

DETERMINATION OF MICROELEMENTS IN GEOLOGICAL SAMPLES

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ABSTRACT

The methods used for the determination of microelements in the USSR Geological Survey are considered. The role of the preconcentration of microelements is discussed, the most important reagents for the preconcentration and the determination of microelements are indicated. Some procedures for the determination of 34 microelements are cited. As a sample of the analysis of unusual objects the analysis of lunar samples is briefly considered.

With respect to geological samples, microelements are usually considered as elements with a concentration not exceeding a definite small value, for example 0.01 or 0.1 per cent. In this case the abundance of an element in nature is not taken into consideration; abundant elements in some samples are considered as microelements, as for instance iron in quartzites or calcium in bauxites. We shall confine examination mainly to less abundant elements (except platinum, rare earths and radioactive ones), the concentration of which in many natural materials is actually small.

The data presented below summarize the experience of laboratories of the USSR including that of the geological survey laboratories. The large and various mineral resources of the USSR and the enormous volume of geological explorations require proper analytical attention. In many laboratories of the geological survey the determination of microelements is a kind of routine analysis; there are laboratories, accomplishing between two and three thousands of determinations of microelements monthly.

METHODS OF MICROELEMENT DETERMINATION

Methods used for this purpose must be highly sensitive and sufficiently accurate; moreover, the speed, the simplicity and especially the universality (i.e. the slight dependence of the results on the bulk composition of samples) are also essential. Although demands put to sensitivity are most important, but unlimited: a sensitivity corresponding to 0.1 clark suffices. Thus, methods ensuring (at a 'conditional' weighed amount of 1 g) the determination of microelements within the range from tens of micrograms (fluorine, strontium) to 10^{-3} – 10^{-4} of a microgram (rhenium, gold, bismuth) are suitable for this purpose.

The following techniques are widely used in the Soviet geological survey

(the order corresponds to the scale of practice): photometry, emission spectroscopy, fluorimetry, atomic absorption, neutron activation, a.c. polarography, flame photometry and kinetic methods. The scope of application of the above methods for the determination of 34 main microelements is shown in *Table 1*. This only includes methods being used for routine analysis in at least two laboratories; the most frequent determinations are separately marked. The table also gives general sensitivity characteristics: the determination limit is compared with the clark value and 0.1 clark.

Table 1. Use of different methods for the determination of 34 microelements

Methods	Number of microelements		Number of microelements being determined at contents	
	being determined by the given method (in all)	being very frequently determined	equal to 1 clark or less	equal to 0.1 clark or less
Photometric	28	19	16	7
Emission spectroscopic	22	9	11	4
Fluorimetric	15	5	10	5
Atomic absorption	8	4	5	2
Activation	8	2	6	2
Polarographic	7	—	3	1
Flame-photometric	4	4	4	3
Kinetic	3	2	1	—

More detailed information about these techniques may be found in *Table 2*. The techniques being most often used for the determination of a given element are printed in bold type. In the column (4) the threshold sensitivity of a method as such is indicated: for photometric, fluorimetric and kinetic methods—as a microgram of the element under determination in a volume of a solution prepared for measurement; for atomic absorption, polarographic and flame-photometric methods—as micrograms per millilitre in the same solution (marked by an asterisk); for emission spectroscopy and activation methods—as a microgram of element in a weighed amount of a powder sample. The column (5) gives the lower limit of concentrations which may be determined in real geological objects with an average relative error of a single result equal to 25–30 per cent (3σ -criterion). The quoted sensitivity values are mainly relevant to optimum determination conditions and to devices of the Soviet technology. The ratio of the value from the column (4) to a corresponding value from the column (5) is the weighed amount of a sample in grams, but for atomic absorption, polarographic and flame-photometric methods—a weighed amount in grams, contained in 1 ml of the solution prepared for the determination of a microelement.

In all methods except emission spectroscopy and activation the determination is preceded by dissolution of the sample. These two methods are used in the instrumental variant for the analysis of powder samples and in the variant with preliminary chemical preparation (dissolution of the sample and preconcentration of microelements) for the analysis of solutions. The variants including chemical treatment are marked in the table; the absence of marks

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Table 2. Sensitivity of methods for the determination of microelements (description in the text)

Element	Clark g/t	Method of determination	Sensitivity	
			$\mu\text{g}(\ast\mu\text{g}/\text{ml})$ in the sample	g/t
1	2	3	4	5
Antimony	0.5	Photometric	0.5-1	3-5
		Fluorimetric	0.02-0.1	0.5
		Polarographic	0.1*	3-5
		Emission spectroscopy with concentrating	1	1
Arsenic	1.7	Activation	0.1	1
		Photometric	0.5-1	10
Beryllium	3.8	Activation	0.1	1
		Photometric	0.1-0.2	0.1-0.2
Bismuth	0.009	Fluorimetric	0.1	0.2
		Emission spectroscopy	0.03-0.1	1-3
		Photometric	5-10	10-20
		Polarographic	0.04*	2
		Emission spectroscopy	0.02	5-10
Boron	12	Emission spectroscopy with concentrating	0.12	0.2
		Photometric	0.5-1	30
		Emission spectroscopy	0.6-3	20-100
Cadmium	0.13	Polarographic	0.05*	2
		Atomic absorption	0.01-0.05*	2-10
Caesium	3.7	Flame-photometric	0.02*	2
		Emission spectroscopy	1-2	30
		Activation	0.1	1
Cobalt	18	Photometric	1-2	2-3
		Atomic absorption	0.01-0.05*	5-25
Copper	47	Photometric	0.2	2-3
		Polarographic	0.1*	5
		Atomic absorption	0.01-0.03*	2-5
		Emission spectroscopy with concentrating	0.03	0.2-2
Fluorine	660	Fluorimetric	0.5-1	0.5-1
		Photometric	2	10-50
		Emission spectroscopy	10-15	300-500
Gallium	19	Photometric	0.2-0.3	10
		Fluorimetric	0.003-0.01	0.5-1
		Emission spectroscopy	0.3	10
Germanium	1.4	Photometric	0.5-1	1-2
		Fluorimetric	0.2-0.5	0.3-1
		Emission spectroscopy	0.03-0.06	1-2
Gold	0.0043	Photometric	0.5-1	0.05-0.1
		Fluorimetric	0.018-0.03	0.003
		Atomic absorption	0.02-0.1*	0.1-0.5
		Emission spectroscopy with concentrating	0.05	0.005-0.01
		Activation with chemical isolation	0.0001	0.001
Indium	0.25	Photometric	0.5-1	0.5-1
		Fluorimetric	0.02-0.1	0.02-0.1
		Emission spectroscopy	0.06-0.15	2-5

Table 2 (continued)

Element	Clark g/t	Method of determination	Sensitivity	
			$\mu\text{g}(*\mu\text{g/ml})$ in the sample	g/t
1	2	3	4	5
Iodine	0.4	Photometric	0.5-1	1-2
		Fluorimetric	0.2-0.5	0.5
		Kinetic	0.05	0.2
Lead	16	Photometric	1-2	5-10
		Polarographic	0.1*	5
Lithium	32	Flame-photometric	0.005*	0.5
Mercury	0.083	Photometric	0.05	0.1
		Fluorimetric	0.05-0.1	0.1-0.2
		Atomic absorption	0.5-1*	0.0001
Molybdenum	1	Photometric	0.5	0.5
		Emission spectroscopy	0.03	1-2
Nickel	58	Photometric	1-2	2-3
		Atomic absorption	0.01-0.05*	5-25
Niobium	20	Photometric	1	2
		Emission spectroscopy	0.3	10
Rhenium	0.0007	Photometric	0.5-1	0.2-0.5
		Fluorimetric	0.1-0.2	0.05-0.1
		Kinetic	0.002-0.005	0.002-0.005
		Emission spectroscopy with concentrating	0.5	1
Rubidium	150	Flame-photometric	0.05*	5
		Emission spectroscopy	0.6	20
		Activation	1	10
Scandium	10	Photometric	5-10	5-10
		Emission spectroscopy	0.3	10
		Activation	0.05-0.1	0.05-1
Selenium	0.05	Photometric	1-2	1-2
		Fluorimetric	0.005	0.005-0.1
		Activation with chemical isolation	0.01	0.1
		Fluorimetric	1	1
Silver	0.07	Kinetic	0.02-0.05	0.1
		Atomic absorption	0.01-0.05*	0.1-0.2
		Emission spectroscopy	0.03	1
		Flame-photometric	0.03*	10-20
Strontium	340	Emission spectroscopy	1	30
		Photometric	1-2	1-2
Tantalum	2.5	Fluorimetric	0.2-0.5	0.2-0.5
		Emission spectroscopy	1	30
		Emission spectroscopy with concentrating	1	3-5
		Activation	0.1-0.2	1-2
Tellurium	0.001	Photometric	0.5-1	0.5-1
Thallium	1	Photometric	0.5-1	1-2
		Fluorimetric	0.02-0.05	0.02-0.05
		Emission spectroscopy	0.06-0.15	2-5
Tin	2.5	Photometric	0.5	1
		Fluorimetric	0.2	0.5
		Polarographic	0.05*	5

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Table 2 (continued)

Element	Clark g/t	Method of determination	Sensitivity	
			$\mu\text{g}(*\mu\text{g/ml})$ in the sample	g/t
1	2	3	4	5
[Tin]	[2.5]	Emission spectroscopy	0.3	10-20
		Emission spectroscopy with concentrating	0.3	0.3-1
Tungsten	1.3	Photometric	0.5-1	0.5-1
Zinc	83	Photometric	0.2	5-10
		Polarographic	0.2*	30-50
		Atomic absorption	0.01-0.03*	10-30
Zirconium	170	Photometric	0.1-0.2	10
		Emission spectroscopy	0.3	10-20

signifies that powder samples are analysed. Atomic absorption and flame-photometric determinations are carried out with the use of solutions directly obtained after dissolution of the sample, with the exception of the atomic-absorption determination of gold, silver and the highly sensitive determination of mercury. If concentration is used, the enrichment factors are on the average equal to 15-50.

The sensitivity of several determinations is limited by a considerable correction for the blank experiment. This is true for the photometric determination of As, B, Cu, F, Pb, Sn, Zn, emission spectroscopic determination of Ag, Cu, Sn, fluorimetric determination of Au, I, Sb, Sn, Tl, atomic-absorption determination of Cu and Zn, and the kinetic determination of I. Sensitivity can be increased in these cases as a result of using conditions established for the analysis of high-purity substances.

The special feature of the USSR geological survey is the wide use of fluorimetric methods, taking the third place in frequency after photometric and emission spectroscopic techniques, as well as the application of kinetic methods. The fluorimetric procedures used have been mainly developed by Soviet analytical chemists (see, for instance, ref. 1). The introduction of kinetic methods has allowed the first approach to the determination of clark amounts of rhenium and to reach this level during the determination of iodine and silver. Atomic absorption methods are relatively rarely used.

It can be seen from the data of *Tables 1* and *2* that the available set of procedures permits the determination of clark amounts of 29 elements out of 34. Moreover, 16 elements can be defined at their concentrations of 0.1 clark. The sensitivity of methods for Bi, Cd, Rh and Te determination is not sufficiently satisfactory.

PRECONCENTRATION OF MICROELEMENTS

The ratio of the concentration of the element under determination to the sum of concentrations of the components present has a value from 10^{-4} to

10^{-9} . The amount of accompanying elements in geological samples can change within a wide range and is in general not known to the analyst. Therefore the determination of elements without separation from other components present, i.e. in the powder sample or directly after its dissolution, is by no means always possible. Without separation lithium and rubidium can be determined by the flame-photometric method; beryllium, tin and scandium in rocks by emission spectroscopy; copper and some other elements by atomic absorption; tantalum, caesium, scandium by the activation method. During the analysis of relatively simple geological objects directly after dissolution of the sample selenium is determined with diamionaphthalene by the fluorimetric method, copper with diquinolyl, nickel with dimethylglyoxime by the photometric method. Frequently, especially during geochemical searches a direct emission spectroscopic determination of a number of microelements is carried out.

However, in many other cases a separation of microelements from associated components is needed. The latter cause errors during the determination of microelements in connection with the fact that they themselves possess the same analytical property—light absorption, fluorescence, etc. or as a result of the 'matrix effect'. Extraction, coprecipitation, distillation of the microelement or of the accompanying elements were most frequently used as the method of concentrating (separation) of the microelement.

It is usually thought that concentration facilitates an increase in the sensitivity of the determination. This is indeed true, but in addition concentration simplifies the solution of the problem of standard samples for physical methods of analysis. Thus during emission spectral analysis the use of a single base for concentrates (coal powder, etc.) permits exclusion in practice of the problem of the influence of 'third elements' which is traditional in emission analysis. Concentrating facilitates sampling; in this case large weighed samples may be used and at the expense of this the undesirable influence of sample heterogeneity may be lowered. In addition concentrating simplifies the introduction of internal standards where this is needed.

The effectiveness of concentrating depends on many factors among which not the least is the mutual influence of the microelement under determination and the presence of accompanying elements. During precipitation or coprecipitation of the microelement this may be the entrapping of the accompanying elements by the precipitate or the decrease of the completeness of microelement precipitation in the presence of interfering elements. During precipitation of the accompanying components there may occur coprecipitation of the microelement under determination, a diminution of the separation factor owing to the solubility increase of the element being precipitated in the presence of others. During extraction of the microelement the coextraction of the accompanying elements sometimes takes place or the latter may suppress extraction of the microelement. In the case of extraction separation of the interfering elements the coextraction of the microelement under determination or a diminution of the separation factor at the expense of suppression of interfering element extraction by other elements is not ruled out.

All these effects are studied in a general theoretical scheme; in particular their mechanism is disclosed. During recent years particularly great attention has been paid to the natural influence of elements during extraction, especially

in halide systems. If concentrating is carried out by the extraction of the ionic associates of macroelements with ethers, coextraction of the microelements under determination may take place. Therefore others except dichlorodiethyl are not advisable for this purpose. Much more effective are highly-polar and highly-basic solvents of the tributylphosphate or methylisobutylketone type. In this case not only the coextraction is lacking, but, on the contrary, the suppression of microelement extraction is observed which increases the separation factor². Such investigations give general recommendations for analysts which can be easily used. Thus a recent report³ dealt with the elimination of coextraction during the determination of tellurium microamounts.

All the above enumerated effects of mutual influence depend on absolute concentrations of the microelement and the accompanying elements and their ratios. The magnitude of the interferences being brought in by the accompanying elements, are usually non-additive. Therefore neither the separate study of the behaviour of the microelement and the accompanying elements, nor even the investigation of the pairs of microelement-accompanying element (which is naturally also necessary) gives sufficient information about the behaviour under the real conditions of analysis. The study of multicomponent systems imitating various kinds of natural objects is needed. This laborious work, chiefly being carried out by practical analysts, permits a choice of the most rational methods. As a result methods are elaborated which allow determination of the microelements disposing of minimum knowledge about the composition of the samples under analysis.

Experience shows that the least dependence of the microelement output and of the separation factors of the system is observed in extraction concentrating from strongly acidic, and especially halide-containing, solutions. Therefore such methods are widely used. Their successful application is favoured by good knowledge concerning the extraction of metals from halide solutions with oxygen-containing solvents⁴.

REAGENTS FOR CONCENTRATION AND DETERMINATION OF MICROELEMENTS

The 'natural selection' of reagents for concentrating and determination of microelements has led to the allotment of a relatively small group of reagents in analytical practice. The main ones being used at least for the determination of three microelements are listed in *Table 3*. When the table was drawn up, some new elaborations were taken into account which are being developed for use in routine analyses.

The basic dyes are widely used⁵. Of triphenylmethane dyes Crystal Violet and Brilliant Green are most frequently used and of rhodamine dyes, Ethylrhodamine B and Butylrhodamine B. Most photometric determinations of thallium, tantalum, boron, antimony, gold, tellurium, and fluorimetric determinations of gallium, indium, thallium, tantalum, rhenium, gold and tellurium are carried out with the aid of the basic dyes. Probably within the next few years mercury, tin, germanium, bismuth, and possibly cadmium and

silver will enter this list. The sensitivity of reactions with the basic dyes is very high, but the main reason for the success of these reagents consists in the possibility of reaching high sensitivity during analysis of real objects (right-handmost column in *Table 1*).

Table 3. Reagents used for concentrating or determination of not less than three microelements

Reagents	Total number of microelements	Method of application	Microelements
Basic dyes	17	Extraction concentrating	Au, Cd, Ga, Hg, In, Nb, Re, Sb, Sn, Ta, Te, Tl
		Photometric or fluorimetric determination	Ag, As, Au, B, Cd, Ga, Ge, Hg, I, In, Re, Sb, Sn, Ta, Te, Tl
Dithizone	8	Extraction concentrating	Ag, Pb
		Concentrating by precipitation or coprecipitation	Ag, Cd, Co, Cu, Ni, Pb, Zn
		Photometric determination	Hg, Pb, Zn
Halides	8	Extraction concentrating	As, Au, Ga, Ge, I, In, Sb, Tl
Reagents of the arsenazo group	5	Extraction concentrating	Zr
		Photometric determination	Cu, F, Nb, Sc, Zr
Thionalide	5	Concentrating by precipitation	Ag, Bi, Cu, Sb, Sn
Diethyldithiocarbamate	3	Extraction concentrating	Bi, Cd
		Photometric determination	Cu

During the last few years the use of basic dyes has also been started for microelement concentration⁶. Thus, during fluorimetric determination of microelements with rhodamine dyes a preliminary extraction of the microelement in the form of an associate with triphenylmethane dye is frequently carried out, the separation from a number of accompanying elements reacting with rhodamines having been ensured. The basic dyes permit us to accomplish separations based on the difference of stability of ionic associates with different metal-containing anions or on the different stability of the latter. A two-step extraction of associates with the basic dyes is possible, the first stage (concentrating) being accomplished with an excess of complex-forming reagents in the aqueous phase.

The reagents of the arsenazo-group: arsenazo III, sulphochlorophenol C—have become more and more widely used and their use is being extended⁷. On the other hand, the role of dithizone and diethyldithiocarbamate is substantially less than might be expected.

DETERMINATION OF SEPARATE MICROELEMENTS

*Photometric and fluorimetric determination*⁵⁻¹³

Antimony is determined by the photometric method as chloroantimonate of Crystal Violet¹⁰ or by the fluorimetric method after substitution in the extract of the cation of Crystal Violet for a cation of Ethylrhodamine B.

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Arsenic is determined as a molybdenum blue or by the modified Gutzeit method.

Beryllium is extracted as acetylacetonate by carbon tetrachloride, the extractant is removed, the residue is dissolved and the element is determined with Beryllon II⁸. In the case of fluorimetric determination beryllium is precipitated on titanium phosphate or extracted as acetylacetonate; in both cases the precipitate (residue) is dissolved and beryllium is determined with morin¹¹.

Bismuth is photometrically determined as an iodide complex after extraction separation with diethyldithiocarbamate.

Boron is determined by the photometric method transferring it during heating in the fluoride complex and extracting by benzene the Crystal Violet fluoroborate^{5, 9}.

Cobalt is photometrically determined with nitroso-R-salt or 1-nitroso-2-naphthol.

Copper is determined as a complex with diquinolyl or diethyldithiocarbamate.

Fluorine is determined by the indirect photometric method; it is separated by distilling it off or by hydrolytic precipitation of the accompanying elements and the element content is determined according to the discolouration of the thorium complex with Arsenazo or zirconium with Alizarine Red^{9, 10}.

Gallium is determined by the fluorimetric or the photometric methods with Rhodamine B.

Germanium is determined photometrically in the form of a compound with phenylfluorone or is fluorimetrically determined with Rezarson (after GeCl_4 extraction).

Gold is precipitated in an elemental state on a collector (tellurium, coal powder), extracted and determined photometrically in the form of tetrachloro-aurate of Crystal Violet or Brilliant Green. For fluorimetric determination the method is the same except that Butylrhodamine B is introduced into the final extract.

Indium is first separated by extraction methods from interfering elements (some stages), then determined fluorimetrically with Rhodamine 6G¹⁰ or Ethylrhodamine B⁵.

Iodine after extraction is determined by the photometric and the fluorimetric methods with one of the rhodamine dyes¹¹.

Lead is determined photometrically in the form of dithizonate or a compound with Sulpharsazene after multistage concentrating.

Mercury is determined by the nephelometric method according to Polezhaev's reaction after distilling it off directly from the powdered sample.

Molybdenum is determined by the photometric method in the form of a dithiol complex after extraction or precipitation by α -benzoinoxime.

Nickel is determined photometrically as dimethylglyoximate.

Niobium is determined by the photometric method with Sulphochlorophenol C⁷; with a content less than 30 g/t, niobium is preliminarily concentrated by precipitation with tannin or by extraction of Butylrhodamine B fluoroniobate¹².

Rhenium is extracted in the form of perrhenate of Ethylrhodamine B and determined by the fluorimetric method.

Scandium is, after multistage separation from accompanying elements, photometrically determined with Arsenazo III or other reagents of this group^{7,9}.

Selenium is photometrically or fluorimetrically determined with 3,3'-diaminobenzidine or fluorimetrically with diaminonaphthalene¹³.

Silver is determined fluorimetrically as an associate of the bromide complex of the element with Butylrhodamine B after extraction of dithizonate⁸.

Tantalum is precipitated by tannin and determined photometrically in the form of fluorotantalate of Rhodamine 6G⁹ or of Crystal Violet or is extracted as fluorotantalate of Brilliant Green and the extract is determined photometrically⁵; if in the organic phase Brilliant Green is substituted for Butylrhodamine B, tantalum may be fluorimetrically determined.

Tellurium is determined by the photometric or fluorimetric methods as bromotellurite of Ethylrhodamine B after precipitation in the elemental state on a collector (arsenic) and extraction in the form of an associate with Ethylrhodamine B⁵.

Thallium is extracted and determined photometrically in the form of chlorothallate of Crystal Violet¹⁰ or is assessed fluorimetrically after substitution in the organic phase of Crystal Violet for Butylrhodamine B⁵.

Tin is concentrated by precipitation in the form of hydroxide from a solution containing EDTA and by extraction; it is photometrically or fluorimetrically determined as an associate of the chloride complex of the element with Butylrhodamine B or with Ethylrhodamine B.

Tungsten is photometrically determined with dithiol after extraction or precipitation by α -benzoinoxime.

Zinc is determined photometrically with dithizone.

Zirconium is extracted in the form of a complex with Picramine R and determined with Arsenazo III⁷.

Kinetic determination

Iodine is determined according to its catalytic effect on the reaction of arsenic(III) oxidation with cerium(IV); separation from accompanying elements is attained during the sample agglomeration with the mixture of potassium sodium-carbonate and zinc oxide¹⁴.

Rhenium is determined according to the catalytic effect on the reaction of tellurium(IV) reduction to the elemental state by tin(II); rhenium is preliminarily separated from accompanying elements by extraction as Ethylrhodamine B perrhenate.

Silver catalyses the reaction of manganese(II) oxidation to manganese(IV); it is on this effect that its determination is based. Silver may be separated from precious metals as a dithizonate¹⁵.

Determination by other methods

Information about the use of emission spectroscopy for microelement determination in geological samples is gathered in the books by Rusanov *et al.*^{16,17}. Methods of flame-photometric determination of microelements are given in Poluektov's¹⁸ and Britske's¹⁹ manuals. Instrumental methods

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of determination by activation of microelements are elucidated in the book by Yakubovich *et al.*²⁰ and methods with chemical isolation appear in the collective paper²¹.

ANALYSIS OF SEPARATE NATURAL OBJECTS

What has been said above concerns routine analyses of more or less ordinary geological samples. When complicated and unusual natural objects are analysed, of course diverse methods are used including also those which have not yet gained wide use in industrial laboratories. In analytical laboratories of research institutes the assortment of methods and reagents being used is much more extensive.

Table 4. Determination of microelements in lunar soil returned by the automatic station 'Luna-16,

Microelement	Determination method			
	Emission spectroscopy	Atomic absorption and flame photometry	Mass spectroscopy	Activation
1	2	3	4	5
Antimony			+	
Arsenic			+	
Beryllium	+			
Bismuth			+	
Boron	+		+	
Cadmium		+	+	
Caesium			+	
Cobalt	+		+	+
Copper	+		+	
Fluorine	+		+	
Gallium		+	+	
Germanium			+	
Gold			+	
Indium			+	
Iodine			+	
Lead	+		+	
Lithium		+		
Mercury		+	+	
Molybdenum	+		+	
Nickel	+		+	
Rubidium			+	
Scandium	+		+	+
Selenium			+	
Silver		+		+
Strontium			+	
Tellurium			+	
Thallium		+	+	
Tin	+		+	
Tungsten			+	
Zinc			+	
Zirconium			+	

As an example of an analysis of uncommon objects we may consider the analysis of lunar soil. For the determination of microelements in samples of lunar soil returned by the automatic stations 'Luna-16' and 'Luna-20', spark mass spectrometry, various techniques of emission spectroscopy, radioactivation and a number of other methods were used (*Table 4*).

Particularly widely used was the spark mass spectrometry. With its aid 60–70 elements may be determined in a single experiment with a sensitivity up to 10^{-7} per cent and even better. The precision of the method was, however, not high; this is connected with the different probabilities of ionization of the atoms of the analysed sample in the spark discharge, with superpositions of lines of polyatomic matrix ions as well as oxides, nitrides, etc. upon the analytical lines. In the Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences we succeeded in raising the reproducibility of the method by isolation from the whole spectrum only such ions which are formed in the very first phases of the discharge. This permitted us to elaborate and utilize for the analysis of lunar soil the probe method of analysis of non-conducting multicomponent solids without additions of graphite and silver²². For a complete high precision analysis it was necessary to take 20–25 mg of lunar substance. The powdered sample is pressed in the form of a thin layer into a crucible of high-purity aluminium, the main components of the sample are determined by x-ray spectrography; afterwards the same sample is used in mass-spectrometric determination of microelements. The diabase W-1 (NBS) served as standard sample.

Emission spectroscopy was used in various ways for the analysis of terrestrial rocks of basalt type, but with diminution of the weighed sample. Beryllium and fluorine were determined with a plasma generator for the spectrum excitation of powder samples. Nickel, lead, scandium, cobalt and vanadium were determined with the use of a direct current arc and a diffraction spectrograph. The analysis was carried out with two parallel weighed samples of 20 mg each. Lithium and gallium were determined by flame photometry, silver and cadmium by atomic absorption with an impulse selective atomizer of powder samples²³, thallium and mercury—by atomic fluorescence spectroscopy with atomization of solid samples.

PROSPECTS

Within the next few years in the determination of microelements physical methods of analysis will be more and more put into practice, both with preliminary concentration and without it. Even now in a number of countries atomic absorption has almost become the most widespread method of microelement determination. Nuclear-physical methods are also being rapidly introduced including non-destructive ones. Computers will be extensively used in the future.

The prospect of determining all or most microelements of geological materials by instrumental methods alone in the near future will apparently not be realized. Chemical separation and concentration remains an important stage of natural sample analysis. For the determination of a great number of microelements it is expedient to intensively develop atomic absorption and emission spectroscopy in combination with chemical concentration. In

addition to their other advantages the merit of these methods is the positive identification of the element being determined, which allows less stringency in the demands of its purity of isolation.

Many papers appear in the literature in which reagents (frequently scarcely differing from well known ones) and new methods of the determination of one or two microelements in the absence of accompanying elements are described. On the other hand, investigations of reagents having proved themselves to be successful and methods which may be applied to multi-component systems limiting real objects of technical analysis are lacking. As long as 40 years ago the famous American analyst G. E. F. Lundell wrote about that. Let us quote the text from his paper: 'The Chemical Analysis of Things as They Are'²⁵:

... In the field of analytical chemistry, as in other fields of endeavor, there has been a constant drifting toward specialization. As a consequence, there is an increasing tendency to devote more and more time to determinations which deal with the final act of a chemical analysis, and less and less time to chemical analysis itself—in other words, to consider chemical analysis as dealing with one or two variables instead of the dozen or more that are often involved. This gradual loss of the analytical viewpoint is evident in contemporary articles that purport to deal with chemical analysis. . . . Methods of the type described are about as helpful to the analyst as the method for catching a bird which the old folks used to recommend to children—namely, to sprinkle salt on its tail. To do that, one obviously must have the bird in hand, and in that case there is no need for the salt. So it is with much of the advice that the analyst receives. Minute directions are given for the salting away of the quarry after it has been separated from its fellows.

Many practical analysts, working in the field of mineral raw material analysis, could subscribe to Lundell's words even now in the 'seventies.

Undoubtedly the determination of microelements in geological samples will still remain for a long time an important and complicated field of analytical chemistry.

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