Eds.)**, *Colorimetric Determination of Nonmetals*, 2nd ed., John Wiley & Sons, New York, 1978.
7. **Nazarenko, V. A. and Flyantikova, G. V.**, *Zh. Anal. Khim.*, 32, 1217 (1977).
8. **Savvin, S. B.**, *Crit. Rev. Anal. Chem.*, 8, 55 (1979).
9. **Ayres, G. H. and Narang, B. D.**, *Anal. Chim. Acta*, 24, 241 (1961).
10. **Yarbro, S. and Flaschka, H. A.**, *Microchem. J.*, 21, 415 (1976).
11. **Tölg, G.**, *Talanta*, 19, 1489 (1972); 21, 327 (1974).
12. **Jackwerth, E., Mizuike, A., Zolotov, Y. A., Berndt, H., Höhn, R., and Kuzmin, N. M.**, *Pure Appl. Chem.*, 51, 1195 (1979).
13. **Marczenko, Z.**, *Zavod. Lab.*, 45, 1 (1979).
14. **Vanderborght, B. M. and Van Grieken, E.**, *Anal. Chem.*, 49, 311 (1977).
15. **Tölg, G.**, *Pure Appl. Chem.*, 50, 1075 (1978).
16. **Mizuike, A. and Pinta, M.**, *Pure Appl. Chem.*, 50, 1519 (1978).
17. **Hughes, R. C., Mürau, P. C. and Gunderson, G.**, *Anal. Chem.*, 43, 691 (1971).
18. **Kuehner, E. C., Alvarez, R., Paulsen, P. J., and Murphy, T. J.**, *Anal. Chem.*, 44, 2050 (1972).
19. **Al-Sibaai, A. A. and Fogg, A. G.**, *Analyst*, 98, 732 (1973).
20. **Struempler, A. W.**, *Anal. Chem.*, 45, 2251 (1973).
21. **Rothman, L. D., Crouch, S. R., and Ingle, J. D., Jr.**, *Anal. Chem.*, 47, 1226 (1975).
22. **Marczenko, Z. and Minczewski, J.**, in *Achievements of Analytical Chemistry* (in Russian), Izd. Nauka, Moscow, 1974, 164.
23. **Koch, O. G.**, *Pure Appl. Chem.*, 50, 1531, 1951 (1978).
24. **Perrin, D. D.**, *Masking and Demasking of Chemical Reactions*, Interscience, New York, 1970.
25. **Perrin, D. D.**, *Crit. Rev. Anal. Chem.*, 5, 85 (1975).
26. **Holzbecher, Z., Diviš, L., Kral, M., Sucha, L. and Vlačil, F.**, *Handbook of Organic Reagents in Inorganic Analysis*, Horwood-Wiley, Chichester, England, 1976.
27. **Sommer, L., Langova, M. and Kubaň, V.**, *Scripta Fac. Sci. Nat. Univ. Purkynianae Brun.*, 8, 13 (1978).
28. **Irving, H. M. N. H.**, *Dithizone*, Burlington House, London, 1977.
29. **Iwantscheff, G.**, *Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse*, 2nd ed., Verlag Chemie, Weinheim, Germany, 1972.
30. **Savvin, S. B.**, *Organic Reagents of Arsenazo III Group* (in Russian), Atomizdat, Moscow, 1971.
31. **Ivanov, V. M.**, *Usp. Khim.*, 45, 456 (1976).
32. **Shibata, S., Furukawa, M., and Tôei, K.**, *Anal. Chim. Acta*, 66, 397 (1973).
33. **Shibata, S., Kamata, E., and Nakashima, R.**, *Anal. Chim. Acta*, 82, 169 (1976).
34. **Johnson, D. A. and Florence, T. M.**, *Talanta*, 22, 253 (1975).

35. Hovind, H. R., *Analyst,* 100, 769 (1975).
36. Nazarenko, V. A. and Antonovich, V. P., *Trihydroxyfluorones* (in Russian), Izd. Nauka, Moscow, 1973.
37. Asmus, E. and Kraetsch, J., *Z. Anal. Chem.,* 223, 401 (1966).
38. Nazarenko, V. A. and Yagnyatinskaya, G. Y., *Zavod. Lab.,* 38, 1427 (1972); 40, 21 (1974).
39. Asmus, E. and Klank, W., *Z. Anal. Chem.,* 265, 260, 267 (1973).
40. Singh, R. B., Garg, B. S., and Singh, R. P., *Talanta,* 26, 425 (1979).
41. Peshkova, V. M., Savostina, V. M., and Ivanova, E. K., *Oximes* (in Russian), Izd. Nauka, Moscow, 1977.
42. Majumdar, A. K., *N-Benzoylphenylhydroxylamine and Its Analogues,* Pergamon Press, Oxford, 1972.
43. Katyal, M. and Prakash, S., *Talanta,* 24, 367 (1977).
44. Schilt, A. A., *Analytical Applications of 1,10-Phenanthrolines and Related Compounds,* Pergamon Press, New York, 1969.
45. Pilipenko, A. T. and Tananaiko, M. M., *Talanta,* 21, 501 (1974).
46. Tananaiko, M. M. and Pilipenko, A. T., *Zh. Anal. Khim.,* 32, 430 (1977).
47. Marczenko, Z., *Chem. Anal. (Warsaw),* 24, 551 (1979).
48. Blum, I. A., *Extractive-Photometric Methods of Analysis with Use of Basic Dyes* (in Russian), Izd. Nauka, Moscow, 1970.
49. Marczenko, Z., *Mikrochim. Acta,* II, 651 (1977).
50. Kish, P. P., Balog, I. S., Spivakov, B. Y., and Zolotov, Y. A., *Zh. Anal. Khim.,* 31, 1114 (1976).
51. Alexandrow, A. and Dimitrow, A., *Mikrochim. Acta,* 680 (1972).
52. Burke, R. W., *Talanta,* 17, 240 (1970).
53. Lomonosov, S. A., Sorokin, G. S., and Shukolukova, N. I., *Zh. Anal. Khim.,* 28, 2085 (1973).
54. Blum, I. A. and Brushtein, N. A., *Zh. Anal. Khim.,* 31, 1669 (1976).
55. Ackermann, G. and Köthe, J., *Chem. Anal. (Warsaw),* 17, 445 (1972).
56. Fogg, A. G., Burgess, C., and Burns, D. T., *Talanta,* 18, 1175 (1971).
57. Courtot-Coupez, J. and Guerder, P., *Bull. Soc. Chim. Fr.,* 1961, 1942.
58. Mirzoyan, F. V., Tarayan, V. M., and Karapetyan, Z. A., *Zh. Anal. Khim.,* 34, 1515 (1979).
59. Babko, A. K. and Ivashkovich, E. M., *Zh. Anal. Khim.,* 27, 120 (1972).
60. Chwastowska, J. and Pruszkowski, K., *Chem. Anal. (Warsaw),* 21, 525 (1976).
61. Ganago, L. I. and Prostak, I. A., *Zh. Anal. Khim.,* 26, 104 (1971).
62. Flyantikova, T. V. and Korolenko, L. I., *Zh. Anal. Khim.,* 30, 1349 (1975).
63. Ganago, L. I. and Ivanova, I. F., *Zh. Anal. Khim.,* 27, 713 (1972).
64. Marczenko, Z. and Uścińska, J., *Anal. Chim. Acta,* 123, 271 (1981).
65. Marczenko, Z. and Jarosz, M., Talanta, in press.
66. Pilipenko, A. T. and Shkaravskii, Y. F., *Zh. Anal. Khim.,* 29, 716 (1974).
67. Marczenko, Z. and Maruszak, J., *Chem. Anal. (Warsaw),* 24, 341 (1979).
68. Marczenko, Z. and Kowalczyk, E., *Anal. Chim. Acta,* 108, 261 (1979).
69. Gołkowska, A. and Pszonicki, L., *Talanta,* 20, 749 (1973).
70. Skripchuk, V. G. and Murashova, V. I., *Zh. Anal. Khim.,* 29, 1823 (1974); 32, 452 (1977).
71. Ivanova, I. F. and Ganago, L. I., *Zh. Anal. Khim.,* 30, 1395 (1975).
72. Dedkov, Y. M. and Podvigina, T. I., *Zh. Anal. Khim.,* 32, 437 (1977).
73. Bailey, B. W., Dagnall, R. M., and West, T. S., *Talanta,* 13, 753 (1966).
74. Dagnall, R. M., El-Ghamry, M. T., and West, T. S., *Talanta,* 15, 1353 (1968).
75. Tananaiko, M. M. and Bilenko, N. S., *Zh. Anal. Khim.,* 30, 689 (1975).
76. Tananaiko, M. M. and Bilenko, N. S., *Zavod. Lab.,* 42, 761 (1976); Zh. Anal. Khim., 34, 1899 (1979).
77. El-Ghamry, M. T. and Frei, R. W., *Anal. Chem.,* 40, 1986 (1968).
78. Tananaiko, M. M. and Bilenko, N. S., *Zavod. Lab.,* 42, 1161 (1976).
79. Alinovskaya, L. A. and Ganago, L. I., *Zh. Anal. Khim.,* 25, 2347 (1970).
80. Kobyakova, S. O., Savostina, V. M., and Peshkova, V. M., *Zh. Anal. Khim.,* 29, 300 (1974).
81. Stolyarov, K. P. and Firyulina, V. V., *Zh. Anal. Khim.,* 33, 2102 (1978).
82. Hulanicki, A. and Nieniewska, J., *Talanta,* 21, 896 (1974).
83. Gershuns, A. L., Adamovich, L. P., and Skorobogatov, V. M., *Zh. Anal. Khim.,* 29, 1905 (1974).
84. Skorobogatov, V. M., Gershuns, A. L., Adamovich, L. P., and Kogan, I. M., *Zh. Anal. Khim.,* 30, 1704 (1975).
85. Skorobogatov, V. M., Gershuns, A. L., and Adamovich, L. P., *Zh. Anal. Khim.,* 32, 1450 (1977).
86. Svoboda, V. and Chromy, V., *Talanta,* 12, 431, 437 (1965); 13, 237 (1966).
87. Dagnall, R. M., West, T. S., and Young, P., *Analyst,* 92, 27 (1967).
88. Bailey, B. W., Chester, J. E., Dagnall, R. M., and West, T. S., *Talanta,* 15, 1359 (1968).
89. Sommer, L. and Kubaň, V., *Collect. Czech. Chem. Commun.,* 32, 4355 (1967).
90. Chester, J. E., Dagnall, R. M., and West, T. S., *Talanta,* 17, 13 (1970).
91. Tananaiko, M. M. and Vdovenko, O. P., *Zh. Anal. Khim.,* 30, 1095 (1975); 32, 1121 (1977).

92. Leong, C. L., *Talanta*, 18, 845 (1971).
93. Chernova, R. K., Kharlamova, L. N., Belousova, V. V., Kulapina, E. G., and Sumina, E. G., *Zh. Anal. Khim.*, 33, 858 (1978).
94. Ashton, A., Fogg, A. G., and Burns, D. T., *Analyst*, 98, 202 (1973).
95. Marczenko, Z. and Kałowska, H., *Chem. Anal. (Warsaw)*, 22, 935 (1977).
96. Tikhonov, V. N. and Ekaterinina, L. A., *Zh. Anal. Khim.*, 30, 1507 (1975).
97. Tikhonov, V. N. and Karpeeva, L. A., *Zh. Anal. Khim.*, 33, 2267 (1978).
98. Evtimova, B. and Nonova, D., *Anal. Chim. Acta*, 67, 107 (1973).
99. Evtimova, B., *Anal. Chim. Acta*, 68, 222 (1974).
100. Leong, C. L., *Anal. Chem.*, 45, 201 (1973).
101. Evtimova, B., *Anal. Chim. Acta*, 83, 397 (1976).
102. Marczenko, Z. and Kałowska, H., *Microchem. J.*, 23, 71 (1978).
103. Tikhonov, V. N. and Vashurkina, E. A., *Zh. Anal. Khim.*, 33, 1298 (1978).
104. Marczenko, Z. and Kałowska, H., *Mikrochim. Acta*, 2, 507 (1979).
105. Marczenko, Z. and Kałowska, H., *Chem. Anal. (Warsaw)*, 25, 555 (1980).
106. Tikhonov, V. N. and Samarkina, T. V., *Khim. Khim. Tekhnol.*, 21, 1116 (1978).
107. Marczenko, Z. and Kałowska, H., *Anal. Chim. Acta*, 123, 279 (1981).
108. Duchkova, H., Malat, M., and Čermakova, L., *Anal. Lett.*, 9, 487 (1976).
109. Tikhonov, V. N., Petukhova, Y. A., and Vashurkina, Y. A., *Khim. Khim. Tekhnol.*, 21, 43 (1978).
110. Uesugi, K. and Miyawaki, M., *Microchem. J.*, 21, 438 (1976).
111. Uesugi, K. and Shigematsu, T., *Anal. Chim. Acta*, 84, 377 (1976).
112. Uesugi, K. and Miyawaki, M., *Bunseki Kagaku*, 27, 209 (1978).
113. Ramakrishna, T. V. and Murthy, R. S. S., *Talanta*, 26, 499 (1979).
114. Chernova, R. K., *Zh. Anal. Khim.*, 32, 1477 (1977).
115. Savvin, S. B., Chernova, R. K., Belousova, V. V., Sukhova, L. K., and Shtykov, S. N., *Zh. Anal. Khim.*, 33, 1473 (1978).
116. Nazarenko, V. A., Ibragimov, G. I., Połuektova, E. N., and Shitareva, G. G., *Zh. Anal. Khim.*, 33, 938 (1978).
117. Chernova, R. K., Sukhova, L. K., and Amelin, V. G., *Zh. Anal. Khim.*, 33, 1934 (1978).
118. Mori, I., Fujita, Y., Nakamura, N., and Enoki, T., *Bunseki Kagaku*, 26, 344 (1977).
119. Poluektov, N. S., Lauer, R. S., and Ovchar, L. A., *Zh. Anal. Khim.*, 28, 1490 (1973).
120. Nazarenko, V. A., Poluektova, E. N., Shitareva, G. G., and Ibragimov, G. I., *Zavod. Lab.*, 44, 929 (1978).
121. Shijo, Y. and Takeuchi, T., *Bunseki Kagaku*, 22, 1341 (1973).
122. Wyganowski, C., *Mikrochim. Acta*, 1979 I, 399.
123. Belousova, V. V. and Chernova, R. K., *Zh. Anal. Khim.*, 32, 1669 (1977); Zavod. Lab., 44, 658 (1978).
124. Sekine, K., *Z. Anal. Chem.*, 273, 103 (1975).
125. Sekine, K., *Mikrochim. Acta*, 1976 II, 559.
126. Ueda, K., *Bull. Chem. Soc. Jpn.*, 52, 1215 (1979).
127. Korenaga, T., Motomizu, S., and Tôei, K., *Anal. Chim. Acta*, 104, 369 (1979).
128. Kudryavtseva, L. M. and Chernova, R. K., *Zavod. Lab.*, 44, 522 (1978).
129. Röbisch, G., *Chem. Anal. (Warsaw)*, 21, 1061 (1976).
130. Savvin, S. B., Chernova, R. K., and Kudryavtseva, L. M., *Zh. Anal. Khim.*, 33, 2127 (1978).
131. Savvin, S. B., Chernova, R. K., and Kudryavtseva, L. M., *Zh. Anal. Khim.*, 34, 66 (1979).
132. Goto, K., Taguchi, S., Fukue, Y., Ohta, K., and Watanabe, H., *Talanta*, 24, 752 (1977).
133. Watanabe, H., *Talanta*, 21, 295 (1974).
134. Sakai, Y., *Bunseki Kagaku*, 28, 10 (1979).
135. Watanabe, H. and Yamaguchi, N., *Bunseki Kagaku*, 28, 154 (1979).
136. Nemodruk, A. A., Arevadze, N. G., Egiazarova, N. V., and Supatashvili, G. D., *Zh. Anal. Khim.*, 34, 1266 (1979).
137. Pilipenko, A. T., Shpak, E. A., and Zulfigarov, O. S., *Zh. Anal. Khim.*, 29, 1074 (1974); 30, 1007 (1975).
138. Pilipenko, A. T., Shpak, E. A., and Eremenko, M. V., *Zh. Anal. Khim.*, 30, 1535 (1975).
139. Ganago, L. I. and Mosina, L. A., *Zh. Anal. Khim.*, 31, 1470 (1976).
140. Tsykhanskii, V. D., Konusova, V. V., and Nazarenko, V. A., *Zh. Anal. Khim.*, 30, 2390 (1975).
141. Olenovich, N. L., Kovalchuk, L. I. and Kozitskaya, E. P., *Zh. Anal. Khim.*, 29, 47 (1974).
142. Halász, A. and Pungor, E., *Talanta*, 18, 557, 569 (1971).
143. Lukin, A. M., Chernyshova, T. V., Avgushevich, I. V., and Kulikova, E. S., *Zavod. Lab.*, 40, 22, (1974).
144. Belcher, R., *Talanta*, 15, 357 (1968); 24, 533 (1977).
145. Flaschka, H. A. and Hornstein, J. V., *Microchem. J.*, 23, 488 (1978).

146. Hinze, W. L. and Humphrey, R. E., *Anal. Chem.*, 45, 385 (1973).
147. Umland, F. and Wünsch, G., *Z. Anal. Chem.*, 213, 186 (1965).
148. Halász, A., Polyak, K. and Pungor, E., *Talanta*, 18, 691 (1971).
149. Malyutina, T. M., Savvin, S. B., Orlova, V. A., Mineeva, B. A., and Kirillova, T. I., *Zh. Anal. Khim.*, 29, 925 (1974).
150. Nishida, H., Nishida, T., and Ohtomo, H., *Bull. Chem. Soc. Jpn.*, 49, 571 (1976).
151. Poluektova, N. S., Meshkova, S. B., Beltyukova, S. V., and Tsepik, E. I., *Zh. Anal. Khim.*,27, 1721 (1972).
152. Marczenko, Z., Mojski, M., and Balcerzak, M., *Mikrochim. Acta*, I, 539 (1975).
153. Pyatnitskii, I. V., Pinaeva, S. G., and Pospelova, N. V., *Zh. Anal. Khim.*, 30, 2316 (1975).
154. Ferguson, J. W., Richard, J. J., O'Laughlin, J. W., and Banks, C. V., *Anal. Chem.*, 36, 796 (1964).
155. Shibata, S., Uchiumi, A., Sasaki, S., and Goto, K., *Anal. Chim. Acta*, 44, 345 (1969).
156. Svoboda, V. and Chromy, V., *Anal. Chim. Acta*, 54, 121 (1971).
157. Marczenko, Z. and Kałowska, H., *Chem. Anal. (Warsaw)*, 21, 183 (1976).
158. Kuczerpa, A. V., *Anal. Chem.*, 40, 581 (1968).
159. Keil, R., *Z. Anal. Chem.*, 253, 15 (1971).
160. Brittain, H. G., *Anal. Chem.*, 49, 969 (1977); Anal. Chim. Acta, 96, 165 (1978).
161. Kemp, P. J. and Williams, M. B., *Anal. Chem.*, 45, 124 (1973).
162. Uesugi, K., *Anal. Chim. Acta*, 49, 597 (1970).
163. Shimizu, T. and Momo, E., *Anal. Chim. Acta*, 52, 146 (1970).
163a. Jurkevičinte, J. and Malat, M., *Collect. Czech. Chem. Commun.*, 44, 3236 (1979).
164. Savvin, S. B., *Talanta*, 8, 673 (1961); 11, 1 (1964).
165. Onishi, H. and Sekine, K., *Talanta*, 19, 473 (1972).
166. Surin, I. G., Spitsyn, P. K., and Barkovskii, V. F., *Zh. Anal. Khim.*, 34, 1103 (1979).
167. Taketatsu, T., Sato, A., Kurihara, H., and Maeda, S., *Anal. Chim. Acta*, 93, 327 (1977).
168. Men'kov, A. A. and Nepomnyashchaya, N. A., *Zh. Anal. Khim.*, 32, 1409 (1977).
169. Savvin, S. B., Petrova, T. V., and Romanov, P. N., *Talanta*, 19, 1437 (1972).
170. Savvin, S. B., Petrova, T. V., and Romanov, P. N., *Zh. Anal. Khim.*, 28, 272 (1973); 29, 1929 (1974).
171. Verhande, C. and Munshi, K. N., *Microchem. J.*, 23, 28 (1978).
172. Belousova, V. V., Chernova, R. K., and Sukhova, L. K., *Zavod. Lab.*, 44, 390 (1978).
173. Bakhmatova, T. K. and Bochkareva, I. A., *Zavod. Lab.*, 42, 1164 (1976).
174. Cospito, M. and Rigali, L., *Anal. Chim. Acta*, 106, 385 (1979).
175. Yamamoto, T., *Anal. Chim. Acta*, 63, 65 (1973).
176. Lukyanov, V. F., Duderova, E. P., Novak, E. F., Barabanova, T. E., and Polyakova, I. A., *Zavod. Lab.*, 42, 1302 (1976).
177. Perez-Bustamante, J. A. and Delgado, F. P., *Analyst*, 96, 407 (1971).
178. Keil, R., *Z. Anal. Chem.*, 297, 384 (1979).
179. Strelow, F. W. and Van der Walt, T. N., *Talanta*, 26, 537 (1979).
180. Yamamoto, T., *Anal. Chim. Acta*, 65, 329 (1973).
181. Bykhovtsova, T. T. and Tserkovnitskaya, I., A., *Zh. Anal. Khim.*, 32, 745 (1977).
182. Dubey, S. C. and Nadkarni, M. N., *Talanta*, 24, 266 (1977).
183. Tarayan, V. M., Ovsepyan, E. N., and Petrosyan, A. A., *Zh. Anal. Khim.*, 26, 322 (1971).
184. Tribalat, S. and Caldero, J. M., *Bull. Soc. Chim. Fr.*, 3187 (1964).
185. Tananaiko, M. M. and Lozovik, A. S., *Zh. Anal. Khim.*, 24, 844 (1969).
186. Talipov, S. T., Karibyan, E. E., Shesterova, I. P., and Smolkova, O. A., *Zh. Anal. Khim.*, 32, 724 (1977).
187. Tamhina, B., Maul, V., and Herak, M. J., *Microchem. J.*, 22, 275 (1977).
188. Antonovich, V. P., Shelikhina, E. I., and Lozovaya, S. A., *Zh. Anal. Khim.*, 28, 1506 (1973).
189. Pakalns, P., *Anal. Chim. Acta*, 44, 73 (1969).
190. Nemodruk, A. A. and Boganova, A. N., *Zh. Anal. Khim.*, 32, 1131 (1977).
191. Yamamoto, T., Muto, H., and Kato, Y., *Bunseki Kagaku*, 26, 515 (1977).
192. Shtokalo, M. I., Ryzhenko, V. L., and Ostrovskaya, T. V., *Zavod. Lab.*, 44, 925 (1978).
193. Janssen, A. and Umland, F., *Z. Anal. Chem.*, 254, 286 (1971).
194. Kiss, E., *Anal. Chim. Acta*, 77, 205 (1975).
195. Savvin, S. B., Mineeva, V. A., Okhanova, L. A., and Pachadzhanov, D. N., *Zh. Anal. Khim.*, 26, 2364 (1971).
196. Simonzadeh, N., Muraskas, E., and Jaselskis, B., *Talanta*, 26, 935 (1979).
197. Minczewski, J., Chwastowska, J., and Pham thi Hong Mai, *Analyst*, 100, 708 (1975).
198. Pilipenko, A. T. and Eremenko, O. M., *Zh. Anal. Khim.*, 25, 1330 (1970).
199. Lobanov, F. I., Zatonskaya, V. M., and Gibalo, I. M., *Zh. Anal. Khim.*, 29, 826 (1974).
200. Belcher, R., Ramakrishna, T. V., and West, T. S., *Talanta*, 9, 943 (1962); 10, 1013 (1963).
201. Široki, M., Marič, L., Herak, M. J., and Djordjević, C., *Anal. Chem.*, 48, 55 (1976).

202. Belcher, R., Ramakrishna, T. V., and West, T. S., *Talanta,* 12, 681 (1965).
203. Alimarin, I. P., Savvin, S. B., and Okhanova, L. A., *Talanta,* 15, 601 (1968).
204. Gerkhardt, L. I., Okhanova, L. A., Savvin, S. B., and Vagan, V. F., *Zavod. Lab.,* 39, 769 (1973).
204a. Ganago, L. I. and Bukhteeva, L. N., *Zh. Anal. Khim.,* 34, 2186 (1979).
205. Nevzorov, A. N., Mordvinova, S. N., and Kapitsa, A. V., *Zh. Anal. Khim.,* 29, 2281 (1974).
206. Eberle, A. R. and Lerner, M. W., *Anal. Chem.,* 39, 662 (1967).
207. Tarayan, V. M., Ovsepyan, E. N., and Barkhudaryan, S. R., *Zh. Anal. Khim.,* 27, 19 (1972).
208. Elinson, S. V., Nevzorov, A. N., Belogortseva, M. V., Mirzoya, N. A., and Mordvinowa, S. N., *Zh. Anal. Khim.,* 29, 1234 (1974).
209. Podchainova, V. N. and Freidenzon, L. N., *Zh. Anal. Khim.,* 31, 1312 (1976).
210. Adam, J. and Přibil, R., *Talanta,* 21, 616 (1974).
211. Onishi, H. and Koshima, H., *Bunseki Kagaku,* 27, 726 (1978).
211a. Shimogawa, K., Mori, H., and Takada, H., *Bunseki Kagaku,* 28, 437 (1979).
212. Yotsuyanagi, T., Takeda, Y., Yamashita, R., and Aomura, K., *Anal. Chim. Acta,* 67, 297 (1973).
213. Silva, M. E., *Analyst,* 100, 517 (1975).
214. Tamhina, B., Herak, M. J., and Jagodić, V., *Anal. Chim. Acta,* 76, 417 (1975).
215. Haddad, P. R., Alexander, P. W., and Smythe, L. E., *Talanta,* 22, 61 (1975).
216. Savvin, S. B., Mineeva, V. A., Okhanova, L. A., and Pachadzhanov, D. N., *Zh. Anal. Khim.,* 26, 532 (1971).
217. Fogg, A. G., Marriott, D. R., and Burns, D. T., *Analyst,* 95, 848 (1970).
218. Yatirajam, V. and Dhamija, S., *Talanta,* 22, 760 (1975).
219. Chernova, R. K., Kharlamova, L. N., and Belousova, V. V., *Zh. Anal. Khim.,* 32, 2197 (1977).
220. Nazarenko, V. A., Poluektova, E. N., and Shitareva, G. G., *Zh. Anal. Khim.,* 28, 1966 (1973).
221. Marczenko, Z., *Anal. Chim. Acta,* 31, 224 (1964).
222. Adam, J. and Přibil, R., *Talanta,* 19, 1105 (1972).
223. Giné, M. F., Zagatto, E. A., and Filho, H. B., *Analyst,* 104, 371 (1979).
224. Betteridge, D., Fernando, Q., and Freiser, H., *Anal. Chem.,* 35, 294 (1963).
225. Nonova, D. and Evtimova, B., *Talanta,* 20, 1347 (1973).
226. Ahrland, S. and Herman, R. G., *Anal. Chem.,* 47, 2422 (1975).
227. Marczenko, Z. and Mojski, M., *Anal. Chim. Acta,* 54, 469 (1971).
227a. Akaiwa, H., Kawamoto, H., and Kogure, S., *Bunseki Kagaku,* 28, 498 (1979).
228. Savvin, S. B., Petrova, T. V. and Dzherayan, T. G., *Zh. Anal. Khim.,* 33, 516 (1978).
229. Pollock, E. N. and Zopatti, L. P., *Anal. Chim. Acta,* 32, 418 (1965).
230. Stefanov, S., Jordanov, N., and Pavlova, M., *Mikrochim. Acta,* II, 449 (1976).
231. Savariar, C. P. and Hariharan, T. R., *Mikrochim. Acta,* I, 477 (1975).
232. Fogg, A. G., Burgess, C., and Burns, D. T., *Analyst,* 95, 1012 (1970).
233. Gagliardi, E. and Füsselberger, E., *Mikrochim. Acta,* 385 (1972).
234. Tarayan, V. M., Bartanyan, S. V., and Eliazyan, L. A., *Zh. Anal. Khim.,* 24, 1040 (1969).
235. Lebedeva, S. P. and Tarayan, V. M., *Zh. Anal. Khim.,* 30, 1403 (1975).
236. Analytical Methods Committee, *Analyst,* 103, 391 (1978).
237. Perry, R. D. and San Clemente, C. L., *Analyst,* 102, 114 (1977).
238. Analytical Methods Committee, *Analyst,* 103, 521 (1978).
239. Stephens, B. G. and Suddeth, H. A., *Anal. Chem.,* 39, 1478 (1967).
240. Stookey, L. L., *Anal. Chem.,* 42, 779 (1970).
241. Carter, P, *Mikrochim. Acta,* 1972, 410.
242. Schilt, A. A. and Hoyle, W. C., *Anal. Chem.,* 39, 114 (1967).
243. Kiss, E., *Anal. Chim. Acta,* 72, 127 (1974).
244. Tôei, K., Motomizu, S., and Korenaga, T., *Analyst,* 100, 629 (1975).
245. Korenaga, T., *Mikrochim. Acta,* II, 419 (1977).
246. Shijo, Y., *Bull. Chem. Soc. Jpn.,* 48, 2793 (1975).
247. Likussar, W., Wawschinek, O., and Beyer, W., *Anal. Chim. Acta,* 40, 538 (1968).
248. Imai, H. and Yamada, T., *Bull. Chem. Soc. Jpn.,* 42, 237 (1969).
249. Korenaga, T., Motomizu, S., and Tôei, K., *Anal. Chim. Acta,* 65, 335 (1973); Talanta, 21, 645 (1974).
250. Wünsch, G., *Talanta,* 26, 177 (1979).
251. Motomizu, S., *Anal. Chim. Acta,* 64, 217 (1973); Talanta, 21, 654 (1974).
252. Tôei, K. and Motomizu, S., *Analyst,* 101, 497 (1976).
253. Shibata, S., Furukawa, M., Ishiguro, Y., and Sasaki, S., *Anal. Chim. Acta,* 55, 231 (1971).
254. Kiss, E., *Anal. Chim. Acta,* 66, 385 (1973); 77, 320 (1975).
255. Shibata, S., Furukawa, M., and Kamata, E., *Anal. Chim. Acta,* 73, 107 (1974).
256. Kotelanskaya, L. I. and Kish, P. P., *Zh. Anal. Khim.,* 28, 1999 (1973).
257. Minczewski, J., Chwastowska, J., and Lachowicz, E., *Chem. Anal. (Warsaw),* 21, 373 (1976).
258. Zolotov, Y. A. and Vlasova, G. E., *Zh. Anal. Khim.,* 28, 1540 (1973).

259. Afghan, B. K. and Ryan, D. E., *Anal. Chim. Acta,* 41, 167 (1968).
260. Chwastowska, J. and Lachowicz, E., *Chem. Anal. (Warsaw),* 24, 369 (1979).
260a. Toei, K., Motomizu, S., and Yokosu, H., *Anal. Chim. Acta,* 110, 329 (1979).
261. Umland, F. and Thierig, D., *Z. Anal. Chem.,* 197, 151 (1963).
262. Basargin, N. N., Rozovskii, Y. G., and Merzlyakova, A. N., *Zavod. Lab.,* 38, 260 (1972).
263. Savvin, S. B., Propistsova, R. F., and Rozovskii, Y. G., *Zh. Anal. Khim.,* 27, 1554 (1972).
264. El-Ghamry, M. T. and Frei, R. W., *Talanta,* 16, 235 (1969).
265. Gurieva, R. F., Savvin, S. B., Romanov, P. N., Akimova, T. G., and Syanava, E. M., *Zh. Anal. Khim.,* 32, 1009 (1977).
266. Cheng, K. L. and Goydish, B. L., *Microchem. J.,* 10, 158 (1966).
266a. Tsukahara, I., *Bunseki Kagaku,* 28, 253 (1979).
267. Pilipenko, A. T., Danilova, V. N., and Lisichenok, S. L., *Zh. Anal. Khim.,* 25, 1154 (1970).
268. Duchkova, H., Čermakova, L., and Malat, M., *Anal. Lett.,* 8, 115 (1975).
269. Hara, T. and Sandell, E. B., *Anal. Chim. Acta,* 23, 65 (1960).
270. Kamra, L. C. and Ayres, G. H., *Anal. Chim. Acta,* 78, 423 (1975).
271. Goldstein, G., Manning, D. L., Menis, O. and Dean, J. A., *Talanta,* 7, 307 (1961).
272. Marczenko, Z. and Kułaga, J., *Chem. Anal. (Warsaw),* 24, 841 (1979).
273. Turkington, R. W. and Tracy, F. M., *Anal. Chem.,* 30, 1699 (1958).
274. Stoner, R. E. and Dasler, W., *Anal. Chem.,* 32, 1207 (1960).
275. Sims, G. G. and Ryan, D. E., *Anal. Chim. Acta,* 44, 139 (1969).
275a. Koh, T., Aoki, Y., and Suzuki, Y., *Anal. Chem.,* 50, 881 (1978).
276. Shijo, Y., *Bull. Chem. Soc. Jpn.,* 47, 1642 (1974).
276a. Asmus, E., Kossmann, U., and Ortlepp, W., *Z. Anal. Chem.,* 298, 150 (1979).
277. Cheng, K. L., *Mikrochim. Acta,* 1967, 820.
278. Gur'eva, R. F., Trutneva, L. M., and Savvin, S. B., *Zh. Anal. Khim.,* 33, 632 (1978).
278a. Savvin, S. B., Gur'eva, R. F., and Trutneva, L. M., *Zh. Anal. Khim.,* 34, 1493 (1979).
279. Dagnall, R. M. and West, T. S., *Talanta,* 11, 1533 (1964).
280. Tananaiko, M. M. and Gorenshtein, L. I., *Ukr. Khim. Zh.,* 40, 275 (1974).
281. Likussar, W. and Raber, H., *Anal. Chim. Acta,* 50, 173 (1970).
282. Shestidesyatnaya, N. L., Kotelanskaya, L. I., and Chuchulina, I. A., *Zh. Anal. Khim.,* 30, 1303 (1975).
283. Koh, T. and Katoh, M., *Anal. Chim. Acta,* 109, 107 (1979).
284. Nabivanets, B. I., Zadorozhnaya, E. M., and Maslei, N. N., *Zh. Anal. Khim.,* 28, 1901 (1973).
285. Kothny, E. L., *Analyst,* 94, 198 (1969).
286. Stanton, R. E. and McDonald, A. J., *Analyst,* 89, 767 (1964).
287. Gorbunova, N. N., Busev, A. I., and Ivanov, V. M., *Zh. Anal. Khim.,* 25, 461 (1970).
288. Tsukahara, I., *Talanta,* 24, 633 (1977).
289. Pilipenko, A. T., Ryabushko, O. P., and Matsibura, G. S., *Zh. Anal. Khim.,* 34, 1088 (1979).
290. Lichtenstein, I. E., *Anal. Chem.,* 47, 465 (1975).
291. Borissova, R., *Talanta,* 22, 797 (1975).
292. Propistsova, R. F., Savvin, S. B., and Rozovskii, Y. G., *Zh. Anal. Khim.,* 26, 2424 (1971).
293. Ackermann, G. and Köthe, J., *Talanta,* 26, 693 (1979).
294. Shibata, S., Furukawa, M., and Sasaki, S., *Anal. Chim. Acta,* 51, 271 (1970).
295. Flaschka, H. and Weiss, R., *Microchem. J.,* 14, 318 (1969); 15, 653 (1970).
296. Nonova, D., Nenov, V., and Lihareva, N., *Talanta,* 23, 679 (1976).
297. Kish, P. P. and Balog, I. S., *Zh. Anal. Khim.,* 32, 482 (1977).
297a. Kish, P. P. and Balog, I. S., *Zh. Anal. Khim.,* 34, 2326 (1979).
298. Tsubouchi, M., *Anal. Chem.,* 42, 1087 (1970).
299. Tarayan, V. M., Ovsepyan, E. N., and Lebedeva, S. P., *Zh. Anal. Khim.,* 26, 1745 (1971).
299a. De, A. K. and Pal, B. K., *Mikrochim. Acta,* 2, 201 (1979).
300. Pilipenko, A. T., Kish, P. P., and Witenko, G. M., *Ukr. Khim. Zh.,* 40, 850 (1974).
301. Kish, P. P., Spivakov, B. Y., Roman, V. V., and Zolotov, Y. A., *Zh. Anal. Khim.,* 32, 1942 (1977).
302. Ackermann, G. and Röder, H., *Talanta,* 24, 99 (1977).
303. Shibata, S., Furukawa, M., and Nakashima, R., *Anal. Chim. Acta,* 81, 131 (1976).
304. Dougan, W. K. and Wilson, A. L., *Analyst,* 99, 413 (1974).
305. Martynov, A. P., Novak, V. P., and Reznik, B. E., *Zh. Anal. Khim.,* 33, 51 (1978).
306. Biryuk, E. A. and Ravitskaya, R. V., *Zh. Anal. Khim.,* 27, 459 (1972).
307. Prabhu, B. N. and Khopkar, S. M., *Talanta,* 25, 109, (1978).
308. Armeanu, V. and Costinescu, P., *Talanta,* 14, 699 (1967).
309. Fogg, A. G., Burgess, C. and Burns, D. T., *Analyst,* 98, 347 (1973).
310. Kish, P. P. and Bukovich, A. M., *Zh. Anal. Khim.,* 24, 1653 (1969).
311. Tarayan, V. M., Ovsepyan, E. N., and Pogosyan, A. N., *Zavod. Lab.,* 36, 656 (1970).
312. Kish, P. P. and Bukovich, A. M., *Ukr. Khim. Zh.,* 35, 1290 (1969).

313. Uesugi, K. and Shigematsu, T., *Talanta*, 24, 391 (1977).

314. Akhmedly, M. K., Glushchenko, E. L., and Gasanova, Z. L., *Zh. Anal. Khim.*, 26, 1947 (1971).

315. Široki, M. and Herak, M. J., *Anal. Chim. Acta*, 87, 193 (1976).

316. Zolotov, Y. A., Kish, P. P., Bagreev, V. V., and Pogoida, I. I., *Zh. Anal. Khim.*, 29, 221 (1974); 30, 1692 (1975).

317. Kish, P. P. and Pogoida, I. I., *Zh. Anal. Khim.*, 29, 52 (1974).

318. Garčic, A. and Sommer, L., *Collect. Czech. Chem. Commun.*, 35, 1047 (1970).

319. Marczenko, Z., Kałowska, H., and Mojski, M., *Talanta*, 21, 93 (1974).

320. Kish, P. P. and Monich, E. E., *Zh. Anal. Khim.*, 25, 272 (1970).

321. Tarayan, V. M., Ovsepyan, E. N., and Artsruni, V. Z., *Zh. Anal. Khim.*, 25, 691 (1970).

322. Nazarenko, V. A., Makrinich, N. I., and Shustova, M. B., *Zh. Anal. Khim.*, 25, 1595 (1970).

323. Nazarenko, V. A., Lebedeva, N. V., and Vinarova, L. I., *Zh. Anal. Khim.*, 27, 128 (1972).

324. Nazarenko, V. A., Vinarova, L. I., Lebedeva, N. V., and Lyakh, R. A., *Ukr. Khim. Zh.*, 43, 1325 (1977).

325. Dymov, A. M., Ivanov, I. G., and Romantseva, T. I., *Zh. Anal. Khim.*, 26, 2360 (1971).

325a. Kulkarni, V. H. and Good, M. L., *Anal. Chem.*, 50, 973 (1979).

326. Shestidesyatnaya, N. L., Kotelyanskaya, L. I., and Yanik, M. I., *Zh. Anal. Khim.*, 31, 67 (1976).

327. Ackermann, G. and Heegn, H., *Talanta*, 21, 431 (1974).

328. Nazarenko, V. A., Lebedeva, N. V., and Vinarova, L. I., *Zh. Anal. Khim.*, 28, 1100 (1973).

329. Ducret, L. and Maurel, H., *Anal. Chim. Acta*, 21, 79 (1959).

330. Shestidesyatnaya, N. L., Milyaeva, N. M., and Koshelyanskaya, L. I., *Zavod. Lab.*, 41, 653 (1975).

331. Trinder, N., *Analyst*, 91, 587 (1966).

332. Dagnall, R. M., West, T. S., and Young, P., *Talanta*, 12, 583 (1965).

333. Klečkova, Z., Langova, M., and Havel, J., *Collect. Czech. Chem. Commun.*, 43, 3163 (1978).

334. Gusev, S. I. and Nikolaeva, E. M., *Zh. Anal. Khim.*, 24, 1674 (1969).

335. Schnepfe, M. M., *Talanta*, 20, 175 (1973).

336. Fogg, A. G., Jillings, J., Marriott, D. R., and Burns, D. T., *Analyst*, 94, 768 (1969).

337. Yadav, A. A. and Khopkar, S. M., *Bull. Chem. Soc. Jpn.*, 43, 693 (1971).

338. Kish, P. P. and Onishchenko, Y. K., *Zh. Anal. Khim.*, 29, 102 (1974).

339. Kish, P. P., Onishchenko, Y. K., and Pogoida, I. I., *Zh. Anal. Khim.*, 28, 1746 (1973).

340. Kish, P. P. and Onishchenko, Y. K., *Zh. Anal. Khim.*, 26, 514 (1971).

341. Nevskaya, E. M., Antonovich, V. P., and Nazarenko, V. A., *Zh. Anal. Khim.*, 28, 1104 (1973).

342. Antonovich, V. P., Nevskaya, E. M., Suvorova, E. N., and Nazarenko, V. A., *Zh. Anal. Khim.*, 33, 458 (1978).

343. Shestidesyatnaya, N. L. and Milyaeva, N. M., *Ukr. Khim. Zh.*, 41, 84 (1975).

344. Busev, A. I., Shestidesyatnaya, N. L., and Kish, P. P., *Zh. Anal. Khim.*, 27, 298 (1972).

345. Antonovich, V. P., Shelikhina, E. I., Nevskaya, E. M., and Yakovleva, T. P., *Zh. Anal. Khim.*, 30, 1566 (1975).

346. Rosenfeld, H. J. and Selmer-Olsen, A. R., *Analyst*, 104, 983 (1979).

347. Kuwada, K., Motomizu, S., and Tôei, K., *Anal. Chem.*, 50, 1788 (1978).

348. Nicholson, R. A., *Anal. Chim. Acta*, 56, 147 (1971).

349. Buldini, P. L., *Anal. Chim. Acta*, 82, 187 (1976).

350. Kruse, J. M. and Thibault, L. E., *Anal. Chem.*, 45, 2260 (1973).

351. Gilbert, B. L., Olson, B. L., and Reuter, W., *Anal. Chem.*, 46, 170 (1974).

352. Nagashima, S., *Anal. Chim. Acta*, 91, 303 (1977).

353. Dagnall, R. M., El-Ghamry, M. T., and West, T. S., *Talanta*, 15, 107 (1968).

354. Buhl, F. and Kania, K., *Chem. Anal. (Warsaw)*, 24, 689 (1979).

355. Guerrero, A. H. and Roig, A. M., *Anal. Chem.*, 45, 1943 (1973).

356. Koh, T. and Iwasaki, I., *Bull. Chem. Soc. Jpn.*, 40, 569 (1967).

357. Einaga, H. and Ishii, H., *Talanta*, 20, 1017 (1973).

358. Pakalns, P. and Flynn, W. W., *Anal. Chim. Acta*, 38, 403 (1967).

359. Bazzi, A. and Boltz, D. F., *Microchem. J.*, 20, 462 (1975).

360. Pilipenko, A. T. and Shkaravskii, Y. F., *Ukr. Khim. Zh.*, 42, 1183 (1976).

361. Trudell, L. A. and Boltz, D. F., *Talanta*, 19, 37 (1972).

362. Krug, F. J., Ružička, J., and Hansen, E. H., *Analyst*, 104, 47 (1979).

363. Glebko, L. I., Ulkina, Zh. I., and Lognenko, E. M., *Mikrochim. Acta*, II, 641 (1975).

364. Patton, C. J. and Crouch, S. R., *Anal. Chem.*, 49, 464 (1977).

365. Oliver, R., *Analusis*, 6, 126 (1978).

366. Celardin, F., Marcantonatos, M., and Monnier, D., *Anal. Chim. Acta*, 68, 61 (1974).

367. Dougherty, J. A. and Laban, G. A., *Anal. Chem.*, 47, 1130 (1975).

368. Keh-Chung Chao, Higuchi, T., and Sternson, L. A., *Anal. Chem.*, 50, 1670 (1978).

368a. Fox, J. B., Jr., *Anal. Chem.*, 51, 1493 (1979).

369. Elton-Bott, R. R., *Anal. Chim. Acta*, 108, 285 (1979).
370. Norwitz, G. and Keliher, P. N., *Anal. Chim. Acta*, 98, 323 (1978); 109, 373 (1979).
371. Norwitz, G., Farino, J., and Keliher, P. N., *Anal. Chim. Acta*, 105, 335 (1979).
372. Ciesielski, H., Soignet, G., Catoire, M., and Vancayzeele, P., *Analusis*, 6, 38 (1978).
373. Baca, P. and Freiser, H., *Anal. Chem.*, 49, 2249 (1977).
374. Ohashi, K., Yasu, K., Suzuki, C., and Yamamoto, K., *Bull. Chem. Soc. Jpn.*, 50, 3202 (1977).
375. Matsuo, T., Shida, J., and Kurihara, W., *Anal. Chim. Acta*, 91, 385 (1977).
376. Altmann, H. J., Fürstenau, E., Gielewski, A., and Scholz, L., *Z. Anal. Chem.*, 256, 274 (1971).
377. Djurkin, V., Kirkbright, G. F., and West, T. S., *Analyst*, 91, 89 (1966).
378. Morosanova, S. A., Grishko, G. A., and Shkatova, L. A., *Zh. Anal. Khim.*, 29, 529 (1974).
379. Gastinger, E., *Mikrochim. Acta*, 1972, 526.
380. Kopp, J. F., *Anal. Chem.*, 45, 1786 (1973).
381. Basadre-Pampin, M., Alvarez-Devesa, A., Bermejo-Martinez, F., and Bollain-Rodriguez, M. H., *Microchem. J.*, 23, 360 (1978).
382. Budesinsky, B. W., *Microchem. J.*, 24, 80 (1979).
382a. Ganago, L. I. and Ishchenko, N. N., *Zh. Anal. Khim.*, 34, 1768 (1979).
383. Matheson, N. A., *Analyst*, 99, 577 (1974).
384. Kirsten, W. J., *Mikrochim. Acta*, II, 403 (1978).
385. Arikawa, Y., Ozawa, T., and Iwasaki, I., *Bull. Chem. Soc. Jpn.*, 41, 1454 (1968).
386. King, H. G. and Pruden, G., *Analyst*, 94, 43 (1969).
387. Basargin, N. N., Menshikova, Z. S., Biełova, Z. S., and Myasishcheva, R. G., *Zh. Anal. Khim.*, 23, 732 (1968).
388. Reijnders, H. F., Stadeuvan, J. J., and Griepink, B., *Z. Anal. Chem.*, 295, 122 (1979).
389. Hinze, W. L. and Humphrey, R. E., *Anal. Chem.*, 45, 814 (1973).
390. Shkrobot, E. P. and Shebarshina, N. I., *Zavod. Lab.*, 35, 417 (1969).
391. Mabuchi, H. and Nakahara, H., *Bull. Chem. Soc. Jpn.*, 36, 151 (1963).
392. Shcherbov, D. P., Ivankova, A. I., and Gladysheva, G. P., *Zavod. Lab.*, 33, 683 (1967).
393. Osburn, R. L., Shendrikar, A. D., and West, P. W., *Anal. Chem.*, 43, 594 (1971).
394. Marczenko, Z., Krasiejko, M., and Czarnecka, I., *Chem. Anal. (Warsaw)*, 22, 275 (1977).
395. Nazarenko, V. A., Shitareva, G. G., Połuektova, E. N., and Yakovleva, T. P., *Zh. Anal. Khim.*, 29, 1850 (1974).
395a. Nazarenko, V. A., Shitareva, G. G., Połuektova, E. N., and Veshchikova, N. A., *Zh. Anal. Khim.*, 34, 2359 (1979).
396. Shitareva, G. G., Poluektova, E. M., and Nazarenko, V. A., *Zh. Anal. Khim.*, 30, 1166 (1975).
397. Kish, P. P. and Kremeneva, S. G., *Zh. Anal. Khim.*, 25, 2200 (1970).
398. Vijayakumar, M., Ramakrishna, T. V., and Aravamudan, G., *Talanta*, 26, 323 (1979).
399. Analytical Methods Committee, *Analyst*, 96, 384 (1971).
400. Kirsten, W. J. and Shah, Z. H., *Anal. Chem.*, 47, 184 (1975).
401. Haarsma, J. P. and Agterdenbos, J., *Talanta*, 18, 747 (1971).
402. Marczenko, Z. and Lenarczyk, L., *Chem. Anal. (Warsaw)*, 21, 151 (1976).
403. Rudenko, E. I. and Popov, V. A., *Zavod. Lab.*, 45, 388 (1979).
404. Minin, A. A., Barmina, G. A., and Khakhalkina, I. G., *Zh. Anal. Khim.*, 30, 2196 (1975).
405. Deane, S. F. and Leonard, M. A., *Analyst*, 102, 340 (1977).
406. Deane, S. F., Leonard, M. A., McKee, V., and Svehla, G., *Analyst*, 103, 1134 (1978).
407. Dzhashi, D. O., Dedkova, V. P., and Savvin, S. B., *Zh. Anal. Khim.*, 33, 1164 (1978).
408. Jurkevicinte, J. and Malat, M., *Collect. Czech. Chem. Commun.*, 43, 2885 (1978).
409. Laitinen, H. A. and Boyer, K. W., *Anal. Chem.*, 44, 920 (1972).
410. D'Amboise, M. and Meyer-Grall, F., *Anal. Chim. Acta*, 104, 355 (1979).
411. Scheubeck, E. and Ernst, O., *Z. Anal. Chem.*, 249, 370 (1970); 254, 185 (1971).
412. Rodabaugh, R. D. and Upperman, G. T., *Anal. Chim. Acta*, 60, 434 (1972).
413. Florence, T. M. and Farrar, Y. J., *Anal. Chim. Acta*, 54, 373 (1971).
414. Uchikawa, S., *Bull. Chem. Soc. Jpn.*, 40, 798 (1967).
415. Tsubouchi, M., *Anal. Chim. Acta*, 54, 143 (1971).
416. Fogg, A. G., Burgess, C., and Burns, D. T., *Analyst*, 96, 854 (1971).
417. Dodin, E. I. and Kharlamov, I. P., *Zh. Anal. Khim.*, 31, 102 (1976).
418. Likussar, W., Pokorny, G., and Zechman, H., *Anal. Chim. Acta*, 49, 97 (1970).
419. Brown, L. C. and Boyd, G. E., *Anal. Chem.*, 42, 291 (1970).
420. Lomonosov, S. A., Shukolyukova, N. I., and Chernoukhova, V. I., *Zh. Anal. Khim.*, 28, 2389 (1973).
421. Yamamoto, Y., Tarumoto, T., and Tsubouchi, M., *Bull. Chem. Soc. Jpn.*, 44, 2124 (1971).
422. Yamamoto, Y., Kumamaru, T., Hayashi, Y. and Yamamoto, M., *Anal. Chim. Acta*, 69, 321 (1974).
423. Agterdenbos, J., Jütte, B. A. and Elberse, P. A., *Talanta*, 17, 1085 (1970).
423a. Hamada, S., Motomizu, S., and Tôei, K., *Analyst*, 104, 880 (1979).

424. Fadrus, H. and Malý, J., *Analyst,* 96, 591 (1971).
425. Poe, D. P. and Diehl, H., *Talanta,* 21, 1065 (1974).
426. Altmann, H. J., *Z. Anal. Chem.,* 262, 97 (1972).
427. Hamlin, P. A. and Lambert, J. L., *Anal. Chem.,* 43, 618 (1971).
427a. Goodfellow, G. I. and Webber, H. M., *Analyst,* 104, 1105 (1979).
428. Hofmann, P. and Stern, P., *Anal. Chim. Acta,* 45, 149 (1969); 47, 113 (1969).
429. Sachdev, S. L., Lodge, J. P., and West, P. W., *Anal. Chim. Acta,* 58, 141 (1972).
430. Collard, R. S. and Pryor, W. A., *Anal. Chim. Acta,* 108, 255 (1979).
431. Kornienko, T. G. and Samchuk, A. I., *Ukr. Khim. Zh.,* 38, 917 (1972).
432. Impedovo, S., Traini, A., and Papoff, P., *Talanta,* 18, 97 (1971).
433. Poluektov, N. S., Kirillov, A. I., Makarenko, O. P., and Vlasov, N. A., *Zavod. Lab.,* 37, 536 (1971).
434. Bazzano, E. and Ghersini, G., *Anal. Chim. Acta,* 38, 457 (1967).
435. Korkisch, J. and Krivanec, H., *Talanta,* 23, 295 (1976).
436. Korkisch, J. and Gödl, L., *Anal. Chim. Acta,* 71, 113 (1974).
437. Sekine, K., *Mikrochim. Acta,* 1975 I, 313.
438. Reinhardt, K. H. and Müller, H. J., *Z. Anal. Chem.,* 292, 359 (1978).
439. Nikitina, L. P. and Basargin, N. N., *Zh. Anal. Khim.,* 25, 1521 (1970).
440. Nishimura, M., Matsunaga, K., Kudo, T., and Obara, F., *Anal. Chim. Acta,* 65, 466 (1973).
441. Yoshimura, K. and Ohashi, S., *Talanta,* 25, 103 (1978).
441a. Yamazaki, H., *Anal. Chim. Acta,* 113, 131 (1980).
442. Morgen, E. A., Rossinskaya, E. S., and Vlasov, N. A., *Zh. Anal. Khim.,* 30, 1384 (1975).
443. Kawabuchi, K. and Kuroda, R., *Anal. Chim. Acta,* 46, 23 (1969).
443a. Ohta, N., Fujita, M., and Tomura, K., *Bunseki Kagaku,* 28, 277 (1979).
443b. Crowther, J., *J. Anal. Chem.,* 50, 1041 (1978).
444. Maly, J. and Fadrus, H., *Analyst,* 99, 128 (1974).
445. Matsui, H., *Anal. Chim. Acta,* 69, 216 (1974).
446. Stephens, B. G., Felkel, H. L., Jr., and Spinelli, W. M., *Anal. Chem.,* 46, 692 (1974).
446a. Crowther, J., *Anal. Chem.,* 50, 658 (1978).
447. Fadrus, H. and Malý, J., *Analyst,* 100, 549 (1975).
448. Kiriyama, T. and Kuroda, R., *Z. Anal. Chem.,* 288, 354 (1977).
449. Beaupré, P. and Holland, W. J., *Mikrochim. Acta,* II, 95 (1978).
450. Liardon, O. and Ryan, D. E., *Anal. Chim. Acta,* 83, 421 (1976).
451. Abraham, J., Winpe, M., and Ryan, D. E., *Anal. Chim. Acta,* 48, 431 (1969).
452. Weiss, H. V. and Lai, M. G., *Anal. Chim. Acta,* 28, 242 (1963).
453. Evans, W. H. and Sayers, G. S., *Analyst,* 97, 453 (1972).
454. Watanabe, H., Yamaguchi, N., and Tanaka, H., *Bunseki Kagaku,* 28, 366 (1979).
455. Goldstein, G., Maddox, W. L., and Kelley, M. T., *Anal. Chem.,* 46, 485 (1974).
456. Yoshimura, K., Waki, H., and Ohashi, S., *Talanta,* 25, 579 (1978).
457. Korkisch, J. and Dimitriadis, D., *Talanta,* 20, 1295 (1973).
457a. Korenaga, T., Motomizu, S., and Tôei, K., *Talanta,* 27, 33 (1980).
458. Korkisch, J. and Sorio, A., *Talanta,* 22, 273 (1975).
459. Portmann, J. E. and Riley, J. P., *Anal. Chim. Acta,* 35, 35 (1966).
460. Toshimitsu, Y., Yoshimura, K., and Ohashi, S., *Talanta,* 26, 273 (1979).
461. Bassett, J. and Matthews, P. J., *Analyst,* 99, 1 (1974).
462. Östling, G., *Anal. Chim. Acta,* 78, 507 (1975).
462a. Lambert, J. L., Paukstelis, J. V., and Bruckdorfer, R. A., *Anal. Chem.,* 50, 820 (1978).
463. Yoshimura, K., Kariya, R., and Tarutani, T., *Anal. Chim. Acta,* 109, 115 (1979).
464. Goulden, P. D., Afghan, B. K., and Brooksbank, P., *Anal. Chem.,* 44, 1845 (1972).
465. Royer, J. L., Twichell, J. E., and Muir, S. M., *Anal. Lett.,* 6, 619 (1973).
466. Marczenko, Z. and Kasiura, K., *Chem. Anal. (Warsaw),* 9, 321 (1964).
467. Fanning, K. A. and Pilson, M. E., *Anal. Chem.,* 45, 136 (1973).
468. Truesdale, V. W. and Smith, C. J., *Analyst,* 101, 19 (1976).
469. Matsunaga, K. and Nishimura, M., *Anal. Chim. Acta,* 73, 204 (1974).
470. Hong-Kwen Boo and Ma, T. S., *Mikrochim. Acta,* II, 515 (1976).
471. Matsunaga, K., Oyama, T., and Nishimura, M., *Anal. Chim. Acta,* 58, 228 (1972).
472. Tôei, K. and Kiyose, T., *Anal. Chim. Acta,* 88, 125 (1977).
472a. Okada, M., Miyata, H., and Tôei, K., *Analyst,* 104, 1195 (1979).
473. Davison, W. and Woof, C., *Analyst,* 104, 385 (1979).
474. Ghimicesuc, G. and Dorneanu, V., *Talanta,* 19, 263 (1972).
475. Ramirez-Munoz, J., *Anal. Chim. Acta,* 78, 431 (1975).
475a. Goossen, J. T. H. and Kloosterboer, J. G., *Anal. Chem.,* 50, 707 (1978).
476. Johnson, D. L. and Pilson, M. E., *Anal. Chim. Acta,* 58, 289 (1972).

477. Reay, P. F., *Anal. Chim. Acta,* 72, 145 (1974).
478. Haywood, M. G. and Riley, J. P., *Anal. Chim. Acta,* 85, 219 (1976).
479. Sandhu, S. S. and Nelson, P., *Anal. Chem.,* 50, 322 (1978).
480. Grasshoff, K. M. and Chan, K. M., *Anal. Chim. Acta,* 53, 442 (1971).
481. Bhat, S. R., Eckert, J. M., Geyer, R., and Gibson, N. A., *Anal. Chim. Acta,* 108, 293 (1979).
482. Lambert, J. L. and Ramasamy, J., *Anal. Chim. Acta,* 75, 460 (1975).
483. Quentin, K. E. and Rosopulo, A., *Z. Anal. Chem.,* 241, 241 (1968).
484. Kempf, T., *Z. Anal. Chem.,* 244, 113 (1969).
485. Shahine, S. A. and Mahmoud, R. M., *Microchem. J.,* 21, 286 (1976).
486. Archimbaud, M. and Bertrand, M. R., *Chim. Anal.,* 52, 531 (1970).
487. Peron, A. and Courtot-Coupez, J., *Analusis,* 6, 389 (1978).
488. Tsunogai, S., *Anal. Chim. Acta,* 55, 444 (1971).
489. Mulwani, H. R. and Sathe, R. M., *Analyst,* 102, 137 (1977).
490. Pilz, W., *Z. Anal. Chem.,* 219, 350 (1966).
491. Marshall, B. S., Telford, I., and Wood, R., *Analyst,* 96, 569 (1971).
492. Pines, I., *Chem. Anal. (Warsaw),* 15, 103 (1970).
493. Groffman, D. M. and Wood, R., *Analyst,* 96, 140 (1971).
494. Sorokin, G. K. and Lomonosov, S. A., *Zavod. Lab.,* 40, 23 (1974).
495. Reilly, D. A., *Anal. Chem.,* 49, 322 (1977).
496. Bock, R. and Bockholt, B., *Z. Anal. Chem.,* 260, 274 (1972).
497. Bell, D. R., Reiszner, K. D., and West, P. W., *Anal. Chim. Acta,* 77, 245 (1975).
498. Leithe, W. and Petschl, G., *Z. Anal. Chem.,* 230, 344 (1967).
499. Huygen, I. C., *Anal. Chem.,* 42, 407 (1970).
500. Bultez, A., *Analusis,* 2, 190 (1973).
501. Zutshi, P. K. and Mahadevan, T. N., *Talanta,* 17, 1014 (1970).
502. Pacz, D. M. and Guagnini, O. A., *Mikrochim. Acta,* 220 (1971).
503. Rehme, K. A. and Scaringelli, F. P., *Anal. Chem.,* 47, 2474 (1975).
504. Alekseeva, L. S., Murashova, V. I., Bakunina, L. I., and Skripchuk, V. G., *Zavod. Lab.,* 37, 1299 (1971).
505. Marshall, B. S. and Wood, R., *Analyst,* 94, 493 (1969).
506. Ilinskaya, G. I. and Mudrolyukova, N. S., *Zh. Anal. Khim.,* 34, 1306 (1979).
507. Gabbay, J., Davidson, M., and Donagi, A. E., *Analyst,* 101, 128 (1976).
508. Morsches, B. and Tölg, G., *Z. Anal. Chem.,* 250, 81 (1970).
509. Kotz, L., Kaiser, G., Tschöpel, P., and Tölg, G., *Z. Anal. Chem.,* 260, 207 (1972).
509a. Morrison, G. H., *Crit. Rev. Anal. Chem.,* 8, 287 (1979).
510. Stoeppler, M. and Backhaus, F., *Z. Anal. Chem.,* 291, 116 (1978).
511. Chauhan, U. P. and Pande, P. C., *Talanta,* 14, 575 (1967).
512. Howell, D. S., Pita, J. C., and Marquez, J. F., *Anal. Chem.,* 38, 434 (1966).
513. Petrow, H. G. and Strehlow, C. D., *Anal. Chem.,* 39, 265 (1967).
514. Agterdenbos, J., Van Broekhoven, L., Jütte, B. A., and Schuring, J., *Talanta,* 19, 341 (1972).
515. Nanewar, R. R. and Tandon, U., *Talanta,* 25, 352 (1978).
516. Quin, B. F. and Brooks, R. R., *Anal. Chim. Acta,* 74, 75 (1975).
517. Norheim, G. and Waasjo, E., *Z. Anal. Chem.,* 286, 229 (1977).
518. Beyer, W., Wawschinek, O., and Ott, R. D., *Mikrochim. Acta,* 233 (1967).
519. Traister, G. L. and Schilt, A. A., *Anal. Chem.,* 48, 1216 (1976).
520. Dewey, D. W. and Marston, H. R., *Anal. Chim. Acta,* 57, 45 (1971).
521. Silva de, M. E., *Analyst,* 99, 408 (1974).
522. Pollak, M. and Kubaň, V., *Collect. Czech. Chem. Commun.,* 44, 725 (1979).
523. Tewari, S. N., Harpalani, S. P., and Tripathi, S. S., *Mikrochim. Acta,* I, 13 (1975).
524. Wawschinek, O., Beyer, W., and Paletta, B., *Mikrochim. Acta,* 201 (1968).
525. Oelschläger, W. and Schwarz, E., *Z. Anal. Chem.,* 258, 203 (1972).
526. Mair, J. W. and Day, H. G., *Anal. Chem.,* 44, 2015 (1972).
527. Kaczmarczyk, A., Messer, J. R., and Peirce, C. E., *Anal. Chem.,* 43, 271 (1971).
528. Baumeister, R. and Schievelbein, H., *Z. Anal. Chem.,* 255, 362 (1971).
529. Jacobs, S., *Crit. Rev. Anal. Chem.,* 7, 297 (1978).
530. Shechter, H., Gruener, N., and Shuval, H. I., *Anal. Chim. Acta,* 60, 93 (1972).
531. Fogg, A. G., Soleymanloo, S., and Burns, D. T., *Anal. Chim. Acta,* 88, 197 (1977).
532. Tušl, J., *Analyst,* 97, 111 (1972).
533. Eichhorn, G., Wolf, W., and Berger, S. A., *Mikrochim. Acta,* I, 135 (1976).
534. Keay, J., Menagé, P. M., and Dean, G. A., *Analyst,* 97, 897 (1972).
535. Cummins, L. M., Martin, J. L., and Maag, D. D., *Anal. Chem.,* 37, 430 (1965).
536. Hargreaves, J. A., Ingram, G. S., and Cox, D. L., *Analyst,* 95, 177 (1970).

537. Weiss, J. A. and Staubury, J. B., *Anal. Chem.*, 44, 619 (1972).
538. Slegers, G. and Claeys, A., *Analyst*, 99, 471 (1974).
539. Ssekaalo, H., *Analyst*, 96, 346 (1971).
540. Bergamin, H., Medeiros, J. X., Reis, B. F., and Zagatto, E. A., *Anal. Chim. Acta*, 101, 9 (1978).
541. Ssekaalo, H., *Anal. Chim. Acta*, 51, 503 (1970).
542. Quinsland, D. E. and Jones, D. C., *Talanta*, 16, 282 (1969).
543. Kothny, E. L., *Mikrochim. Acta*, 1, 425 (1978).
544. Middleton, K. R., *Analyst*, 90, 234 (1965).
545. Kerin, Z., *Mikrochim. Acta*, 927 (1968).
546. Reis, B. F., Bergamin, H., Zagatto, E. A., and Krug, F. J., *Anal. Chim. Acta*, 107, 309 (1979).
547. Basson, W. D., Böhmer, R. G., and Stanton, D. A., *Analyst*, 94, 1135 (1969).
548. Stewart, J. W., Ružička, J., Filho, H. B., and Zagatto, E. A., *Anal. Chim. Acta*, 81, 371 (1976).
549. Stewart, J. W. and Ružička, J., *Anal. Chim. Acta*, 82, 137 (1976).
550. Crosby, N. T., *Analyst*, 102, 225 (1977).
551. Stanton, R. E. and Hardwick, A. J., *Analyst*, 93, 193 (1968).
552. Rudnicki, A. and Niewiadomski, H., *Chem. Anal. (Warsaw)*, 13, 755 (1968).
553. Kum-Tatt Lee, Yock-Fong Chang, and Sau-Fun Tan, *Mikrochim. Acta*, II, 505 (1976).
554. Nabrzyski, M., *Anal. Chem.*, 47, 552 (1975).
555. Scheubeck, E., Nielsen, A., and Iwantscheff, G., *Z. Anal. Chem.*, 294, 398 (1979).
555a. Plesch, R., *Z. Anal. Chem.*, 298, 400 (1979).
556. Jones, P. and Nickless, G., *Analyst*, 103, 1121 (1978).
557. Engberg, A., *Analyst*, 98, 137 (1973).
558. Manolov, K., Stamatova, V., and Matschev, A., *Mikrochim. Acta*, II, 343 (1976).
559. Raber, H. and Likussar, W., *Mikrochim. Acta*, 577 (1970).
560. Thaler, H. and Sturm, W., *Z. Anal. Chem.*, 244, 379; 246, 315 (1969); 250, 120; 251, 30 (1970).
561. Kaul, A. K. and Sharma, T. R., *Z. Anal. Chem.*, 280, 133 (1976).
562. Jintakanon, S., Kerven, G. L., Edwards, D. G., and Asher, C. J., *Analyst*, 100, 408 (1975).
563. Analytical Methods Committee, *Analyst*, 104, 434 (1979).
564. Hieke, E. and Kreisel, A., *Z. Anal. Chem.*, 285, 39 (1977).
565. Kretzschmann, F. and Engst, R., *Mikrochim. Acta*, 270 (1970).
566. Joerin, M. M., *Analyst*, 100, 7 (1975).
567. Zolotov, Y. A. and Blyum, I. A., *Pure Appl. Chem.*, 44, 671 (1975); Zh. Anal. Khim., 31, 159 (1976).
568. Bakhmatova, T. K., Dedkov, Y. M., and Ershova, V. A., *Zh. Anal. Khim.*, 31, 292 (1976).
569. Akhmedli, M. K., Granovskaya, P. B., and Melikova, E. G., *Zh. Anal. Khim.*, 28, 1304 (1973).
570. Voldet, P. and Haerdi, W., *Anal. Chim. Acta*, 72, 111 (1974).
571. Karalova, Z. K., *Zh. Anal. Khim.*, 28, 1389 (1973).
572. Korkisch, J. and Dimitriadis, D., *Talanta*, 20, 1199 (1973); Mikrochim. Acta, 25 (1974).
573. Kiriyama, T. and Kuroda, R., *Anal. Chim. Acta*, 71, 375 (1974).
574. Korkisch, J., Steffan, I., Arrhenius, G., Fisk, M., and Frazer, J., *Anal. Chim. Acta*, 90, 151 (1977).
575. Korkisch, J. and Hübner, H., *Talanta*, 23, 283 (1976).
576. Easton, A. J., *Anal. Chim. Acta*, 78, 224 (1975).
577. Ilsemann, K. and Bock, R., *Z. Anal. Chem.*, 274, 185 (1975).
578. Nikolskaya, I. V. and Maksimov, A. V., *Zh. Anal. Khim.*, 31, 892 (1976).
579. Mazzucotelli, A., Franche, R., Dadone, A., and Baffi, F., *Talanta*, 24, 690 (1977).
580. Donaldson, E. M., *Talanta*, 17, 583 (1970).
581. Nazarenko, V. A., Yagnyatinskaya, G. Y., and Antonovich, V. P., *Zh. Anal. Khim.*, 29, 1977 (1974).
582. Mazzucotelli, A., Franche, R., Dadone, A., and Baffi, F., *Analyst*, 102, 825 (1977).
583. Lillie, E. G. and Greenland, L. P., *Anal. Chim. Acta*, 69, 313 (1974).
584. Kawabuchi, K. and Kuroda, R., *Talanta*, 17, 67 (1970).
585. Cogger, N., *Anal. Chim. Acta*, 84, 143 (1976).
586. Korkisch, J. and Dimitriadis, D., *Mikrochim. Acta*, 549 (1974).
587. Görbicz, M. and Upor, E., *Acta Chim. Acad. Sci. Hung.*, 66, 373 (1970).
588. Bodart, D. E., *Z. Anal. Chem.*, 247, 32 (1969).
589. Bocanegra Sierra, L., Perez-Bustamante, J. A., and Burriel-Marti, F., *Anal. Chim. Acta*, 59, 231, 249 (1972).
589a. Coombes, R. J. and Chow, A., *Talanta*, 26, 991 (1979).
590. Maslei, N. N., Nabivanets, B. I., and Zadorozhnaya, E. M., *Zavod. Lab.*, 42, 1165 (1976).
591. Bykhovtsova, T. T., *Zavod. Lab.*, 40, 512 (1974).
592. Korkisch, J. and Dimitriadis, D., *Mikrochim. Acta*, 449 (1974).
593. Leong, P. C. and Ong, H. P., *Anal. Chem.*, 43, 940 (1971).
594. Lypka, G. N. and Chow, A., *Anal. Chim. Acta*, 60, 65 (1972).

595. Flyantikova, G. V., Korolenko, L. I., Vinarova, L. I., and Chekirda, T. N., *Zh. Anal. Khim.*, 32, 1028 (1977).
596. Agterdenbos, J. and Vlogtman, J., *Talanta*, 19, 1295 (1972).
597. Koeva, M., Mareva, S., and Jordanov, N., *Anal. Chim. Acta*, 75, 464 (1975).
598. Nazarenko, V. A., Vinarova, L. I., and Lebedeva, N. V., *Zh. Anal. Khim.*, 30, 617 (1975).
599. Shelton, N. F. and Reed, R. A., *Analyst*, 101, 396 (1976).
600. Farzaneh, A., Troll, G., and Neubauer, W., *Z. Anal. Chem.*, 296, 383 (1979).
601. Bodkin, J. B., *Analyst*, 101, 44 (1976).
602. Whitehead, D. and Malik, S. A., *Analyst*, 101, 485 (1976).
603. Marin, L. and Vernet, M., *Analusis*, 7, 33 (1979).
604. Nazarenko, I. I., Kislova, I. V. and Rabinovich, B. S., *Zh. Anal. Khim.*, 30, 1389 (1975).
605. Hall, A. and Walsh, J. N., *Anal. Chim. Acta*, 45, 341 (1969).
606. Clements, R. L., Sergeant, G. A., and Webb, P. J., *Analyst*, 96, 51 (1971).
607. Huang, W. H. and Johns, W. D., *Anal. Chim. Acta*, 37, 508 (1967).
608. Grimaldi, F. S. and Schnepfe, M. M., *Anal. Chim. Acta*, 53, 181 (1971).
609. Podberezskaya, N. K. and Sushkova, V. A., *Zavod. Lab.*, 39, 774 (1973).
610. Yakovlev, P. Y. and Zhukova, M. P., *Zavod. Lab.*, 36, 1169 (1970); 37, 1292 (1971).
611. Shmanenkova, G. I., Pleshakova, G. P., Romantseva, T. I., and Fileeva, A. M., *Zh. Anal. Khim.*, 33, 699 (1978).
612. Romantseva, T. I. and Kharitonova, L. K., *Zavod. Lab.*, 45, 495 (1979).
613. Polyak, L. Y., *Zh. Anal. Khim.*, 29, 1338 (1974).
614. Ratcliffe, D. B. and Byford, C. S., *Anal. Chim. Acta*, 58, 223 (1972).
615. Busev, A. I., Kharlamov, I. P., and Byzova, E. P., *Zavod. Lab.*, 38, 1433 (1972).
616. Ashton, A., Fogg, A. G., and Burns, D. T., *Analyst*, 99, 108 (1974).
617. Baranova, L. I., Orlova, E. S., and Tserkovnitskaya, I. A., *Zavod. Lab.*, 44, 142 (1978).
618. Gagliardi, E. and Höllinger, W., *Mikrochim. Acta*, 136 (1972).
619. Westland, A. D. and Bezaire, J., *Anal. Chim. Acta*, 66, 187 (1973).
620. Čižek, Z. and Doležal, J., *Anal. Chim. Acta*, 109, 381 (1979).
621. Dolgorev, A. V., *Zavod. Lab.*, 44, 146 (1978).
622. Luke, C. L., *Anal. Chim. Acta*, 37, 97; 39, 404, 447 (1967).
623. Donaldson, E. M., *Talanta*, 18, 905 (1971).
624. Kharlamov, I. P., Eremina, G. V., and Borcheva, T. A., *Zavod. Lab.*, 38, 8, (1972).
625. Basargin, N. N., Yakovlev, P. Y., and Morozova, O. N., *Zavod. Lab.*, 40, 1322 (1974).
626. Sauer, K. H. and Nitsche, M., *Arch. Eisenhuettenwes.*, 47, 153 (1976).
627. Asmus, E. and Weinert, H., *Z. Anal. Chem.*, 249, 179 (1970).
628. Ashton, A., Fogg, A. G., and Burns, D. T., *Z. Anal. Chem.*, 264, 133 (1973).
629. Hulanicki, A. and Głab, S., *Chem. Anal. (Warsaw)*, 15, 1089 (1970).
630. Burgess, C., Fogg, A. G., and Burns, D. T., *Analyst*, 98, 605 (1973).
631. Koch, O. G., *Z. Anal. Chem.*, 265, 29 (1973).
632. Koch, O. G., *Z. Anal. Chem.*, 255, 269 (1971).
633. Tolk, A., Tap, W. A., and Lingerak, W. A., *Talanta*, 16, 111 (1969).
634. Bhargava, O. P. and Hines, W. G., *Talanta*, 17, 61 (1970).
635. Pakalns, P., *Anal. Chim. Acta*, 49, 511 (1970).
636. Bhargava, O. P., Donovan, J. F., and Hines, W. G., *Anal. Chem.*, 44, 2402 (1972).
637. Fogg, A. G., Marriott, D. R., and Burns, D. T., *Analyst*, 97, 657 (1972).
638. Koch, O. G., *Anal. Chim. Acta*, 63, 156 (1973).
639. Zhukova, M. P., Matrosova, T. V., and Yakovlev, P. Y., *Zh. Anal. Khim.*, 26, 2231 (1971).
640. Boganova, A. N. and Nemodruk, A. A., *Zh. Anal. Khim.*, 32, 1961 (1977).
641. Kasiura, K. and Boroch, E., *Chem. Anal. (Warsaw)*, 21, 177 (1976).
642. Graffmann, G. and Jackwerth, E., *Z. Anal. Chem.*, 246, 12 (1969).
643. Mukai, K., *Talanta*, 19, 489 (1972).
644. Pakalns, P., *Anal. Chim. Acta*, 51, 497 (1970).
645. Wood, D. F. and Jones, J. T., *Analyst*, 93, 131 (1968).
646. Hashitani, H., Yoshida, H., and Adachi, T., *Anal. Chim. Acta*, 76, 85 (1975).
647. Mizuike, H. and Kondo, A., *Mikrochim. Acta*, 841 (1971).
648. Walker, R. J. and Holland, W. J., *Mikrochim. Acta*, I, 57 (1977).
649. Jackwerth, E., Graffmann, G., and Lohmar, J., *Z. Anal. Chem.*, 247, 149 (1969).
650. Dukashenkova, N. V., Tolmacheva, N. S., and Shkrobot, E. P., *Zavod. Lab.*, 39, 541 (1973).
651. Nemodruk, A. A., Arevadze, N. G., and Abalakina, V. M., *Zavod. Lab.*, 45, 494 (1979).
652. Tsukahara, I., Sakakibara, M., and Tanaka, M., *Anal. Chim. Acta*, 92, 379 (1977).
653. Norwitz, G. and Galan, M., *Anal. Chim. Acta*, 83, 289 (1976).

654. Donaldson, E. M., *Talanta*, 25, 131 (1978).
655. Pakalns, P., *Analyst*, 94, 1130 (1969).
656. Pugh, H. and Waterman, W. R., *Anal. Chim. Acta*, 55, 97 (1971).
657. Jackwerth, E., *Z. Anal. Chem.*, 235, 235 (1968).
658. Donaldson, E. M., *Talanta*, 24, 441 (1977).
659. Donaldson, E. M., *Talanta*, 23, 823 (1976).
660. Onishi, H. and Sekine, K., *Anal. Chim. Acta*, 62, 204 (1972).
661. Sekine, K. and Onishi, H., *Z. Anal. Chem.*, 288, 47 (1977).
662. Flaschka, H. and Speights, R. M., *Microchem. J.*, 14, 490 (1969).
663. Jackwerth, E. and Döring, E., *Z. Anal. Chem.*, 255, 194 (1971).
664. Hofer, A., *Z. Anal. Chem.*, 240, 229 (1968).
665. Zhukova, M. P. and Yakovlev, P. Y., *Zavod. Lab.*, 39, 661 (1973).
666. Uny, G., Mathien, C., Tardif, J. P., and Tran Van Danh, *Anal. Chim. Acta*, 53, 109 (1971).
667. Kasiura, K. and Meus, M., *Chem. Anal. (Warsaw)*, 23, 305 (1978).
668. Fedorov, A. A. and Krichevskaya, A. M., *Zavod. Lab.*, 36, 1433 (1970).
669. Jackwerth, E., Döring, E., Lohmar, J., and Schwark, G., *Z. Anal. Chem.*, 260, 177 (1972).
670. Jadhav, S. G., Murugaiyan, P., and Venkateswarlu, C., *Anal. Chim. Acta*, 82, 391 (1976).
671. Chainani, P. A., Murugaiyan, P. and Venkateswarlu, C., *Anal. Chim. Acta*, 57, 67 (1971).
672. Tsukahara, I., Sakakibara, M., and Yamamoto, T., *Anal. Chim. Acta*, 83, 251 (1976).
673. Mizuike, A. and Hiraide, M., *Anal. Chim. Acta*, 69, 231 (1974).
674. Krasiejko, M. and Marczenko, Z., *Mikrochim. Acta*, I, 585 (1975).
675. Alexandrow, A., *Mikrochim. Acta*, 664 (1972).
676. Cyrankowska, M., *Chem. Anal. (Warsaw)*, 15, 209 (1970).
677. Vita, O. A., Levier, W. A., and Litteral, E., *Anal. Chim. Acta*, 42, 87 (1968).
678. Korkisch, J. and Hübner, H., *Mikrochim. Acta*, I, 25 (1976).
679. Motomizu, S., *Analyst*, 100, 39 (1975).
680. Rajković, D., *Z. Anal. Chem.*, 255, 190 (1971).
681. Kukisheva, T. N., Sinitsyna, E. S., and Efimova, N. S., *Zh. Anal. Khim.*, 26, 953 (1971).
682. Gordon, H. and Norwitz, G., *Talanta*, 19, 7 (1972).
683. Zhukova, M. P., Shemyakin, F. M. and Yakovlev, P. Y., *Zh. Anal. Khim.*, 28, 1705 (1973).
684. Wood, D. F. and Jones, J. T., *Anal. Chim. Acta*, 47, 215 (1969).
685. Ghersini, G. and Mariottini, S., *Talanta*, 18, 442 (1971).
686. Pakalns, P., *Anal. Chim. Acta*, 50, 103 (1970).
687. Donaldson, E. M., *Talanta*, 16, 1505 (1969).
688. Neef, B. and Döge, H. G., *Talanta*, 14, 967 (1967).
689. Donaldson, E. M. and Inman, W. R., *Talanta*, 13, 489 (1966).
690. Kallmann, S., Hobart, E. W., Oberthin, H. K., and Brienza, W. C., Jr., *Anal. Chem.*, 40, 332 (1968).
691. Lassner, E., Püschel, R., and Katzengruber, K., *Mikrochim. Acta*, 527 (1969).
692. Vadasdi, K., Buxbaum, P., and Salamon, A., *Anal. Chem.*, 43, 318 (1971).
693. Chkanikova, O. K., Krivtsova, V. Y., and Dorokhova, E. N., *Zh. Anal. Khim.*, 34, 944 (1979).
694. Orlova, V. A., Spivakova, B. Y., Sharova, N. A., and Malyutina, T. M., *Zh. Anal. Khim.*, 32, 1591 (1977).
695. Tumanov, A. A., et al., *Zavod. Lab.*, 45, 796 (1979).
696. Nazarenko, V. A. and Shustova, M. B., *Zavod. Lab.*, 37, 146 (1971).
697. Grossmann, O., *Z. Anal. Chem.*, 245, 135 (1969).
698. Kallmann, S., Hobart, E. W., and Oberthin, H. K., *Talanta*, 15, 982 (1968).
699. Fukasawa, T. and Yamane, T., *Anal. Chim. Acta*, 84, 195 (1976).
700. Davis, W. F., Graab, J. W., and Merkle, E. J., *Talanta*, 18, 263 (1971).
701. Marczenko, Z., Kasiura, K., and Krasiejko, M., *Chem. Anal. (Warsaw)*, 14, 1277 (1969).
702. Marczenko, Z., Kasiura, K., and Krasiejko, M., *Mikrochim. Acta*, 625 (1969).
703. Kasiura, K., *Chem. Anal. (Warsaw)*, 20, 809 (1975).
703a. Krasiejko, M., Marczenko, Z., and Kowalski, T., *Chem. Anal. (Warsaw)*, 24, 1037 (1979).
704. Jackwerth, E., Döring, E., and Lohmar, J., *Z. Anal. Chem.*, 253, 195 (1971).
705. Marczenko, Z. and Krasiejko, M., *Chem. Anal. (Warsaw)*, 15, 1233 (1970).
706. Marczenko, Z. and Balcerzak, M., *Chem. Anal. (Warsaw)*, 24, 867 (1979).
707. Marczenko, Z. and Lenarczyk, Ł., *Chem. Anal. (Warsaw)*, 19, 679 (1974).
708. Demina, L. A., Petrukhin, O. M., and Zolotov, Y. A., *Zh. Anal. Khim.*, 27, 593 (1972).
709. Goryushina, V. G. and Esenina, N. V., *Zavod. Lab.*, 40, 628 (1974).
710. Marczenko, Z., Mojski, M., and Skibe, H., *Chem. Anal. (Warsaw)*, 17, 881 (1972).
711. Saulnier, J., Bauer, D., and Rosset, R., *Analusis*, 7, 242 (1979).

712. Sugawara, K. F. and Yao-Sin Su, *Anal. Chim. Acta,* 80, 143 (1975).
713. Marczenko, Z., Kasiura, K., and Mojski, M., *Chem. Anal. (Warsaw),* 16, 203 (1971).
714. Kasterka, B. and Weppe, J., *Chem. Anal. (Warsaw),* 18, 879 (1973).
715. Dobrowolski, J., Szwabski, S., and Sienkiewicz, K., *Chem. Anal. (Warsaw),* 15, 647, 1033 (1970).
716. Kasterka, B. and Dobrowolski, J., *Chem. Anal. (Warsaw),* 15, 303 (1970); 16, 619 (1971).
717. Wilczewski, T., Kozera, F., and Dobrowolski, J., *Chem. Anal. (Warsaw),* 18, 137 (1973); 19, 577 (1974).
718. Chwastowska, J. and Grzegrzółka, E., *Chem. Anal. (Warsaw),* 20, 1065 (1975).
719. Marczenko, Z., Mojski, M., and Kasiura, K., *Chem. Anal. (Warsaw),* 14, 133 (1969).
720. Lanza, P. and Buldini, P. L., *Anal. Chim. Acta,* 70, 341 (1974).
721. Dias, C. C., Jani, K. P., Murugaiya, P., and Venkateswarlu, G., *Analyst,* 100, 259 (1975).
722. Różycki, C. and Suszczewski, W., *Chem. Anal. (Warsaw),* 19, 1231 (1974).
723. Marczenko, Z. and Podsiadło, E., *Mikrochim. Acta,* II, 317 (1976).
724. Fano, V. and Zanotti, L., *Anal. Chim. Acta,* 72, 419 (1974).
725. Zanotti, L. and Licci, F., *Mikrochim. Acta,* II, 225 (1976).
726. Marczenko, Z. and Mojski, M., *Chem. Anal. (Warsaw),* 12, 1155 (1967).
727. Beskova, E. S. and Zhuravlev, G. I., *Zh. Anal. Khim.,* 28, 1411 (1973).
728. Marczenko, Z. and Mojski, M., *Chem. Anal. (Warsaw),* 14, 495 (1969).
729. Chriswell, C. D. and Schilt, A. A., *Anal. Chem.,* 46, 992 (1974).
730. Tôei, K., Motomizu, S., and Korenaga, T., *Analyst,* 101, 974 (1976).
731. Marczenko, Z., *Mikrochim. Acta,* 281 (1965).
732. DePooter, M., Holland, W., and Bozic, J., *Mikrochim. Acta,* II, 443 (1975).
733. Dunbar, W. E. and Schilt, A. A., *Talanta,* 19, 1025 (1972).
734. Nazarenko, V. A., Kostenko, I. G., and Biryuk, E. A., *Zh. Anal. Khim.,* 34, 1942 (1979).
735. Asmus, E. and Jahny, J., *Z. Anal. Chem.,* 255, 186 (1971).
736. Joy, E. F., Bonn, J. D., and Barnard, A. J., Jr., *Anal. Chem.,* 45, 856 (1973).
737. Pantaler, R. P. and Ivkova, T. I., *Zh. Anal. Khim.,* 32, 1975 (1977).
738. Kirsten, W. J., *Anal. Chem.,* 48, 84 (1976).