INTERNATIONAL UNION OF
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ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON MICROCHEMICAL TECHNIQUES
AND TRACE ANALYSIS

TRACE ANALYSIS APPLICABLE TO THE DETERMINATION OF MINOR AMOUNTS OF IMPURITIES IN CHEMICALS:

I—GENERAL SURVEY

Prepared for publication by
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LONDON
BUTTERWORTHS

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1. INTRODUCTION

This preliminary study was designed to show and define accurately the interest in trace analysis with regard to practical problems. It was thus expected to determine fields of application and to examine the means used. An investigation was set up with the aim of gathering from the analysts their own opinions and ideas on trace analysis and of finding out how much they would be interested in a cooperative study. This report presents the results obtained, based on the experience of experts in trace analysis. However, it is not claimed that the people consulted constitute a completely representative population of such experts.

The reporter first compiled, from the scientific literature of the last five years, a list of the authors of papers on elemental trace determinations in very varied chemical media. Afterwards the question had to be answered whether the investigation should be immediately limited to given classes of chemicals. This might have meant tackling the problem from a very restricted viewpoint, the more so as a first survey showed that among about 100 papers on trace analysis only 14 dealt with chemicals and 4 with 'high grade' ones; full particulars are given later.

Consequently in order to attain a worthwhile idea of the interest in trace analysis, it was decided not to limit the investigation to 'high grade chemicals' but, on the contrary, to enlarge it so as include, among others, all natural products (animal or vegetable), industrial products. metals and alloys, waters.

In a very general way this investigation must enable us to define a classification of chemical elements called 'traces'. The latter is the result of the

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Associate members: M. Grasserbauer (Austria); R. Levy (France); J. Minczewski (Poland); A. Mizuike (Japan); E. A. Terent'eva (USSR); M. Vecera (Czechoslovakia).

important part played by the element in the analysed media and enables us to appreciate the role of trace analysis in relation to the media.

The words 'traces' or 'trace elements' are often used for chemical elements in low or very low concentrations; we propose to give them a narrower definition and use them only for parts per million (p.p.m.) contents between a fraction of one p.p.m. (10^{-1}–10^{-2}) and a few hundred p.p.m., the lower figure depending on the detection limits which may be possibly attained using our present physical techniques of analysis. This subject will be brought up again in the discussion on fields of application of techniques such as mass spectrometry or radioactivation. Within the framework of this investigation it is proposed to define the concentration to be determined appropriate to each specific case.

It was not considered reasonable to report on trace analysis without considering the determination techniques, which are almost entirely physical ones: methods will be classified with regard to chemical elements or vice versa.

Trace analysis is not only a question of the actual determination (determination of a specific physical property of the element): the sensitivity and limit of detection of the presently available techniques sometimes make a direct determination impossible. Very often it is necessary to separate the element to be determined, especially when the concentration level is lower than a few parts per million; this is why the methods of separation used find a place in the investigation questionnaire.

The whole of the information collected thus gives an account of the present state of trace analysis and its practical applications.

Inorganic and organic compounds were excluded from the field covered, in which only chemical elements were considered and not their combinations inside the products to be analysed. Trace gases (oxygen, hydrogen, rare gases . . .) were also excluded particularly as their determination often requires very different means and techniques.

With a view to preparing a continuation of this project, the recipients of the questionnaire were asked whether they would be willing to cooperate in a study on trace analysis.

Before discussing the results of this investigation, it seems appropriate to describe how the consultants were selected. As already pointed out, the names of authors of papers dealing either with research on techniques or with a new application of a technique were picked up in the scientific literature from 1965 to 1970. Within the limits previously defined the highest impartiality was aimed at, in order that no chemical medium, technique or element should be omitted. The recipients of our questionnaire were selected after a thorough study of the following analytical abstracts reviews: *Bulletin signalétique du Centre National de la Recherche Scientifique* (France) and *Analytical Abstracts* (UK). As it seemed that the other analytical reviews would not provide any additional information they were not taken into consideration.

2. CONTRIBUTION TO THE INVESTIGATION

Questionnaires were sent to about 1000 consultants, all over the world.

In fact as authors or co-authors of papers were the recipients and 40 per cent of them belonged to research teams, only 600 laboratories were involved; generally answers were not individual ones but were made by laboratories.

Replies from 208 laboratories, about one third of the total number, were obtained; 20 laboratories indicated that either they had no interest in the investigation or were unable to answer because of their confidential field of activity. 188 laboratories answered the questionnaire in a very complete way.

These 188 answers are dealt with in this report.

Geographic distribution

Table 1 gives the national distribution of the answers.

Table 1. National distribution of the replies

Argentina	1	Israel	1
Australia	6	Italy	2
Austria	2	Japan	21
Belgium	8	Netherlands	1
Brazil	1	Norway	2
Bulgaria	1	Poland	1
Canada	3	Rumania	1
Chile	1	South Africa	2
Czechoslovakia	7	Spain	3
Ethiopia	1	Sweden	1
Finland	1	Switzerland	1
France	34	UK	11
GDR	2	USA	43
GFR	12	USSR	3
Hungary	5	Pakistan	1
India	8	Yugoslavia	1
	Total = 188		

32 countries answered, in other words the majority of those which were consulted. Such a distribution may not be absolutely representative; in fact it does not correspond with that of the questionnaires sent out.

3. CHEMICAL MEDIA INVOLVED IN TRACE ANALYSIS

The few instances given in the questionnaire 'Instances' showed the range which might be attributed to the word 'Chemicals'; the recipients understood it perfectly. However, the answers were classified as follows:

(*a*) *Metals and alloys* whatever the use of the product may be; for instance nuclear metals fall into this category; obviously ordinary alloys are the concern of most trace analysts in this field.

(*b*) *Rocks, soils and minerals*: inorganic natural soil and subsoil products fall into this category; it is the field of geology, geochemistry, pedology and agronomy; it concerns not only earth sciences but also numerous industries.

(*c*) *Plant materials*: leaves, stems and roots and also derived products such as foods of vegetable origin.

(*d*) *Waters*: detection and determination of trace elements are increasingly used for waters: natural waters, river waters, thermal mineral waters, spring waters, sea water, industrial waste waters, drinking water.

(*e*) *Biological media*: trace analysis is used for animal tissues, biological liquids, blood, urine; not only the usual trace elements (oligoelements) are concerned but very often also toxic inorganic ones.

(*f*) *Air and atmosphere*: testing of air pollution makes use of trace analysis, this new application will grow in importance and scope.

(*g*) *Industrial products*: in this category are to be found glasses, cements, plastics and also oil products, lubricants, motor fuels . . .

(*h*) *Pure chemicals*: under the 'chemicals' category falls a great variety of high grade products: chemicals for industrial use, catalysts, semiconductors, high grade chemicals, chemical reagents, inorganic acids, inorganic bases . . .

A complete examination of the results of this investigation is given below.

Table 2 shows the distribution of the laboratories consulted within the above-mentioned categories.

Table 2.

Metals and alloys	58	Biological media	30
Rocks, soils and minerals	74	Air and atmosphere	17
Plant materials	33	Industrial products	18
Waters	65	Pure chemicals	34

Some of the laboratories are concerned with the study of several media. *Table 3* gives a classification of laboratories carrying out trace analysis.

Table 3.

Materials	Percentage of total number of laboratories making tests	Materials	Percentage of total number of laboratories making tests
Rocks, soils and minerals	39	Plant materials	17.5
Waters	34.5	Biological media	16
Metals and alloys	31	Industrial products	9.5
Pure chemicals	18	Air and atmosphere	9

4. TRACE ELEMENTS IN VARIOUS CHEMICAL MEDIA

The results of the inquiry allow the chemical elements present as traces to be classified as a function of their interest in each of the above-defined materials.

(a) Metals and alloys

Among the laboratories analysing metals and different alloys, the distribution is as follows:

(1) Cu, Mn, Ni, Pb are determined in more than 20 laboratories

(2) Al, As, B, Cd, Co, Cr, Fe, Mg, Mo, Sn, W, Zn are determined in 11–20 laboratories, depending on the element

(3) Ag, Au, Be, Bi, Ca, Ce, K, La, Li, Na, Si, Nb, P, Pd, S, Se, Te, Tl, V, Zr, Ti are determined in 3–10 laboratories

(4) Ba, Cl, F, Hg, Pt are determined in 1–2 laboratories.

The most important elements can be listed as follows (in order of decreasing importance): Cu, Ni, Mn, Pb, Zn, Fe, Co, Mo, Mg.

(b) Rocks, soils and minerals

Trace analysis finds its greatest application in the study of natural minerals for a variety of reasons, as mentioned above; this is to be expected, for the earth's crust is the source of the chemical elements. With the exception of the 'major' elements (Fe, Si, Al, Mg, Ca, Na, K) almost any other element can be present as traces in this medium; however, interest varies with each element, for two reasons: the concentration may be too small to be determined conveniently, or the importance of the element may be unknown or little known.

The following classification results from the inquiry (for 74 laboratories):

(1) Co, Cr, Cu, Mn, Ni are determined in more than 30 laboratories

(2) Mo, Pb, V, Zn are determined in 21–30 laboratories

(3) Ag, Au, B, Ba, Li, Mg, Rb, Sn, Sr, U are determined in 11–20 laboratories

(4) Al, Be, Bi, Ca, Cd, Fe, Hg, K, La, Na, Pd, Pt, Sb, Se, Ti, W, Zr and rare earths are determined in 3–10 laboratories

(5) F, Cl, Nb, Te, Tl are determined in 1–2 laboratories.

In this classification, it is preferable to ignore the elements Fe, K, Na, Ti, which are much more frequently found in concentrations above 1000 p.p.m. than as traces.

The elements which are most often sought are:

Cu (38 laboratories), Cr (32), Co (32), Mn (32), Zn (29), Pb (26) (out of 74 laboratories).

(c) Waters

All the elements can occur as traces in waters (natural waters, drinking waters, industrial effluents, waste waters).

In order of interest, the elements determined are:

(1) Cd, Cr, Cu, Fe, Mn, Pb, Zn are determined in more than 20 laboratories

(2) Ag, Al, As, B, Ba, Ca, Cl, Co, F, Hg, K, Li, Mg, Mo, Na, Ni, Sn, Sr, V are determined in 11–20 laboratories

(3) Au, Be, Bi, I, La are determined in 3–10 laboratories

(4) Ga, Rb, Sb, Se, Te, Ti are determined in 1–2 laboratories.

A more precise classification is as follows (the number of laboratories out of 65 studying the element is given in brackets):

Cu (36), Pb (34), Zn (32), Mn (28), Cr (27), Cd (25), Fe (25), As (20), Mo (19).

In this list are found the elements Pb, Cr, Cd, As, which are highly toxic in nature not only for plant but also for animal life. Evidence is thus provided of the importance of trace analysis in toxicology.

(d) Plant materials

Trace analysis applied to plant materials, which also include derived agricultural products, is much more restricted than for the materials considered above. The elements which are sought basically are the biologically active elements or oligoelements (Co, Cu, Fe, Mn, Zn) and the toxic element, Pb.

The classification of these elements in order of interest is as follows: Cu (25), Zn (20), Fe (17), Mn (16), Pb (12), Co (10). (The numbers in brackets are the numbers of laboratories studying the element, out of 33 laboratories.)

It should be noted that the elements P, K, Ca, Mg, considered as 'major' elements in plant materials, can also be present as traces and be determined as such; trace analysis extends also to these elements, particularly in certain problems of mineral deficiencies.

Some other elements of interest in the vegetable kingdom are Al, As, B, Cr, F, Mo, Rb, S, Se, Si, Sr.

Finally, although vegetable food products are included in the above classification, it should be noted that in foods, the greatest interest is shown in As, Cu, Fe, Mn, Pb, Sn, Zn. The toxic role of As, Pb and Sn particularly, should be stressed again.

(e) Biological materials

Thirty laboratories replied to the questionnaire (16 per cent). The remarks made for plant materials are applicable here also: analysis is concerned with the dynamic oligoelements and the toxic minerals. The elements which are most often sought and determined are: Cu, Zn (in more than 10 laboratories), and As, Cd, Co, Cr, Fe, Hg, Mg, Mn, Pb (in 5–10 laboratories).

More occasionally, the elements Al, Au, Ca, F, K, Na, Ni, Sb, Se, Tl can be sought.

The most important elements can be listed in the following order:

Cu, Zn, Pb, Co, Hg, Mn, As, Fe, Cd, Cr.

Among these, the oligoelements (Cu, Zn, Co, Mn, Fe) and the toxic elements (Pb, Hg, As, Cd, Cr) can be differentiated.

(f) Industrial products

This class consists of finished products composed of many constituents; chemical products, pure products and high-purity reagents are dealt with later. Scrutiny of the inquiry shows that trace analysis is mainly applied to the following materials:

(1) *Glasses and cements*, in which Al, Ca, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sr, Zn and Ti are determined.

(2) *Petroleum products, lubricating oils, used oils*: According to the number of laboratories applying trace analysis (7 laboratories replied to the questionnaire), the classification in decreasing order of importance, is as follows:

Pb (6), Cu, V (5), Ca, Cr, Fe, Mg, Zn, Cl (4), Be, Si, Sn, F, S (3).

The relatively small number of laboratories makes it essential not to place too much significance on these figures.

(3) *Plastics*: The following elements are determined as traces in industrial plastic materials (only 6 laboratories replied to the inquiry).

Be, Cl, Cr, Co, Cu, Fe, K, Mg, Mn, N, Ni, Pb, S, Zn.

(g) Chemical products

The field of application of trace analysis is very extensive. However, it is possible to distinguish three classes: *industrial chemical products*, e.g. nuclear products, semiconductors, catalysts, sulphides, phosphorescent or luminescent compounds; chemical products acting as *intermediate products* in the development of defined products, e.g. organic solvents; and *chemical reagents* for analytical use when very high purity is essential.

Although all these products were mentioned in the replies to the inquiry, it is very difficult to group them with respect to the purpose of the analysis, because the questionnaire did not require precise information on this point. This question is of great importance, particularly with regard to the application of trace analysis to products of high purity, but it would have considerably limited the number of replies on account of the often confidential nature of activities within certain Companies. *Table 4* indicates some of the products analysed.

Table 4. Trace analysis applied to some chemical products

Chemical product		Elements sought
$CsCl$		Zn, Cu, Pb, Cd, Tl, Mn
$SnCl_4$		Cu, Pb, Mn, Fe, Co, Ni, Mo
$AgCl$		Cu, Pb, Co, Ni, Fe, Mn
$NaCl$		Mo
$NiCl_2$		Cu, Mn
$SiCl_4$		Al, B, V, Mg, Cu, As
$SiHCl_3$		Al, B, V, Mg, Cu, As
$NaCl$, KCl, $SrCl_2$, Li_2CO_3		alkalis, alkaline earths, Mg
$AgNO_3$		Cu, Pb, Cd, Ni, Zn, Fe, Mn
$Pb(NO_3)_2$		Se, Cu
Ni, Co, Zn, Cu, Mg salts		Cr, Fe, Co
Diverse products:	(1)	Mn, Mg, K
	(2)	Mn, Co, Ni, Cr, Cu, Re
	(3)	Br, I, As, SO_4
	(4)	Zn, Mn, Co, Ni, P, Cu
	(5)	Cr, Fe, Co
	(6)	Cu, Pb, Cd, I, Zn, Mn, As, Ni, Co
Nuclear products:	$Th(NO_3)_4$	Cu, Mn, Cd, Co, Zn, Cr
	$Zr(NO_3)_4$	Cu, Mn, Cd, Co, Zn, Cr
	$NiCl_2$	Cu, Mn
	HCl, HNO_3, H_2O_2	Rare earths, Mg, Mn, Cu, Si, Ag, Ca, Fe, Cr, As, Ba, Bi, B, Zn, Zr, Co, La, Mo, Pt
	Rare earths	Fe, Mn, Mg, Pb, Cu, rare earths
	Various (1)	Ag, Hf, Sc
Metallic oxides:	WO_3, H_2WO_4, MoO_3	Mo, Mn, Ni, Co, Na, K, Ca, Pb, Cu, Si
	As_2O_3	Fe, Cu
	rare earth oxides	Zn, Pb, Cu, rare earths
Mineral acids:	HCl, HF	B
	HCl	All traces
	H_3PO_4	Cd, Pb, Cu
	H_2SO_4	B
	various mineral acids (1)	All traces
	(2)	Cu, Bi, Cd, Zn, Pb, Tl
Organic acids:	CH_3COOH (1)	Zn, Cd, Cu
	(2)	Na, Cu, Au, Al
	Various	Co, Fe, Ni, Br

Table 4 (continued)

Chemical products		Elements sought
Mineral bases:	NaOH, KOH	B, Li, Cl
	Various	Mn, Pb
Various products:	CdS	Cu, Zn, Si, Mg, Pb, Ag
	Semiconductors	Cu, Pb, Cd, In, Zn, Re
	GaAs, GaP, GaAsP	Ag, Se, Cu, Mg, Sr, Ba, Co, Fe, Ge, Mn V, Al, Be, In, Pt, Sn, Sb, Zn
Chemical reagents of high purity (see also chemical products and analytical reagents)		
	Na_2CO_3	Zn
	$CaCO_3$, $BaCO_3$, $SrCO_3$	All traces, especially alkalis, alkaline earths, Pb, Tl
	NaOH, KOH	B, Li, Cl
	NaOH	All traces
	HCl, H_2SO_4, HF	B
	HCl, HF	All traces
	Lithium pyrosulphate	All traces
	Lithium borate	All traces
	Sodium hydrogen sulphide	Pb, Cd, Zn
	Various reagents (1)	Zn, Cu, Pb, Cd, Tl, Mn
	(2)	Pb, Bi, Fe, Ti
	(3)	Cu, Pb, Cd, I, Zn, Mn, As, Ni, Co

Note: Some laboratories did not give details of the products studied and these have been listed as (1), (2), (3) with an indication of the trace elements sought.

A study of the above table shows the whole range and variety of the determination of impurities in pure products. To be exact, of the 30 laboratories which replied to the questionnaire,

17 dealt with pure products for industrial use,

5 dealt with pure products applied in nuclear energy (with the exception of the metals mentioned above),

14 dealt with chemical reagents for analytical purposes.

5. ANALYTICAL TECHNIQUES USED IN TRACE ANALYSIS

Since almost all chemical, physicochemical and physical methods are exploited for the determination of trace elements, it is of interest to establish

Table 5. Analytical techniques and number of laboratories carrying out trace analysis

1	Colorimetry and absorption spectrometry	78
2	Atomic absorption spectrometry	75
3	Emission spectrography (arc and spark)	43
4	Polarography	35
5	Radioactivation	26
6	X-ray (emission and fluorescence)	25
7	Flame spectrometry	17
8	Spark mass spectrometry	12
9	Electrical methods	10
10	Direct potentiometry (specific electrodes)	8
11	Direct reading spectrometry	6
12	Chromatography	6

their distribution in terms of the number of users. *Table 5* shows the classification of 188 answers to the questionnaire.

It must be stressed that this classification refers to the activity of the laboratories in recent years, during which period there has been a considerable development of certain techniques, e.g. atomic absorption spectrometry, mass spectrometry, radioactivation. The classification will certainly not be valid in two or five years time. However, it is interesting to see that the traditional colorimetric methods still remain at the top of the list, closely followed by atomic absorption.

Methods of concentration and separation

Direct determinations on samples or sample solutions are obviously not always possible. *Table 6* gives the most frequently used separation methods, with an indication of the number of laboratories involved. It is clear that classical chemical methods remain very widely used in trace analysis. Organic solvent extraction is generally used in conjunction with the following techniques: colorimetry, atomic absorption spectrometry, emission spectrography, polarography and x-ray spectrometry; either the selective separation of one element or the separation of groups of trace elements is possible.

Table 6. Separation methods used in trace analysis

1	Solvent extraction of organic complexes	79
2	Ion exchange	21
3	Precipitation of organic or mineral complexes	18
4	Distillation or sublimation	8
5	Electrolytic deposition	5

Range of application of techniques

The answers to the questionnaire show that none of the analytical techniques is specific for a particular material. Most of the methods are applied to solutions, so that sample dissolution is necessary; some methods, e.g. arc and spark spectrometry, and x-ray fluorescence, allow direct analysis of powdered samples. Occasionally, recovery of the analysed sample is necessary; a non-destructive technique such as x-ray fluorescence must then be used. Finally, it is clear that the determination of some special element may demand a certain technique.

The investigation shows clearly that the techniques listed above are exploited for the analysis of all types of material. The practical application of a technique is limited only by the chemical elements sought and by their concentration.

Table 7. Range of application of techniques and number of laboratories

Colorimetry and molecular absorption spectrometry							
Ag	2	Cr	14	Nb	8	Sn	8
Al	14	Cu	24	Ni	15	Te	2
As	16	F	11	P	15	Ti	12
Au	3	Fe	22	Pb	15	Tl	2

Table 7 (continued)

B	16	Ga	2	Pd	4	V	6
Be	7	Hg	4	Pt	2	W	5
Ca	2	I	3	S	7	Zn	7
Cd	5	Mg	3	Sb	5	Zr	4
Cl	9	Mn	15	Se	6	U	5
Co	14	Mo	17	Si	11	rare earths	1

Atomic absorption spectrometry

Ag	6	Cd	16	K	11	Ni	22
Al	6	Co	19	Li	10	Pb	22
Au	5	Cr	15	Mg	24	Rb	7
Ba	4	Cu	41	Mn	26	Sn	3
Be	3	Fe	22	Mo	7	Sr	15
Ca	14	Hg	7	Na	10	V	5
						Zn	36

Spectrography (arc and spark)

Ag	14	Cd	8	Mn	12	Sn	15
Al	15	Co	13	Mo	14	Sr	6
As	5	Cr	14	Nb	5	Ti	10
B	16	Cu	19	Ni	15	V	12
Ba	6	Fe	11	Pb	18	W	3
Be	8	La	4	Pt	4	Zn	9
Bi	4	Li	8	Rb	3	Zr	4
Ca	9	Mg	13	Si	9	rare earths	11

Polarography

As	4	Cu	19	Ni	7
Bi	3	Fe	3	Pb	26
Cd	16	Mn	8	Sb	3
Co	7	Mo	6	Sn	5
				Tl	3
				Zn	16

Radioactivation

As	8	Fe	5	Na	5	W	4
Au	7	Ga	4	Ni	6	Zn	8
Co	6	K	4	Rb	3	rare earths	5
Cr	5	Mn	4	Sb	4		
Cu	11	Mo	4	Si	3		
				Sr	3		

X-ray (emission and fluorescence)

As	3	Cs	4	Nb	3	Sn	3
Ba	4	Cu	10	Ni	5	Sr	3
Ca	3	Fe	5	P	3	Ti	4
Co	4	Mn	7	Pb	5	Zn	8
Cr	5	Mo	3	Rb	3	Zr	3
						V	5
						rare earths	4

Flame spectrometry

Ca	5
K	8
Li	8
Na	7
Rb	3

Table 7 shows, for each technique, the elements which can be analysed and the number of laboratories actually using the technique. *Table 8* shows,

Table 8. Techniques used for particular elements*

Element	Techniques
Ag	SE (15), AA (6), C (2)
Al	SE (16), C (14), AA (6)
As	C (16), RA (9), SE (6), P (5), SX (3)
Au	RA (8), AA (5), C (3)
B	SE (20), C (16)
Ba	SE (12), SX (4), AA (4)
Be	SE (11), C (7), AA (3)
Bi	SE (5), P (3), RA (2)
Ca	AA (14), SE (9), EF (5), SX (3)
Cd	AA (16), P (16), SE (9)
Cl	C (19)
Co	AA (19), SE (17), C (14), P (7), RA (6)
Cr	SE (19), AA (15), C (14), P (7), RA (5), SX (5)
Cs	SX (4), RA (2), SE (2)
Cu	AA (41), C (24), P (19), SE (19), RA (11), SX (10)
F	C (11), I (8)
Fe	C (22), AA (22), SE (11), RX (5), RA (5), P (3)
Ga	RA (4), SE (3)
Hg	AA (7), C (4), RA (2)
I	C (3), P (2), RA (2)
K	AA (11), EF (10), RA (4)
Li	AA (10), EF (10), SE (8)
Mg	AA (24), SE (14), C (3)
Mn	AA (26), C (15), SE (14), P (8), SX (7), RA (4)
Mo	C (17), SE (16), AA (7), P (6), RA (4), SX (3)
Na	AA (10), EF (8), RA (5)
Nb	C (8), SE (6), SX (3)
Ni	AA (22), SE (20), C (15), P (7), RA (6), SX (5)
P	C (15), SE (4), SX (3)
Pb	P (26), SE (23), AA (22), P (15), SX (5)
Pd	C (4)
Pt	SE (4)
Rb	AA (7), SE (3), RA (3), SX (3)
S	C (7)
Sb	C (5), SE (4), RA (4), P (3)
Se	C (6)
Si	C (11), SE 10), RA (3)
Sn	SE (16), C (8), P (5), SX (3), RA (3)
Sr	AA (15), SE (10), SX (3)
Te	C (2), SX (2), SM (2)
Ti	C (12), SE (11), SX (4)
Tl	P (3), AA (2), SE (2), C (2)
U	C (5), SX (5), SM (3)
V	SE (20), C (6), AA (5), SM (3)
W	C (5), RA (4), SE (4)
Zn	AA (36), P (16), SE (13), RA (8), SX (8), C (7)
Rare earths	SE (12), RA (5), SX (4)

* AA, Atomic Absorption; EF, Flame Emission; SE, Emission Spectrography; P, Polarography; C, Molecular Absorption Spectrometry or Colorimetry: SX, X-ray Spectrometry (emission and fluorescence); SM, Mass Spectrometry; RA, Radioactivation; I, Potentiometry. The number after each technique is the number of laboratories carrying out the analysis.

for each element, the most frequently used techniques. In *Table 7*, only those elements which are analysed by at least three laboratories by the same method are included. The results for direct-reading spectrometry (a special application of emission spectrography) and for mass spectrometry (used for multielement analysis of many elements) are not included here because the methods are used by very few laboratories. Other techniques such as electrical, chromatographic and titrimetric are applied only in rare cases. It should be noted that direct potentiometry (selective electrodes) is used by 8 laboratories for the determination of traces of fluoride.

For some elements, especially the common elements, it can be seen from *Table 8*, that there is a choice of several methods. This is the case for Al, As, Au, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Si, Sn, Sr, Ti, V and Zn, although one particular technique emerges clearly as most often used for certain elements: As (C), Ba (SE), Be (SE), Ca (AA), Cu (AA), Hg (AA), Mg (AA), Mn (AA), P (C), Rb (AA), Sn (SE), V (SE), Zn (AA). The choice is limited to two techniques for a few elements: Al (SE or C), Bi (SE or C), Cd (AA or P), F (C or I), Fe (C or AA), K (AA or EF), Li (AA or EF), Mo (C or SE), Sr (AA or SE), Ti (C or SE), Sb (C or SE). Finally, for some elements, only one technique is applied: Cl (C), Ga (SE), Pd (C), Pt (SE), S (C) and Se (C). In this classification, radioactivation methods have been omitted, because they cannot be considered as available to all laboratories.

Multielement analytical techniques

In many cases, trace analysis or impurity analysis which involves several elements, is limited by the capability of the technique used. A considerable number of the answers to the questionnaire did not give information on the elements determined but only mentioned that all traces were detected.

Multielement analysis is most frequently applied to rocks, soils, minerals, waters, metals, alloys and chemical products. Several techniques are convenient for multielement analysis: emission spectrography is applied in 20 laboratories, atomic absorption and flame emission in 19 laboratories, radioactivation in 8 laboratories, mass spectrometry in 7 laboratories, and x-ray spectrometry in 5 laboratories.

Application of radioactivation and mass spectrometry

Although these techniques are included in the above comments, it is important to distinguish them from the more 'classical' techniques. These methods require very expensive equipment so that their use is confined to a very small number of laboratories. Furthermore, they often differ from other methods in their great sensitivity, which can enable either direct trace analysis at concentrations of 10^{-3}–10^{-1} p.p.m., or after separation, 10^{-5}–10^{-3} p.p.m., to be determined.

Finally, in spark mass spectrometry, the elimination of all chemical preparation considerably reduces the risk of contamination. This is also true of radioactivation; if irradiation is done on the original sample, the risk of contamination no longer affects subsequent chemical separations.

Some examples of the application of these methods, culled from the answers to the questionnaire, show the possibilities of the techniques.

Spark mass spectrometry

Pure iron and steels: direct determination of Ca, Co, Cr, Cu, V, As, at 2×10^{-2} p.p.m., Ti, Zn at 5×10^{-3} p.p.m.

Pure metals: direct determination of 0.3 p.p.m. of most elements; determination after electrodeposition or ion exchange of all elements at the 10^{-3} p.p.m. level.

Conductors and insulators: direct determination of all elements at a 10^{-2} p.p.m. level; determination after electrolytic separation for some elements at the 10^{-3} p.p.m. level.

Plant materials: determination of 10^{-1} p.p.m. of Se, Cu, Fe, Ni.

Atmospheric dusts: direct determination of 10^{-5} p.p.m. of most elements.

Radioactivation

Analysis of metals: determination of 10^{-5} p.p.m. Cu and As, 10^{-2} p.p.m. Sb, Re and Mn, 10^{-1} p.p.m. In, Pd, Co and Ir.

Pure iron: direct determination of 10^{-1} p.p.m. Al, Co, As, Sb and V.

Iron alloys: direct determination of 10^{-1} p.p.m. In and Mn.

Rocks, minerals, meteorites, sediments: 10^{-1}–10^{-5} p.p.m. Co, Cu, Zn, Sc, Cr, Ag, Sb, Au, Ir, Os and Ru.

Plants and biological materials: 10^{-1}–10^{-5} p.p.m. Mn, As, Co, Cu, Zn, Sc, Cr, Hg, Sb, As, Cs, La and Sm.

Chemicals: determination of 10^{-2} p.p.m. Na, Al and Br, 10^{-6} p.p.m. Au and Cu in alcohols, of 10^{-5} p.p.m. Au, 10^{-4} p.p.m. Cu and 10^{-2} p.p.m. Na and Al in acetic acid, and of 10^{-4} p.p.m. As, Cu and Au and 10^{-2} p.p.m. Zn in semiconductors.

Further interesting cases of application are to be noted:

(*a*) for elements of the platinum group, little known by classical methods—Pt, Pd, Os, Ir, In, Re;

(*b*) for very low contents of elements (10^{-3}–10^{-5} p.p.m.)—As, Cu, Au;

(*c*) for rare earths—10^{-1}–10^{-4} p.p.m;

(*d*) for all substances of high purity—nuclear materials, semiconductors, analytical reagents.

6. TRACE ANALYSIS OF PURE CHEMICALS

On the preceding pages the interest in trace analysis applied to chemical products and the range of application were seen from several examples.

Below the case of high purity products is considered, especially of analytical reagents, defining elements investigated in relation to materials analysed, their contents found, and the methods applied.

One of the most utilized reagents is water, distilled or deionized. Several laboratories systematically determine impurities (trace elements) above 0.01 μg/ml (10^{-8} per cent), which are detectable by colorimetry, atomic absorption spectrometry, emission spectrometry and x-ray spectrometry; in special cases the following were determined:

	μg/ml		μg/ml
Zn, Cu	0.006	B	0.0002
Pb, Bi	0.02	Cu	0.003
Mn	0.005	Cl	0.05
Mg	0.001	Na	0.01

In individual cases polarography, colorimetry, fluorimetry, radioactivation and atomic absorption spectrometry are used.

Mineral and organic acids (quality 'pure for analysis') are controlled frequently and some laboratories are interested in all impurities, others in a limited number of certain elements.

Cases of application are as follows:

(*a*) *Analysis of strong acids* HCl, HNO_3, H_2SO_4:
determination of Cd, Mg, Mn, Cu, Sc, Ag, Ca, Fe, Cr, rare earths (0.01 μg/ml), In, Ir, Co, Mo (0.1 μg/ml), Be (0.005 μg/ml) by emission spectrography;
determination of Cu, Bi, Cd, Zn, Pb, Tl (0.006–0.001 μg/ml) by polarography;
determination of traces and ultra traces (all methods);
determination of B (0.005 μg/ml) by fluorimetry.

(*b*) *Analysis of phosphoric acid*: determination of Ca, Pb, Cu (0.1 μg/ml) by polarography.

(*c*) *Analysis of acetic acid*: determination of Zn, Cd, Pb, Cu (0.05 μg/ml) by polarography, determination of Co, Fe, Ni (1 μg/ml) by atomic absorption spectrometry, of Br (10 μg/ml) by x-ray spectrometry.

(*d*) *Analysis of alkali carbonates* (Na, K, Li): determination of Zn, Pb, Tl, Cu, Cd, (0.01 p.p.m.) by polarography, determination of traces (all elements) by emission spectrography and mass spectrography.

(*e*) *Analysis of alkali hydroxides* (NaOH, KOH): determination of traces by emission spectrography and mass spectrography;
determination of Mn, Pb (0.02 p.p.m.) by polarography;
determination of B (0.01 p.p.m.) by colorimetry or fluorimetry;
determination of Cl (0.1 p.p.m.) by colorimetry;
determination of Li (0.1 p.p.m.) by radioactivation.

(*f*) *Analysis of alkali chlorides*:
NaCl; determination of K, Rb, Li, Cu by flame emission photometry, determination of Mg by atomic absorption spectrometry, determination of Mo (0.001 p.p.m.) by colorimetry;
KCl; determination of Na, Rb, Cs, Li, Mg, Ca by flame emission photometry or atomic absorption spectrometry.

(*g*) *Analysis of chemical reagents* (without defining their nature). Several laboratories analyse their reagents: all traces are determined by means of emission spectrography or mass spectrography.

One notes also particular determinations:

K, Mg, Mn (5 p.p.m.) by atomic absorption spectrometry.
Ag (0.1 p.p.m.) by radioactivation;
Sc (0.04 p.p.m.) by radioactivation;
Pb, Bi, Fe, Ti (0.05 p.p.m.) by polarography;
Cu, P, Cl, Zn (0.1 p.p.m.) by colorimetry;
Mn, Co, Ni (0.1 p.p.m.) by atomic absorption spectrometry.

According to the answers on the questionnaire of the inquiry it seems that, in general, laboratories are interested most frequently in certain elements in a range of concentration, which is defined by their special problems. With regard to the analytical methods applied one notes that certain methods show very general applicability, such as emission spectrography and spark source mass spectrography, and others—polarography, colorimetry, atomic absorption spectrometry, x-ray spectrometry—are especially convenient for certain elements.

Further we note that for a great number of laboratories the analysis of high purity substances is only part of their activities on investigation of chemical substances.

It is clear that today analytical laboratories can obtain commercially available high-purity substances accompanied by a certificate of analysis, in which one can have confidence. This limits somewhat trace analysis of these substances and analytical reagents. Producers of chemicals frequently apply multielemental methods, such as emission spectrography and spark source mass spectrography, for control of impurities in high-purity products.

Moreover the inquiry shows that analytical laboratories investigate more frequently individual methods of determination, such as atomic absorption spectrometry, colorimetry and polarography.

7. INTEREST IN A COOPERATIVE INVESTIGATION

In the last question of the inquiry the laboratories were asked whether they would be willing to participate in a cooperative trace analysis of samples. From the 188 laboratories returning the questionnaire the answers to this question were: 144 were willing to cooperate, 20 were not able to cooperate and 24 gave no answer. According to these results 76 per cent of the laboratories are in favour of a cooperative investigation. The results require some comment.

The interest in a cooperative investigation is related to all products analysed in the laboratories, such as rocks, soils, minerals, waters, metals and alloys, chemicals. . . . Further the laboratories prefer to analyse those materials which lie in the area of their own analytical technique and experience.

For the performance of the cooperative investigation some viewpoints should be considered; (*a*) the number of samples and participants should be limited, (*b*) information should be sent early to the participants, (*c*) the time available should be sufficient.

Perhaps it will be more efficient to select some standard reference materials serving generally for the control of methods, which are available from several sources—pure metals, analysed alloys, rocks, minerals, industrial products (glasses . . .).

It seems that the laboratories are more interested in trace analysis with respect to one, several, or all elements present than in control of impurities with respect to a defined level of their contents.

Certain cooperative inter-laboratory investigations concerned with defined materials e.g. samples of rock, mineral, alloy, plant . . . . already exist.

The objectives are of several types: control of analytical methods applied in laboratories, reproducibility of results, characterization of calibration samples, comparison of the range of application of the different physical methods of analysis. . . . Here arises the question of whether IUPAC could coordinate such activities.

The preparation of samples or solutions for calibration is also an important problem, which could be the object of cooperative investigation. Further the choice of the most convenient method could be the subject of a discussion between the analysts, because one is not always sure that the most adequate method is used either for the material to be analysed or for the element to be determined.

A classification of analytical techniques in relation to the level of trace element contents in a given material should be studied experimentally.

8. CONCLUSIONS

Questionnaires concerning trace analysis applicable to determination of minor impurities in chemicals were sent to 600 laboratories (1 000 analysts) in all countries; 208 were returned, of which 188 were interested in this work.

The materials most investigated by trace analysis are, in decreasing importance: rocks, soils, minerals, waters, metals, alloys, chemicals. . . . The analytical techniques most utilized are (in decreasing importance): colorimetry, atomic absorption spectrometry, emission spectrography, polarography . . . ; techniques such as spark source mass spectrometry or radioactivation are still reserved for the determination of very low trace contents (10^{-2} p.p.m.) or for multielemental analysis.

Trace analysis is of interest for chemicals, especially high-purity products used in industry or in laboratories, and analytical reagents, each substance often being a special case of analysis depending on its application.

Mineral acids and bases are the reagents which are most frequently controlled.

According to the results of the inquiry 76 per cent of the laboratories are able to participate in a cooperative inter-laboratory investigation. It now remains to define the method and scope of this further investigation.