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Multi-element analysis for environmental characterization†

Bruno Sansoni

Central Department for Chemical Analysis, Kernforschungsanlage Jülich GmbH, D-5170 Jülich-1, Federal Republic of Germany

Abstract - Before starting to characterize the environment by its elemental composition, it may be useful to ask about the objective of these efforts. This includes questions about the scope of environmental protection, the definition of the environment and the limitations of its characterization by elemental composition alone. In the second part of this lecture, examples are given of the elemental composition of well analysed samples from the atmosphere, hydrosphere, lithosphere and biosphere. The third part introduces the principle of multi-element analysis and the fourth part gives examples. Finally, future aspects of modern chemical analysis are outlined with respect to the multi-element principle.

1. INTRODUCTION

There is no doubt that environmental protection stands behind many efforts in environmental research. What, however, does this mean? Is it protection of the environment and nature against man, or is it protection of man against a hostile environment? It has become evident that it can only be protection of the environment in order to protect the health and well-being of man and not the whole of nature itself. This is mainly because of limited economic support and the central role which man gives himself in nature (ref. 57).

What is the environment which has to be characterized? Twenty years ago toxicology defined it as air, water, soil and food surrounding man. Ecology has drawn specific attention to the dynamic equilibrium between the community of all living organisms (biozoen) with their non-living environment (biotope). Based on radiation protection, however, it became quite clear that not only the elemental composition of the surroundings, but the whole world around man can become important and thus has to be considered. Every second or even millisecond, the living organism is in interaction with cosmic rays. They have their origin far outside our planet in the galaxy as well as in the sun of our solar system. The other important natural contribution to the radiation exposure of man on the planet earth is due to the existence of radioactive isotopes of the elements in the outer earths crust (53) (Table 1).

2. ELEMENTAL COMPOSITION OF ENVIRONMENT

In order to characterize the chemical element composition of the environment in the following we shall use frequency distributions of mean element contents or concentrations from geochemistry (ref. 72) and biology. In Fig. 1, they are arranged according to the content of major, minor and trace element levels on the x-axis and the corresponding number of elements within one content range (according to increasing conent) on the y-axis.

† 5th Contribution to the Principles of Trace Analysis of Elements and Radionuclides. 4th Contribution (ref. 59).
Dedicated to the 60th birthday of Professor Dr. Ludwig Feinendegen, Jülich.

Comparing the mean composition of the surface of the earth and moon, it becomes evident that there is not much difference except in the large amounts of water on the surface of the earth. Returning from moon, astronauts observing our blue planet earth are able to differentiate between continents, oceans and clouds. These are typical parts of the lithosphere, hydrosphere, atmosphere and biosphere of the earth. The atmosphere mainly consists of air (Fig. 1) which above ground additionally contains solid and liquid aerosol particles. In the histograms, the so-called toxic elements are characterized by a point in their box.

Table 1: Natural and Artificial Radionuclides in Nature

Natural Radionuclides in Nature

1. Primeordial radionuclides

   Half-life times longer than 10^8 years (a)

   - K-40 $1{,}26 \cdot 10^9$ a
   - Rb-87 $4{,}70 \cdot 10^{10}$ a
   - Th-232 $1{,}41 \cdot 10^{10}$ a

     Th-232 decay series:

     Th-232, Ra-228, Ac-228, Th-228, Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Po-212, Tl-208, Pb-208
   - U-238 $4{,}47 \cdot 10^9$ a

     U-238 decay series:

     U-238, Th-234, Pa-234, U-234, Th-230, Ra-226, Rn-222, Po-216, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210, Pb-206

2. Cosmogenic radionuclides

   Produced by reaction of cosmic rays in atmosphere and earth

   - Be-7, Na-22, Na-24
   - He-3, C-14 and others

Artifical Radionuclides in Nature

1. Nuclear Power Production

   Mining and milling: U, Th, Ra; Rn
   Fuel fabrication: U
   Reactor operation, normal:
   - Atmosphere: Kr, Xe, Ar; H-3, C-14, I-131; Cs, Sr, Co, Ru
   - Water: H-3; Cs, Co, Mn, I
   - Water effluent of Stanford reactor, 4 hours after irradiation (1959): Mn-56, Cu-64, Na-24, Cr-51, Np-239, As-76, Si-31, Zn-69, Ga-72, Sr-92, U-239, I-133, Y-92, Nb-97, Sr-91, Zn-65, P-32, Y-30, I-135, Y-93

   Fuel reprocessing:
   - Atmosphere: Kr-85; H-3, C-14; I-131, I-129; Cs, Ru, Sr
   - Water: H-3, I-129; Cs, Ru, Sr

   Global contribution from fuel reprocessing and reactor operation: H-3, Kr-85, C-14, I-129

2. Nuclear Explosions

   Exposure by more long-lived fission products (internal)
   H-3; C-14; Mn-54, Fe-55; Kr-89, Sr-90; Ru-106; I-131; Cs-137, Cs-136; Ba-140; La-140, Ce-144, Pu-239, Pu-240; Pu-238, Pu-241; Am-241, Cm-242

   Exposure by shorter-lived radionuclides (external)
   Fission products: Sr-89, Y-90, Y-91, Zr-95, Nb-95, Ru-103, Rh-106, Cs-134, Cs-136, Ba-137, Ce-141, Pr-143, Pr-144, Pm-147, Sm-151.
   Activation products from mantle:
   Cr-51, Co-57, Co-58, Fe-59, Co-60, Zn-65

   Unfissioned nuclear explosives:
   U-235, Pu-239; (U-238, Np-239) etc.

3. Burn-up of satellite batteries in atmosphere

   Pu-238; Sr-90

4. Nuclear power reactor accidents

   - Chernobyl reactor No. 4, Type RMBK

     Gaseous radionuclides:
     H-3, C-14; Ar-41, e.g., Kr-83m, Kr-85, Kr-85m, Kr-87, Kr-88; Xe-133, Xe-133m, Xe-135, Xe-135m, Xe-137, Xe-138

     Volatile at higher temperature:
     J, Te; Cs; Ru

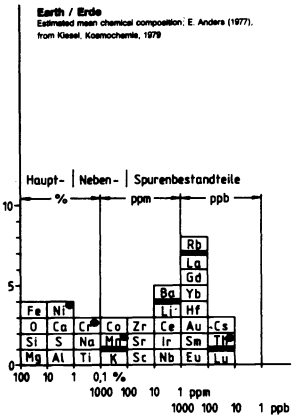
     Main inventory of reactor fuel:
     Nb-95, Zr-95, Mo-99, Tc-99m, Ru-103, Ru-105, Ru-106, Rh-106, (Sb-125), J-131, Cs-134, La-140, Ba-140, J-132, Te-132, Cs-137, Ce-141, Ce-144; Sr-89, Sr-90, Y-91; Np-239

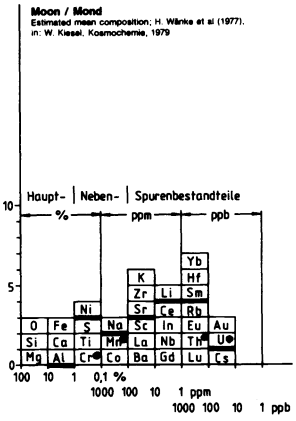
     Transuranium nuclides:
     Pu-238, Pu-239, Pu-240

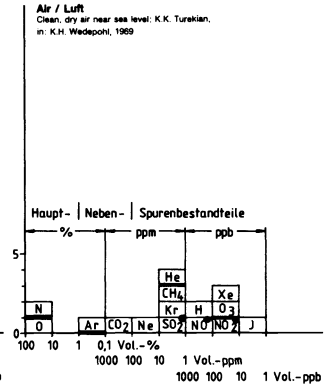
UNSCAR 1977, USSR-Report to IAEA 86, and others

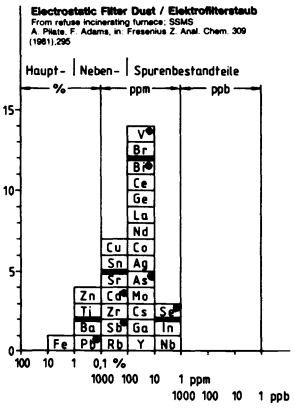
Earth, Moon

Atmosphere

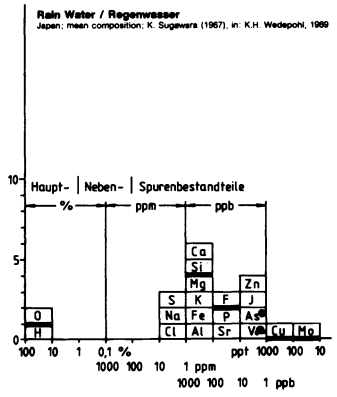


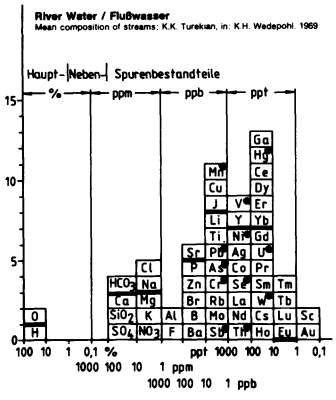


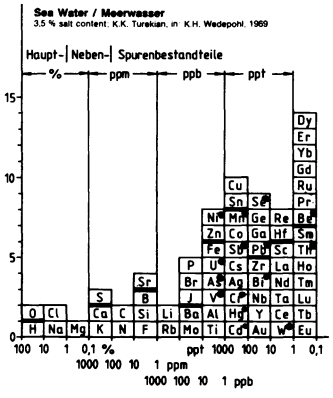




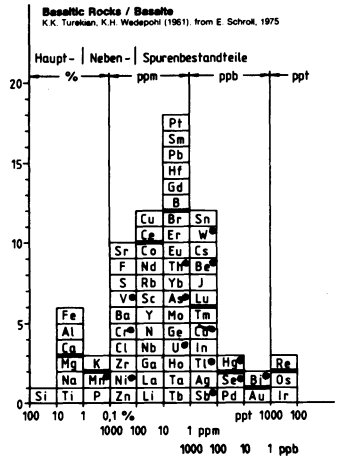
Hydrosphere

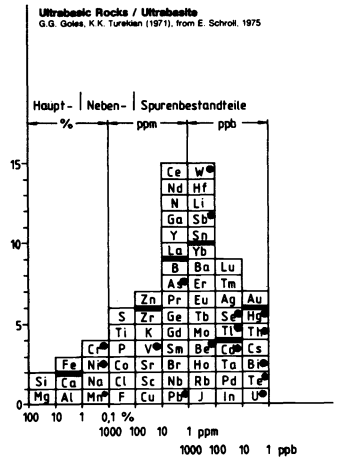






Lithosphere: Rocks, Soil





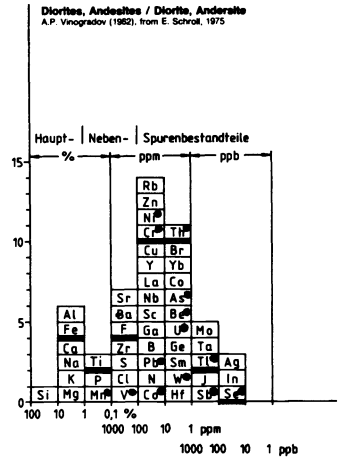
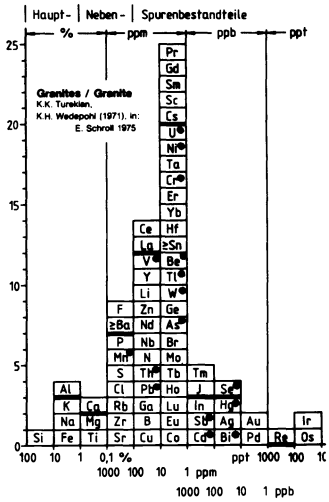
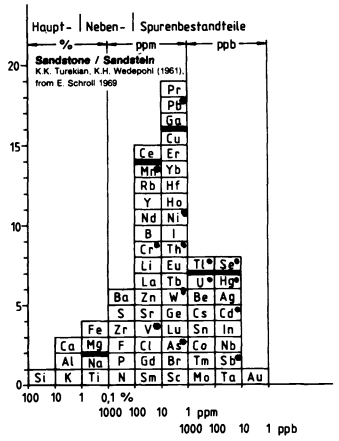
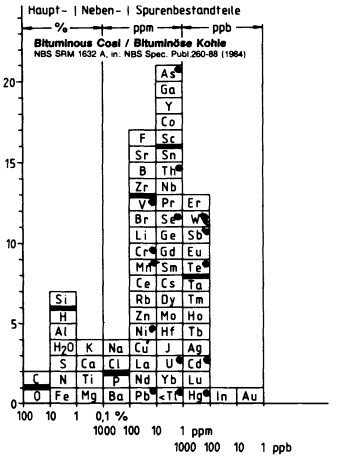


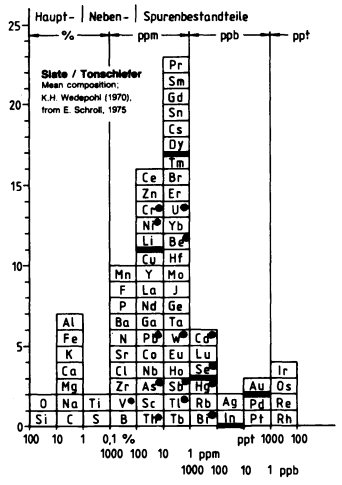
Figure 1

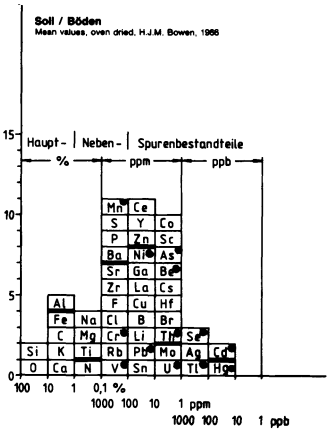
Continuation of Figure 1



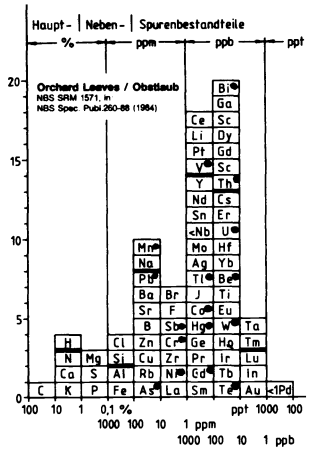


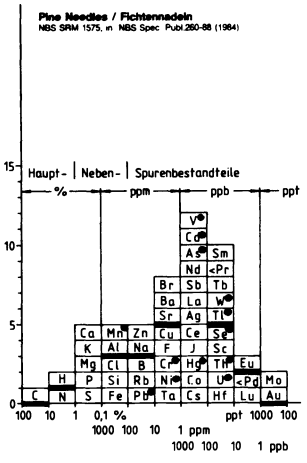


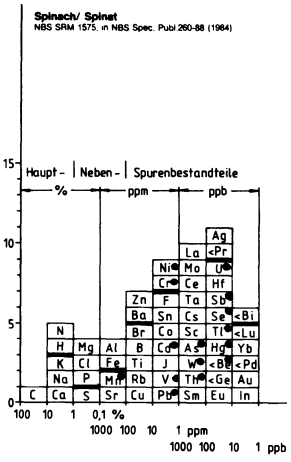


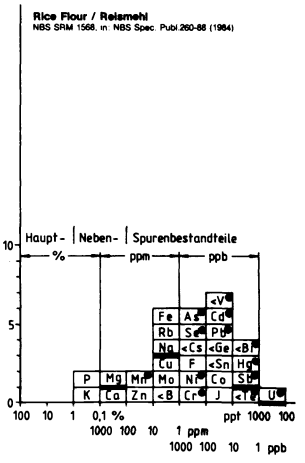


Biosphere: Flora (Plants)



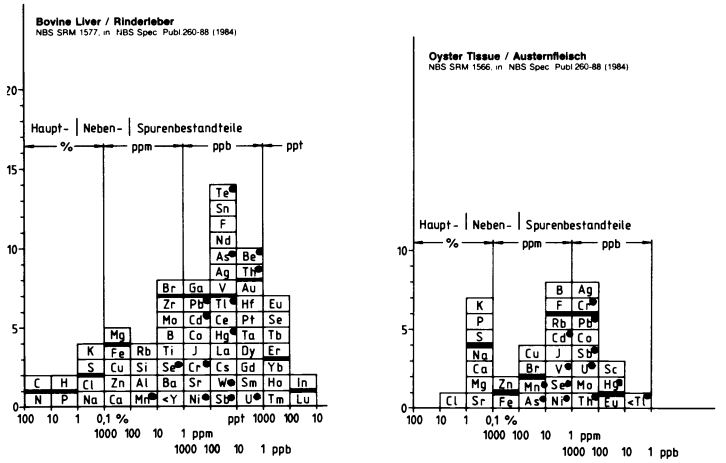






Continuation of Figure 1

Fauna (Animals)



Human Organism

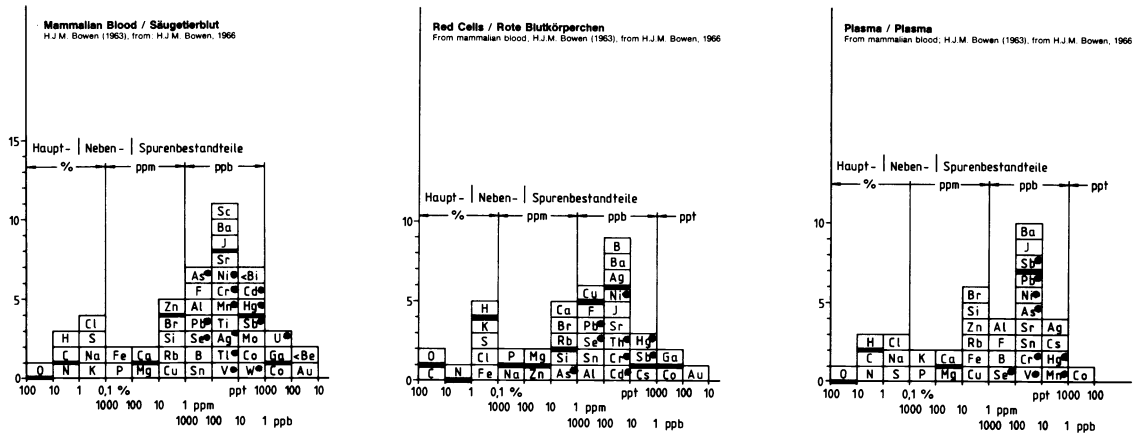


Fig. 1: Elemental Composition of Environmental Material

Frequency distribution of major, minor and trace element concentrations in materials from planet, moon;
atmosphere, hydrosphere, lithosphere and biosphere.
According to (Lit. 60)
X-axis: Element content, decreasing order
Y-axis: Frequency of elements. Increasing content within one order of magnitude.
Bar: half order of magnitude.

The hydrosphere (Fig. 1) is formed by water as a matrix. Depending on the different contents of dissolved elements and components, the hydrogeologist as well as the analyst has to distinguish between a large variety of types of water (44). They may include cloud and rain water, snow; ground, spring; surface, river, lake, sea, ocean, brackish; metamorphic, soil, crystal, percolation; mineral, medicinal, thermal; drinking or technical water; fresh, brackish and salt water or brine. Whereas cloud and rain water are formed by a relatively pure water matrix, especially river, ocean and, of course, waste water may contain a large number of dissolved elements and other components, including toxic ones. In considering the outer crust of the earth, the lithosphere (Fig. 1), one has to differentiate between rocks, minerals and soil. They are characterized by element composition in geochemistry, as well as by crystal habitus and structure of single phases in mineralogy and crystallography and by complex multiphase structures in petrography and pedology. As examples, mean element contents of ultra-basic rocks, granites, sandstone and bituminous coal are given. Slate has an element composition similar to soil, which is one of the most complicated materials of the lithosphere with respect to composition of elements and multiphase systems. As in the case of the simpler water matrix, soil classification has to consider a large variety of different soil types, based on chemical element composition, mineral content and morphology of multiphase systems as well (ref. 65).

As examples of the biosphere, especially the flora, the element composition of the well known standards orchard leaves, pine needles, spinach and flower is given in Fig. 1. The fauna is mentioned by oyster tissue, bovine liver and blood. Together with V. Iyengar in 1978 have been listed more than 140 different sample types for the human organism, which are of special interest to the analyst (ref. 63). They may be grouped under hard, semihard and soft tissues, body fluids and related components. Hard tissues are including enamel and dentin in tooth; gall bladder and kidney stones; in bone the hard and marrow part, cartilage, tendon and connective tissue. Semihard tissues are hair, nail, cartilage and tendon. Among soft tissues the major tissues are muscle, smooth, skeletal, striated, skin with dermis and epidermis. Minor tissues are diaphragm, esophagues, gall bladder, urinary bladder, intestine, larynx, lymph nodes, omentum, thymus, tongue, trachea, urethra. Glands are adrenal, mammary, pancreas, pituitary, prostate, salivary and thyroid. Reproductive organs are ovary, ovum, testis and uterus. To the normal organs are belonging the brain with white and grey matter, prosencephalon (telencephalon, diencephalon), rhombencephalon with mes-, metmylencephalon, spinal cord; eyes; heart; kidney with cortex and medula; liver; lung; spleen and stomach. Other soft tissues are the blood vessels with aorta, intima, media, adventitia; the marrow part and connective tissue from bone; fat; nerves; placenta. Body fluids and related components are: Aqueous humor; blood with erythrocytes, leucocytes, plasma and serum; cerebrospinal fluid; edema; fetal fluids (allantoic fluid, amniotic fluid); intestinal fluids (cecal fluid, duodenal, ileal and jejunal secretion); gastric juice; bile (gall bladder, hepatic); milk with mature, colostrum, transitional; pancreatic juice; pericordial fluid; peritoneal fluid; pleural fluid; phlegm; prostatic fluid; saliva; seminal fluid with seminal plasma and sperm; sputum; sweat; synovial fluid; tears; transudates; urine.

When comparing the distribution of toxic elements within the histograms for different environmental sample types (Figure 1), it is noteworthy that a relatively large number of toxic elements are in the matrix of e.g. granite as well as in river and ocean water, or plant and biomedical material. This reminds of the fact that the toxicity of an element in the human organism always depends greatly on its concentration. For this reason, a given element can be toxic, nontoxic or even essential. No chemical element is "toxic" per se. Furthermore, there is no reason to assume that "toxic" elements in e.g. granite powder might be really toxic for the human organism. It should be possible to eat granite powder without being poisoned by toxic elements!

This draws attention to the important fact that characterizing the environment by element contents alone is not sufficient. Of main importance in environmental research, and especially in ecology, is the chemical (better: molecular) form of the element. It can be the case that the difference between two different elements in the same chemical form is less evident than the difference of the same element in two different molecular forms. Examples are the similarity between the two elements cobalt and nickel, and the big difference in ecological behavior of chromium(III) and chromium(VI) on the other hand. According to Fig. 2, a complete characterization of environmental and other material samples has to be performed in several different dimensions, of which element contents are only one. Element corresponds to atom. So-called "speciation" of the chemical (molecular) form of an element can be determined by analysing the correspon-

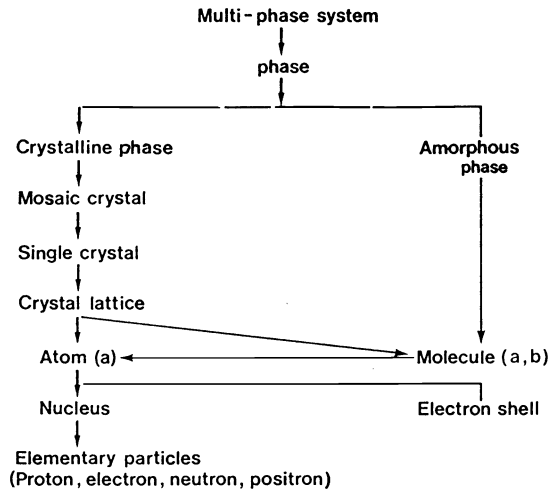


Fig. 2: Constituents of Matter [Based on (59), extended.]
(a) as cation after electron release, as anion after electron acceptance;
(b) complexes between central metal cation and ligands as a special case of molecules

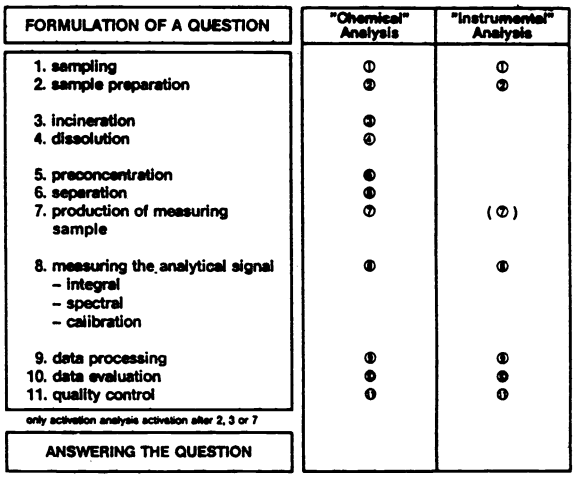


Fig. 3: Steps in the General Course of Analysis for almost all Elements in all Materials [according to (57, 59)]

ding molecules, including ions, instead of the elements alone. Other dimensions of material characterization are the analysis of the habitus and crystal lattice of crystals, as well as the composition and structure of phases and multiphase systems. If in addition radioactivity has to be considered, the type of the atomic nucleus is important too.

These limitations in characterizing the environment by element contents alone should be borne in mind when discussing element composition of samples from the environment.

For all compartments of the environment mentioned above, an enormous large variety of sample types and sub-types is characteristic. With water and biomedical materials, only two examples have been mentioned above. For many of them special analytical standard methods have been developed or are still under development in numerous laboratories and committees.

Sampling and sample preparation (ref. 63, 62, 33, 52) in daily routine analysis of "real-world samples" (ref. 60) to the opinion of the author are the most critical steps of the whole analytical scheme (ref. 57, 63) (Fig. 3). They are often much more critical than the physical measurement of the analytical signal itself. The first law of sampling states, that the mean element composition of the analytical sample used for measuring the analytical signal (e.g. 10 µl solution in case of electrothermal AAS) has to be exactly the same composition as in the totality of environmental compartment to be investigated, e.g. "air over the city of Munich", "water of lake Biwa" or "mean composition of a ships load of scrap metal". There are cases, where the instrumental error of signal measurement in trace element analyses is only 3 - 5%, whereas the sampling error exceeds thousand percent (ref. 63, 57).

Inspite of its importance, because of the topic of this lecture, sampling and sample preparation (ref. 63, 62, 33), pre-concentration (ref. 34) and separation as well as data evaluation (8, 39, 64) can not be mentioned in the following. These factors have, however, to be kept in mind, when evaluating the total analytical error of the result of an analysis.

3. MULTI-ELEMENT ANALYSIS APPROACH

We shall now introduce the instrumental multi-element analysis approach (ref. 58, 59, 61, 43, 54, 66). It allows the instrumental analysis of (a) as many elements as possible, useful and economic, (b) within the same sample, (c) within one analytical step, (d) either simultaneously or fast sequentially. It (e) avoids as many chemical steps from Fig. 3 as possible. As the main advantage one gets much more information about the multi-element composition of the

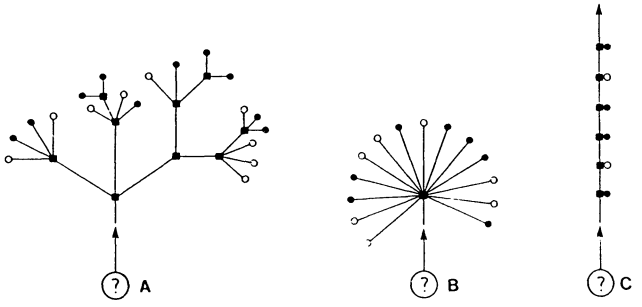


Fig. 4: Structure of Chemical Analysis Methods
[according to H. Kaiser (59)]

ppm	1-10 ppt	10-100 ppt	100-1000 ppt	1-10 ppb	10-100 ppb	100-1000 ppb	1-10 ppm	10-100 ppm	100-1000 ppm	0,1-1 %
Emission Spectroscopy DC Arc						X				
Flame Emission Spectrometry						X				
Atomic Absorption Spectrometry						X				
X-Ray Fluorescence Spectrometry						X				
Emission Spectrometry Cu Sparc						X				
Absorption Spectrophotometry					X					
Atomic Fluorescence Spectrometry					X					
Emission Spectroscopy, Plasma burner					X					
Sparc Source Mass Spectrometry				X						
Instrumental Neutron Activation Analysis				X						

Fig. 5: Range and Median of Detection Limits for Various Methods of Instrumental Element Analysis

Table 2: Survey on Multi-Element Analysis Methods

Mass Spectrometry (MS)	simultaneous
Spark source (SSMS)	
Secondary ion source (SIMS)	
Plasma source (ICP-MS)	
Glow discharge source (GD-MS)	
Laser induced (LMS)	
Neutron Activation Analysis (NAA)	simultaneous
Gammaspectrometry after neutron activation with	
reactor-	
epithermal-	
thermal-	
14 MeV-neutrons	
charged particles	
X-Ray Fluorescence Analysis (XFA)	
energy dispersive	simultaneous
wave-length dispersive	sequential
electron induced	
proton induced (PIXE)	
synchrotron radiation induced (SIXE)	
total reflecting	
Atomic Emission Spectrometry (AES)	simultaneous
arc excitation	
sparc	
ICP-plasma	
glow discharge	
Atomic Fluorescence Spectrometry (AFS)	sequential
ICP excitation (ICP-AFS)	
Forward Scattering Spectrometry	simultaneous
Atomic absorption, with white light sources	

sample with only reasonably increased costs. A disadvantage is the compromise to be made in optimal experimental conditions for each single element, which reduces precision, accuracy and detection limits of numerous elements.

The structure of a chemical analytical method, which Heinrich Kaiser presented at the IUPAC-Congress in 1974 here at Kyoto is given in Fig. 4 (ref. 59). Type A corresponds, for example, to the classical chemical separation scheme for cations, type B to the simultaneous and type C to the sequential instrumental multi-element approach.

The main groups of instrumental methods for multi-element analysis of more than about ten elements according to Table 2 are atomic emission spectrometry, X-ray fluorescence spectrometry, gamma ray spectrometry with and without neutron activation analysis and mass spectrometry. Oligo-element methods with about five to ten elements are voltammetry, alpha-ray spectrometry and isotope-dilution mass spectrometry. Newer multi-element methods to be mentioned are ICP-atomic fluorescence, coherent forward scattering, atomic absorption spectrometry with highly energetic white light source, atomic emission spectrometry with glow discharge excitation (FANES), X-ray fluorescence excited by proton or synchrotron rays and glow-discharge mass spectrometry.

The range of detection limits of elements for several instrumental analytical methods is given in Fig. 5, (ref. 59). The values are taken from different older literature sources and not all are well comparable. Nevertheless, the median of detection limits for elements within one method is decreasing and, therefore, the sensitivity of the method is increasing in the order: DC arc atomic emission, flame emission, atomic absorption, X-ray fluorescence, Cu sparc atomic emission spectrometry, molecular absorption spectrophotometry, atomic fluorescence, plasma atomic emission, sparc source mass spectrometry and instrumental neutron activation analysis. Therefore, from the well established instrumental multi-element analysis methods, sparc source mass spectrometry and neutron activation analysis are the two most sensitive methods, in general.

4. EXAMPLES OF MULTI-ELEMENT ANALYSIS METHODS

4.1 Mass spectrometry (MS)

Unique among all instrumental multi-element methods, mass spectrometry allows at least in principle to detect and determine all elements of the periodical table simultaneously within one sample and one step at detection limits down to about 10 ppb at for electrical detection. Therefore, it might be the dream of the analytical chemist. More precise, it is a multi-isotope analysis method, which is based on complete separation of all isotopes within the sample and to measure the rate of isotope mass/ion charge of the ionized isotopes. From this isotope data, element contents can be calculated by using known isotopic ratios of the individual elements, e.g. their natural isotope ratio. General references are (14, 5, 49, 56).

A solid sample is atomized into single atoms, excited into isotope ions, accelerated as a beam of isotope ions, focused by electrical lenses and separated by combined electrical and magnetic fields into lines with the same isotope mass/ion charge ratio. They are focused on a photographic plate or electrical detector. Especially, the high-resolution and double-focusing arrangement according to MATTAUCH-HERZOG type allows complete separation of all lines of all isotopes. Lines for the same isotope mass number from different elements can be separated because of the small difference due to mass defect however only in instruments with high mass resolution (above 10 000). Whereas the separation is extremely complete and selective, quantitative detection on photo plate by densitometry or electrical detection are extremely unspecific.

For atomizing and exciting solid samples, different types of sources are used. Most familiar to multi-element bulk analysis are the spark sources, either the high-voltage radiofrequency spark or the DC low-voltage arc discharge. For surface analysis mainly, the secondary ion source (SIMS) is well suited, for analysis of non-conducting materials especially the laser ion source. The last two are suited for micro domain analysis. The newer glow-discharge source (GDMS) has advantages for sensitive quantitative analysis of elements. A new type of source has been added to mass spectrometrical multi-element analysis by introducing the ICP-plasma source (ICP-MS) for aqueous solutions.

For bulk analysis of solids, the sample to be analyzed in case of both spark and glow-discharge source must have the shape of one or two small electrode roads and has to show enough electrical conductivity in order to generate the spark.

Conducting metals by mechanical sample preparation alone, can relatively easily be prepared as two electrode rods. Contamination is no serious problem because of pre-sparking within the chamber for surface cleaning. Non-conducting materials, however, have to be grinded extremely fine and mixed with the two- to threefold amount of highest-purity graphite, silver or copper powder. From those conducting mixtures, briquettes with electrode shape are formed under high pressure. The excess of these conducting matrix introduces serious background contaminations. The laser source needs neither electrode shape nor electrical conductivity of the samples. It is promising, therefore, for non-conducting samples. Because of the small beam diameter, the laser source is also well suited for micro analysis of micro domains within the surface of bulk material. The secondary ion source (SIMS) allows surface multi-element analysis down to the 1 ppm range within only two to three atom layers. Depth profiling is possible. In the micro-beam mode of operation, the SIMS-microprobe allows to measure not only vertical, but also horizontal element profiles on surfaces. The glow-discharge source seems to be most promising for quantitative determinations. The ICP-plasma source is most promising for extreme multi-element analysis of aqueous solutions within the sub-ppm range.

Compared with atomic emission spectrometry, the number of spectral lines in MS is much smaller. The extreme high-resolution, double-focusing version is able to separate almost all isotope lines from all elements with no peak overlapping. Compared with X-ray fluorescence spectrometry, the number of spectral lines is somewhat larger. One has to consider all about 290 known stable isotopes instead of about 90 elements, additionally multiply charged isotope lines with up to about five charges per isotope, polyatomic complexes and cluster ions. Fortunately, the intensity of multiply charged ion lines falls by a factor of 3 to 10 for each degree of ionization. Polyatomic ions are always present in the spark source mass spectra, especially in case of semi-metallic elements such as C, Si, Ge, Se and may become a problem in secondary ion or glow discharge source. The relative intensities are in the order of $X_1^+ > X_2^+ > X_3^+ > X_4^+$. Also complex ions such as Fe_2O^+ or AlN^+ as well as cluster ions of the type C_x(x=1 to 15) may interfere. A more serious problem in case of organic material might be fragments of not completely pre-ashed organic molecules.

Accuracies of a factor better than three in general can be obtained in case of SSMS without using standards; with internal standards ± 5 to 20 %, if sample and standard have the same homogeneous distribution. SIMS until now allows only semi-quantitative results because of the complicated processes within this source. Similar problems occour within the laser source, mainly because of the complex mechanisms of volatilization and excitation. Highest precisions and accuracies are obtained with the isotopic dilution method (ID), applied to thermionic (ID-TMS) or spark source mass spectrometry with the high-frequency spark (ID-SSMS).

4.1.1 Spark source mass spectrometry (SSMS)

For bulk analysis of solids, SSMS with high-frequency spark source has become most common until now for conducting and also, to a less degree, for non-conducting materials in mixture with metal powder. The most suitable instrument is the high-resolution, double focusing MATTAUCH-HERZOG type spectrometer. Unfortunately, today only one manufacturer makes this instrument commercial available (ref. 14, 5, 49, 56).

In chemical analysis service of ZCH, up to about ca. 80 elements in metals can be analyzed quantitatively with detection limits around 0,1 atom-ppm for photo plate registration and about 0,01 ppm for electrical detection. In each measurement, the actual detection limits for this special case are printed out. The low-voltage DC arc source allows better quantitative determination of elements by using each isotope and ion charge line of the element for calculating its content.

Main advantages of SSMS are, as for most MS methods, (a) the most extreme multi-element character for up to ca. 80 elements, with (b) similar and extremely low detection limits as mentioned before, (c) simultaneous mode of operation for all 80 elements within one sample and one set of measurements, (d) the closed system of the source with pre-sparking for decontaminating the electrodes, (e) application to solids without chemical sample preparation.

Disadvantages are (a) the restriction to materials with electrical conductivity, (b) need for preparing the sample with the shape of two electrode roads also in case of powders, (c) extremely complex apparatus, especially in case of double-focusing spectrometers, therefore (d) high costs for instrumentation, (f) maintainance and (g) operating costs, (h) need for highly specialized physicist and operators, (i) dropping out for two to three months a year because of failures, (k) line overlapping in case of more simple quadrupole mass spectrometers.

Precisions are in the range of ± 5 to 20 %, accuracies without standards better than factor three and with standards below or equal ± 20 %.

Fig. 6 as an example of the more difficult treatment for non-conducting materials shows the SSMS spectrum of about 38 elements (left) and its numerical results in mean contents ($\bar{x}$, % or ppm) for a soil sample.

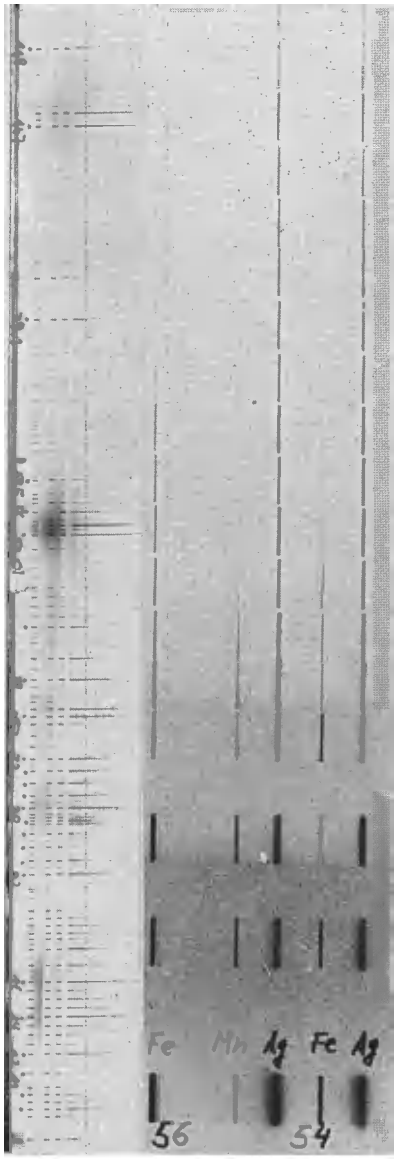
4.1.2 Secondary ion mass spectrometry (SIMS)

It allows multi-element analysis of the first two or three atomic layers of a solid and depth profiling. Most important is application of SIMS as micro probe for measuring vertical and horizontal element distributions in concentration ranges of down to 1 to 10 ppm. With this respect, SIMS ion micro probe is the most important instrumental and micro trace multi-element analysis method. Resolution reaches about 1 µm (5, 19, 20, 21).

Its main disadvantage is the poor accuracy and precision for quantitative element content determination, mainly due to the complex sputtering mechanisms. An ion micro probe (SIMS) costs much more than one million DM.

4.1.3 Laser mass spectrometry (LMS)

Laser energy is high enough, to atomize micro amounts of solids and to ionize its vapor. Therefore, LMS is applicable to metals as well as non-conducting materials too. The small diameter of the laser beam allows micro bulk analysis. Accuracy and precision in multi-element analysis are, however, less than in SSMS. The crater diameter in case of heterogeneous samples can be too small for precise bulk analysis or needs a larger number of laser shots.



	Analysewerte, x_i (% or ppm)					Mittelwert, $\bar{x}$	
B	235	150	250	273	196	220 ± 48	22
C	0.95%	1.3%	1.5%	1.0%	1.1%	1.2% ± 0.22	19
N	711	400	2200	593	3540		
O	42.0%	43.9%	40.0%	47.0%	50.2%	44.6% ± 4.0	9
F	328	252	300	289	310	300 ± 28	10
Na	0.76%	0.59%	1.0%	0.60%	0.90%	0.77% ± 0.17	23
Mg	0.46%	0.95%	1.0%	0.60%	0.87%	0.78% ± 0.23	30
Al	9.0%	8.8%	8.9%	8.1%	9.1%	8.8% ± 0.46	5
Si	38.0%	39.8%	40.0%	35.5%	30.0%	36.5% ± 4.0	11
P	2050	2500	3500	2210	2380	2500 ± 570	22
S	844	684	1000	830	970	870 ± 126	15
Cl	158	80	229	70	200	150 ± 71	47
K	5.9%	6.8%	4.4%	4.3%	7.6%	5.8% ± 1.15	25
Ca	982	1000	1170	2030	2000	1430 ± 533	37
Ti	0.5%	0.31%	0.45%	0.42%	0.53%	0.45% ± 0.1	22
V	44	37	65	100	70	63 ± 25	39
Cr	198	100	250	165	200	170 ± 55	33
Mn	0.17%	0.15%	0.20%	0.16%	0.24%	0.18% ± 0.04	20
Fe	3.7%	3.5%	4.3%	4.1%	4.0%	3.9% ± 0.32	8
Co	26	23	15	19	20	21 ± 4.2	20
Ni	129	154	173	199	240	170 ± 33	19
Co	58	56	80	58	60	62 ± 10	16
Zn	171	208	240	186	200	200 ± 26	13
Ge	30	54	45	26	60	43 ± 15	34
As	34	33	21	30	30	30 ± 5.1	17
Rb	142	148	201	280	253	200 ± 56	28
Sr	100	40	25	41	115		
Y	13	11	20	15	15	15 ± 3.3	23
Zr	340	289	100	188	413	260 ± 120	46
Nb	6.9	7.8	9.0	8.5	7.1	7.9 ± 0.9	11
Mo	1150	1500	2270	700	740	1230 ± 653	52
Sb	210	138	108	126	183	150 ± 42	28
Cs	24	21	32	11	45	27 ± 13	48
La	169	60	51	69	100	90 ± 49	53
Ce	403	178	269	289	300	280 ± 84	21
Nd	103	94	76	110	100	97 ± 13	13
Ta	43	96	82	80	100	74 ± 26	35
Pb	190	200	174	240	340	220 ± 67	30
Bi	<	<	<	<	<		

Fig. 6: Spark Source Mass Spectrometry for 38 Elements in Soil Z (DFG), mixed with Silver Powder

High-resolution, double focussing mass spectrometer (Varian MAT), Mattauch-Herzog type, sample powder briquetts, low voltage arc discharge source.

E. Farah, H. Beske, G. Frerichs, F.-G. Melchers, B. Sansoni, 1979

According to (ref. 74), the bulk method is characterized by the following parameters: element range from Li to U, concentration range from ppb to 100 %, accuracies with standard up to ± 10 %, without standard up to a factor of 3, relative standard deviation up to ± 10 %, absolute detection limits 10^{-12}g, relative detection limits 10 ppb, per shot about 100 µg of material are consumed.

Characteristic for the micro analysis method is, that the spot diameter is 20 µm maximum, spot depth 0,1 to 10 µm, absolute detection limits 10^{-12}g, relative detection limits ± 0,1 %, reproducibility per shot ± 10 %, possibility for thin film and profile analysis.

Further advantages are the simple sample preparation, large variety of sample types which can be analyzed, high degree of ionization and therefore high sensitivity, low degree of vaporization resulting in low memory effects, simple spectra, wide element range and low detection limits.

Disadvantages are the influence of transparency of material on the ion yield; laser optics in source chamber vulnerable to contamination; long analysis time; poorer accuracy compared with SSMS (ref. 74).

4.1.4 Inductively coupled plasma mass spectrometry (ICP-MS)

Combination of a burning ICP-plasma and an open mass spectrometer has made available mass spectrometry for multi-element trace analysis in solutions. The method is relatively new and the first two instruments became commercial in 1982/83 (ref. 22. 23). Its main field of application are sample solutions, for solids the detection power is smaller than for SIMS, GDMS or SSMS.

Over 90 % of all elements are accessable to the method. The detection limits are relatively uniformly distributed through the periodic table. Detection limits down to 0,1 to 1 ppb for many elements have been reported. Compared with ICP-AES, the ICP-MS is reported to be one to two orders of magnitude more sensitive. The detection limits are substantially better for the middle range and heavier elements. The dynamic range is reported to be 6 to 7 orders of magnitude, a necessary presumption for a valuable multi-element method. ICP-MS is attractive also for semi-quantitative analysis of unknown samples. Up to 1 % solid content of the liquid matrix can be tolerated (ref. 22, 23). The time for analyzing one sample is as small as with ICP-AES and lasts a few minutes only. This makes ICP-MS promising for routine analysis of larger sample series. The spectra are much more simple than for ICP-AES. On the other hand, the resolution of the quadrupol mass spectrometer in both commercial instruments is smaller than in double-focusing SSMS. The flexibility is high because of the electrical control of the mass setting and scan as well as peak selection.

The main critical point of the method is the pressure difference at the connection of the burning ICP-plasma and its reaction products with the open mass spectrometer. Serious problems with the vacuum are resulting. On the other hand, introduction of the aqueous sample solution into the plasma by nebulizing is the same as with ICP-AES or even AAS. The method is not so free from matrix effects as ICP-AES. Higher salt content because of promoting ionization gives rise to much more formation of clusters, e.g. even in sea water. The more simple quadrupol mass spectrometer may produce spectral interferences too (ref. 22, 23).

The method is in a stage of rapid increase (ref. 22, 23).

4.1.5 Isotope dilution mass spectrometry

By far the most accurate and precise trace element analysis method in mass spectrometry is the isotope dilution (ID) applied to thermionic (TMS) and sparc source (SSMS) (ref. 31, 37), electron impact, plasma and field desorption mass spectrometry (ref. 31). Whereas ID-TMS is a mono- or oligo-element method (ref. 31), ID-SSMS (ref. 37) has been used as multi-element method.

Isotope dilution is restricted to elements having two or more naturally occuring or longlived radio-isotopes. For each element to be determined, a known amount of a spike is mixed with the sample. The spike is an element whose isotopic composition is different from the natural composition. The unknown concentration of the element in the sample is calculated from the changed isotopic abundances of the mixture and the spike (ref. 31).

ID-SSMS (ref. 37). Sample preparation of complex geochemical material such as rocks, minerals and meteorites has been done either by a sample dissolution method or by the spiked graphite method for up to 20 elements simultaneously. Analysis of 25 elements in these materials has been reported. A complication is, that the sample first has to be dissolved for adding the multi-element spike solution and again prepared as solid electrodes. Also spiking of graphite powder with solutions has been used.

Precisions have been observed between $\pm$ 0,6 to $\pm$ 3 % for photoplate and from $\pm$ 0,5 to $\pm$ 1 % for electrical detection. In an other investigation a mean overall precision of $\pm$ 2 % is reported. The accuracy shows almost always deviations smaller than $\pm$ 10 %, about 75 % of the data deviated less than $\pm$ 5 %. The range of element contents was between 0,05 and 110 ppm (ref. 37).

As a conclusion, application of isotope dilution method makes SSMS to one of the two most precise, accurate and sensitive multi-element analysis methods in the trace level.

4.2 Activation analysis (AA)

Activation analysis (AA) depends on properties of the atomic nucleus of the element to be determined. It is based on the effect, that the inactive elements can be made radioactive by nuclear activation reactions. In case of induced gamma radiation, the radioactivity can be measured most selective and sensitive by gamma spectrometry (ref. 30). In Fermis n, γ-reaction, gamma-rays are emitted, the type of the element remains constant and the largest number of elements can be activated. By these reasons, especially for multi-element analysis neutron activation with thermal neutrons from the reactor is most common in activation analysis (NAA). Other types of activation have more special features. Reviews on AA are given e.g. in (ref. 15, 25, 58, 2, 3).

In detail, the non-radioactive atomic nucleus of one or more isotopes of the element to be analyzed, by the activation is transformed into a radionuclide. The elementary particles emitted by its radioactive decay can be measured highly sensitive and specific by nuclear radiation spectrometry. From these data, the type and concentration of the radionuclide formed can be calculated, using appropriate standards. With knowledge of nuclear chemistry the type and concentration of the corresponding inactive isotope of the element, which has been activated, can be estimated. Therefore, the element content can be calculated, if the isotopic ratios in sample and standard are the same or known.

The sensitivity of AA is proportional to the amount of radionuclides produced from the inactive nuclides of the element to be determined and the intensity of the nuclear radiation emitted. The yield of the nuclear reaction in case of thermal neutron activation is determined by the thermal neutron cross section and for the fraction of epithermal neutrons from the reactor by the resonance integral. The latter is much more dependent on the neutron spectrum than the former. The intensity of the nuclear radiation emitted is a function of the half-life time of the radionuclide induced. The shorter the half-life time, the faster the nuclear decay and the higher the sensitivity of the emitted radiation. More over, the high sensitivity of NAA for a large group of elements has something to do with the highly sensitive radiation detection because of the extremely high energy of the nuclear radiation compared with radiation from the outer electron shell. For a large group of elements, NAA in concurrence with mass spectrometry is the most sensitive instrumental analytical method.

Selectivity largely depends on the separation of the different gamma-ray energies within the gamma-ray spectrum. The highest resolutions are obtained today with a high-purity germanium detector in combination with a multi channel analyzer and automated computer evaluation of the spectra. Also by these reasons, neutron activation with n, γ reactions is most useful. For a good spectral resolution, on the other hand, the gamma energies shall be as different as possible for the different radionuclides to be measured. Whereas the optical atomic spectra are based on the structure of the electron shell of the atom, the gamma spectra are a result of the structure of the nucleus. Chemically similar elements have similar electron shell and, therefore, similar atomic spectra, but may have completely different nuclear properties and nuclear radiation spectra. By this reason, NAA is an extremely selective analysis method for chemically similar elements. Interference of radioactivity measurement by short lived radionuclides can be eliminated by using different irradiation, cooling and measuring times. Furthermore, radiochemical separation of interferring radionuclides after activation is an excellent tool for improving selectivity and sensitivity. For normal chemical analysis service, however, this radiochemical neutron activation analysis (RNAA) is too time consuming and expensive.

Two different approaches for evaluating the element contents from the nuclear data are available (ref. 3, 2, 15). The multistandard method for each element to be determined needs a standard of similar matrix with certified values for all of these elements. The monostandard (or single comparator) method affords only one element, e.g. Co, Fe or Zr as monitor for the neutron flux under the same irradiation conditions. Afterwards the element contents are calculated

with the fundamental activation analysis equation. This mono-standard method for multi-element analysis allows determination of a much larger number of elements in one sample without a standard.

Determination and detection limits of INAA have been calculated by G. Erdtmann and H. Petri (ref. 15) in our laboratory for a reactor with a thermal neutron flux of 8.10^{13} and an epithermal flux of $4.10^{12} n.cm^{-2}.s^{-1}$ under two different conditions, (a) 10 days irradiation, 3 hours measuring time and (b) 1 to 60 minutes irradiation, one half-life time decay, measuring time equal to irradiation time. (c) In addition, the optimal detection limits for radiochemical NAA, estimated by R.C. Koch in 1960 are given as a lower limit.

According to this long-time irradiation, (a) allows to determine about 47 elements with determination limits (definition according to Curry) better than 1 µg/g (ppm), short-term irradiation (b) about 20 elements with better determination limits (c) a maximum of about 70 to 75 elements by radiochemical NAA. The following orders for decreasing sensitivities have been obtained under the experimental conditions given above. // marks one order of magnitude difference in contents:
(a) 9 Ir(9.10^{-6} ppm = 9 ppt)/ 3 Al, Au; 5 Sc; 7 Lu; 9 Eu / 2 Re, Sm, Tb; 3 Hg, Th; 4 Np; 5 Hf, Os; 7 Cs; 9 Sb / 1 Co, Ta, Yb; 2 Se, U, Ce; 3 Cr, Mn, Ru, Ag, La; 5 Pt, Nd, Gd; 6 Pd, Te; 7 In / 1 Ho; 2 Br, Mo; 3 Zn, As, Rb; 5 Cd; 7 Ba; 8 W / 2 Ni; 3 Zr, Sn; 6 Fe (6.10^{-1} ppm).
(b) 2 Eu (2.10^{-5} ppm = 20 ppt), 7 In / 1 Mn, Dy; 4 Pu/1 Rh; 2 V, I, Ho; 3 Cu, Ga; 5 W, Er; 6 Na / 1 Ba; 3 Al, Ge; 6 Cl / 1 Sn; 3 K, Tl (3.10^{-1} ppm).
(c) 6 Eu (6.10^{-8} ppm = 10^{-2} ppt!), 8 Dy / 2 In; 5 Ir, Au, Lu; 7 Ho / 1 Mn, Co, Ag, Re, Sm; 2 Rh, Er, Tm, Yb; 3 Sc, V; 4 As, Tb; 5 Br, La, W, Th; 6 Cu, I; 9 Sb / 1 Ga, Pd, Pr, Gd; 2 Na, Y, Ta, Hg, U; 3 Ge, Nb, Os; 4 Al, Hf; 5 Cr, Cs; 6 P, Rb; 7 Cl; 9 Se / 1 Be, Zn, Cd, Ba; 2 K, Sr, Ru, Te, Pt; 3 Mo; 5 Ce, Nd; 7 Sn; 8 Tl; 9 Ni / 2 Mg, Si, Tl; 3 Bi; 4 S; 6 Zr; 7 Ca / 1 Fe; 2 Pb (2.10^{-1} ppm).

These orders of sensitivities are different from all other instrumental analysis methods.

Under the conditions of (a) and (b), the following elements cannot be determined by NAA with detection limits below 1 ppm:
Li, Be, B, C, N, O, F, Na, Mg, Si, P, S, Cl, K, Ca, Ti, V, Cu, Ga, Ge, Y, Nb, Tc, Rh, I, Tl, Pb, Bi, Po, Ra, Ac, Pa.

Advantages of neutron activation analysis for multi-element analysis are in general (a) very high potential sensitivity and (b) selectivity for many elements, (c) analytical signals with unique and almost complete independence from matrix influence, (d) good precision and accuracy in the trace element level, (e) less and simple sample preparation before activation, therefore a minimum of possible errors by contamination and loss of elements, (f) non-destructive analysis of small samples, (g) freedom of reagent blanks, (h) automatic radioactivity measurement and computer evaluation of gamma spectra, (i) because of (c) easy and accurate calibration, often simply with the solid residue of evaporated aqueous standard solutions, (j) applicable to a large number of materials, mainly solids, (k) because of chemical yield determination, radiochemical RNAA allows also non-quantitative separation methods, (l) difficult chemical operations in the submicrogram range can be avoided by use of inactive carriers.

Disadvantages include (a) very low sensitivity to about 30 elements, which cannot successfully be analyzed by NAA, (b) need for an atomic reactor, which is available only on a few places, (c) availability of an expensive radiochemical laboratory or, at least, a radioactive control area, (d) expensive equipment and instrumentation, (e) often very long analysis time, e.g. in case of long-time irradiation or cooling, (f) possible radioactive and inactive contamination of the sample within the radiochemical laboratory before and after irradiation. Furthermore (g) liquids in the reactor core are often forbidden, (h) strong temperature rise in case of strong neutron absorbers such as B, Cd, (i) radiation and temperature damage of the sample, (j) in case of radiochemical NAA, radiochemical purity of reagents is necessary, (k) both the irradiated element and the inactive carrier element must have the same chemical form, (l) radionuclide interference, if the radionuclide expected during activation from the element to be determined is produced also by other than n,γ reactions from

another element (mainly between adjacent elements in the periodical system) and (m) interferences by fission products of uranium.

In its importance, thermal neutron activation is followed by activation with the fraction of epithermal neutrons within whole reactor neutrons (ref. 3, 2, 15). Irradiation is performed usually under cadmium cover. 14 MeV neutrons can be obtained by a neutron generator, even higher energetic neutrons from cyclotron and suitable targets. One of the most specific instrumental methods in chemical analysis is neutron activation followed by delayed neutron counting. It gives signals only for elements with nuclear fission. Therefore, it is specific for U and to a less extent for Th. High energetic gamma radiation for photon activation is produced in electron accelerators. Other activation methods are using charged particles such as protons, deuterons, tritons, helium-3, helium-4 from accelerator or cyclotron. Expecially the smaller compact cyclotron because of its lower price is used more often. All these methods are handicapped by the expensive instrumentation of nuclear physics which is available only in a few laboratories.

These other activation methods have the following advantages. Epithermal NAA is to be prefered for the elements Rb, Sr, Mo, Sb, Cs, Ba, Ta, Tb, U, Th. 14 MeV is favourable to light elements such as C, N, O, F, S, Si, but allows also analysis of Al, Mg, Fe, Sr, Ca, Ti, Ni, Y, Zr, Nb, Ce. Prompt gamma-ray spectrometry is particularly useful for elements such as H, B, Be, N, O, S, Ni, Cd, Gd. Delayed neutron counting is extremely selective and sensitive for U and Th. Charged particle activation analysis has advantages for light elements of B, C, O, N Li in surface layers. Photon activation analysis has merits also for lighter elements such as C, N, O, F.

In epithermal neutron activation, the corresponding resonance integrals are depending in a complicated function much more on the energy of the epithermal neutrons compared with the cross sections of thermal neutrons. Epithermal neutron activation analysis, therefore, needs an especially careful monitoring of the neutron energy during activation. This can be achieved by a second comparator. Zirconium as mono-standard includes Zr-94 as monitor for the thermal and Zr-95 for the epithermal neutron components in the neutron flux at the irradiation position. As mono-standards Fe, Co, Au as multi comparator Co+Au, Co+A+In and Zr (Zr-94, Zr-95) have been used (ref. 2, 3, 15, 25).

Fig. 7 as an example shows the high-resolution gamma-ray spectrum with high purity Ge-detector for soil. About 35 elements can be identified.

4.2.1 Charged particle activation analysis (CPAA)

This method is characterized by activation with charged particles such as protons, deuterons, tritons, helium-3 and helium-4. It has possibilities for solving special problems (ref. 15, 25, 42).

Depending on the kind and energy of the projectile particles, a large variety of different nuclear reactions can be induced in each target nuclide as compared with thermal neutrons. For example, with 5 to 15 MeV protons, mainly p, n-reactions occour; with deuterons mainly d, n and d, p reactions are used. In general, with a = p, d, He-3, He-4 from the cyclotron or accelerator, mainly (a, n), (a, 2n), (a, p) and (a, α) reactions are induced.

Under optimal conditions, the following detection limits have been reported for all particle types mentioned (42): 1 ppb for B, C, N. O; Ca; Y, Pr, Cd; 1 to 10 ppb: Li, Ti, Cr, Co, Ni, Cu, Zn, Ga, Ge, Br, Rb, Zr, Ru, Cd, Sn, Te, Ba, La, Ce, Eu, Ho, Er, Yb, Lu, Hf, W, Os, Ir, Pt, Tl, Pb, Bi; 10 to 100 ppb: H, He, F, Na, Mg, Al, Si, P, S, V, Fe, As, Se, Sr, Nb, Rh, Pd, Ag, Sb, I, Cs, Dy, Au, Hg; 0,1 - 1 ppm: Be, Cl, Mn, In, Re.

With 5 to 15 MeV proton activation, many elements show detection limits up to 50 ppb, heavier elements with Z between 44 and 82 from 0,01 to 100 ppm. Triton activation has shown for 25 elements detection limits from 0,001 to 30 ppm.

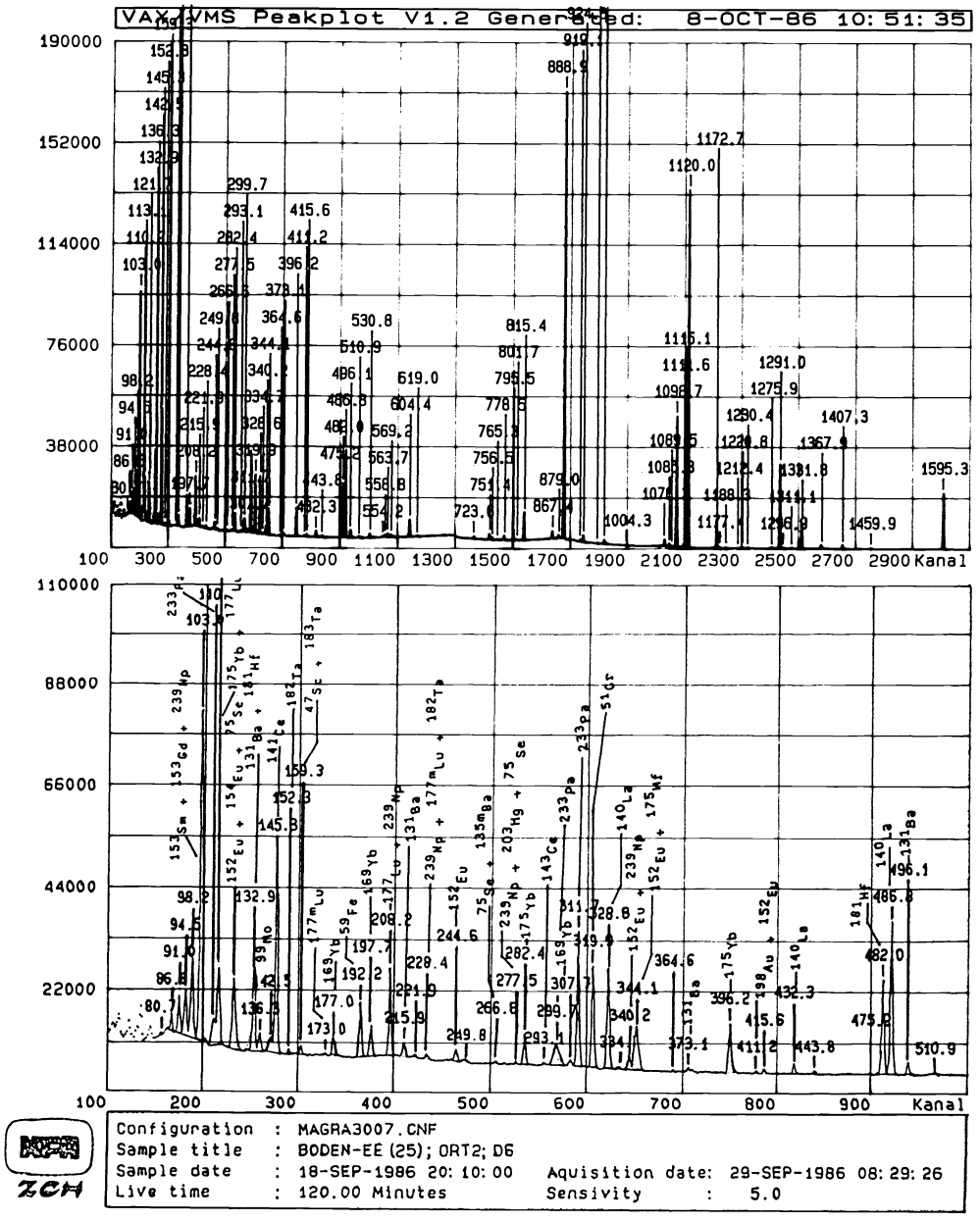


Fig. 7: High-Resolution Gamma Spectrometry of Soil (DFG/EE), with Ge-Detector, after Neutron Irradiation

The following radionuclides could be identified after thermal reactor neutron irradiation 3 days at a flux of $5 \cdot 10^{11}$ n $\cdot cm^{-2} \cdot s^{-1}$ and 3 days cooling:
Sm-153 + Gd-153 + Np-239, La-140, Eu-152, Pa-233, Eu-152 + Np-239, Br-82, Yb-175 + Lu-177, Eu-152 + Hf-175, Rb-86, Eu-152 + Eu-154 + Se-75, Ba-131, La-140, Ba-131 + Hf-181, Yb-175, Fe-59, Mo-99, Au-198 + Eu-152, Eu-152, Ce-141, La-140, Zn-65, Ta-182, Eu-152, Sc-46, Sc-47 + Ta-183, Hf-181, Co-60, Lu-177m, La-140, Ta-182, Yb-169, Ba-131, Ta-182, Fe-59, Br-82, Tb-160, Yb-169, As-76, Fe-59, Lu-177 + Np-239, Sb-122, Ca-47, Ba-131, Cs-134, Tb-160, Np-239 + Lu-177m + Ta-182, Cs-134, Co-64, Eu-152, Br-82, Na-24, Ba-131, Zr-95 + Eu-154, Eu-152, Se-75 + Ba-135m, Zr-95, K-40, Np-239 + Hg-203 + Se-75, Nb-95, La-140, Yb-175, Eu-152, Sb-124, Ce-143, Cs-134, Pa-233, La-140, Yb-169, Eu-152, Pa-233, Sc-46, Cr-51, La-140.
(According to A. Mannan, B. Sansoni, H. Petri, G. Erdtmann)

Main advantages of CPAA are the favourable detection limits for the light elements Li, Be, B, C, N, O, Ca and the possibility to investigate thin layers, films and surfaces. The penetration depth is 5 to 500 μm only.

Because of the intense loss of particle energy in the sample, the sample volume actually activated is rather small and, therefore, not always representative for the investigated material. Standardizing is more complicated compared with NAA, because sample and standard have to be irradiated separately. Serious heat production during irradiation needs effective cooling of the sample, may produce heat and radiation damage; possible losses of volatile elements have to be considered. Only one sample after the other can be irradiated. More abundant interferences with other elements may occour. Last but not least charged particle activation needs extremely expensive instruments.

4.2.2 Photon activation analysis (PHAA)

Photon activation analysis uses photons upto 25 MeV, mainly from an electron accelerator, e.g. LINEAC. The method is based on γ, n and γ,p reactions. Most common, photons between 2 and 15 MeV are used, which induce γ, n reactions in many elements (ref. 15, 25).

Photons penetrate the whole bulk of the sample similar to gamma rays, contrary to charged particles. Another advantage is the determination of the light elements C, N, O, F down to 0,01 ppm, e.g. in metals, alloys and semiconductors, but also Nb and Pb can be determined.

4.3 Low-level alpha- and gammaspectrometry

Reviews on gamma-ray as well as alpha-ray spectrometry especially for multi-radionuclide analysis are given by (ref. 30) and (ref. 28), resp.. Gamma-ray spectrometry has been mentioned also in chapter 4.2 on activation analysis.

4.3.1 Low-level gamma-ray spectrometry

Gamma-ray spectrometry is an extremely effective multi-radionuclide analysis method for gamma-ray emitters. Fig. 7 shows an example in case of higher activities. Main advantage is the extremely low self absorption of gamma-rays within the sample, perhaps the lowest of all instrumental analysis methods discussed within this review. Therefore, no or only little sample preparation is necessary. Solids only have to be grinded carefully to fine powder and measured under standardized conditions. The method is extremely sensitive. Since most gamma-ray emitters have more than one gamma-line, even in case of line overlapping, a suitable line can be selected for determination. However, resolution of modern Ge(Li)- and Ge-detectors with 1,8 to 2,0 keV for the Co-60 line is very high.

Multi-radionuclide trace analysis of gamma-ray emitting radionuclides needs a spectrometer with the highest detector efficiency and resolution as well as the most effective background reduction by careful shielding and anticompton background elimination. As an example, the low-level gamma-ray spectrometer of ZCH has a Ge-detector with 30 % efficiency, 2,0 keV resolution for the Co-60 line and a peak/compton ratio of 55: 1. Anticompton shielding is accomplished by an NaJ-crystal, 12 inch in diameter and 12 inch long. The chamber with an inner size of 2 x 1 x 1 m is shielded by 10 cm Pb, 6 cm Cu and 1 cm plexiglas. As an example, Fig. 8 gives the low-level gamma-ray spectrum of a normal granite from Fichtelgebirge with 25 hours measuring time (W. Matthes, B. Sansoni).

4.3.2 Low-level alpha-ray spectrometry

A review on multi-radionuclide alpha-ray spectrometry is given in (ref. 28), however mainly for higher activities. As an example, Fig, 9 shows the low-level alpha-ray spectrum of the same granite as in Fig. 8, with 50 hours measuring time.

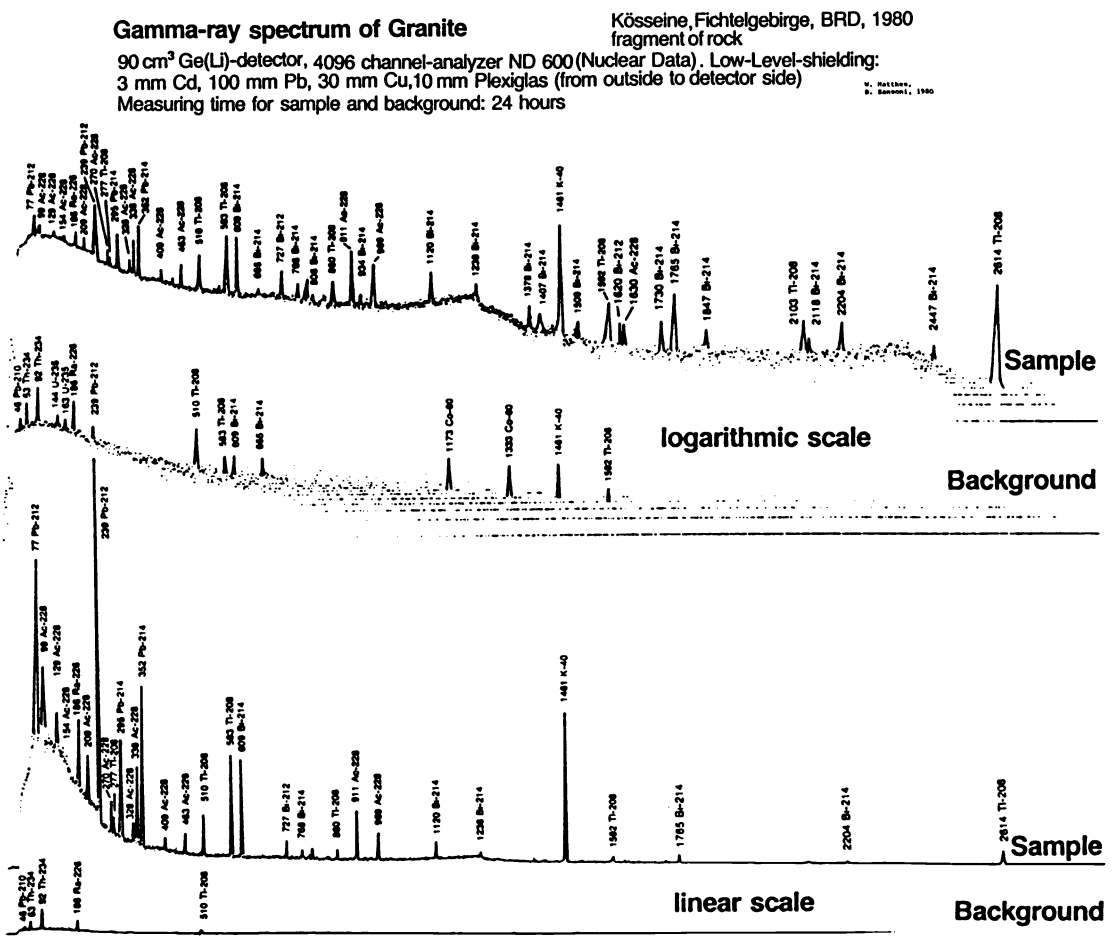


Fig. 8: Low-Level Gamma Spectrometry of Granite

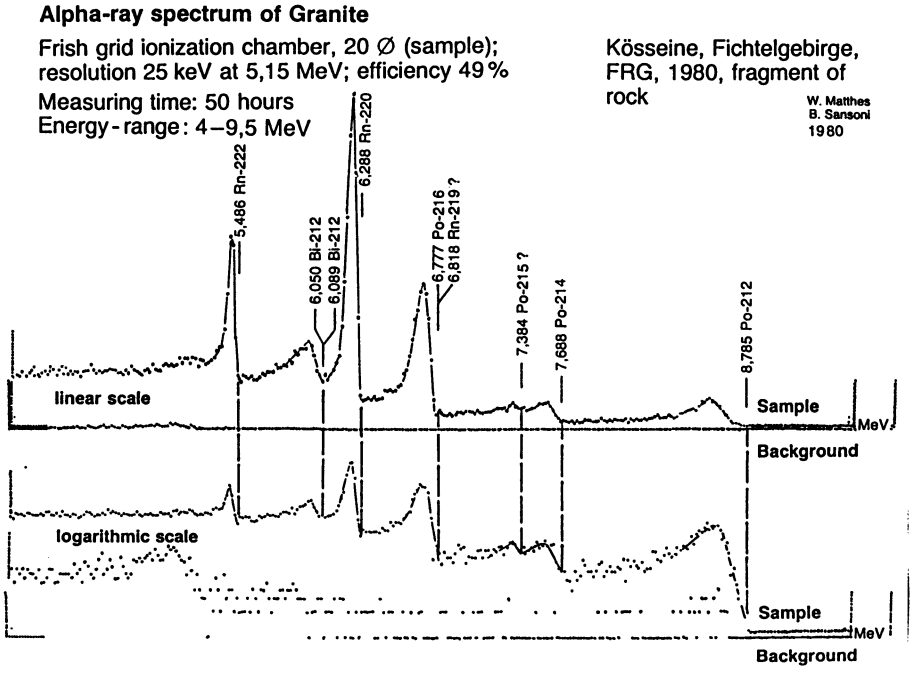


Fig. 9: Low-Level Alpha Spectrometry of Granite

Alpha-ray spectrometry, at least in principle, has almost (a) no problems with shielding and (b) an extremely small radiation background, which (c) results in higher sensitivity compared with gamma-ray spectrometry. The main and serious disadvantage, however, is the extreme large self absorption of the emitted alpha-lines within the sample. It is much larger than e.g. in X-ray spectrometry. Therefore, only the upper layers of the solid sample contribute to the unchanged alpha-ray spectrum and, furthermore, only the upper few atomic layers are emitting alpha-lines with unchanged alpha energies. Alpha particles from deeper layers have retarded and lower energies. This results in a typical asymmetry of the alpha-peaks (Fig. 9) to the side of lower energy. By this reason, for qualitative peak identification, not the top peak energy, but the nadir on the side to the higher energy is used. Quantitative determination from spectra with layers of indefinite thickness as in Fig. 9 is difficult.

Therefore, a main prerequisite for low-level alpha-spectrometry is chemical sample preparation by separation of matrix and carrier-free deposition on a steel disk, e.g. by electro plating from separated solutions. In case of fine powdered solids, only the first upper layer of grains can be used.

The alpha-spectrometer as detector has either a Si-detector or grid ionization chamber. Since the latter has a higher efficiency, it has been preferred for low-level alpha-spectrometry in Fig. 9. The chamber has an efficiency of 49 %, a resolution of 25 keV in Pu-peak, a sample diameter 20 cm Ø, measuring time was 50 hours.

Alpha-spectra, compared with gamma-spectra, have a smaller number of lines per radionuclide. The advantage of lower spectral interference, however, is lost because of peak overlapping in case of infinitely thick sample layers and peak broadening.

4.4 X-ray fluorescence spectrometry (XRF)

Classical XRF is a non-destructive and powerful instrumental multi-element analysis method mainly for the determination of major and minor elements in solids and, less common, in liquids (ref. 27, 29, 35, 36, 40, 24, 4). Light elements below $Z < 13$ are more difficult to analyse, trace elements can be detected only down to about 10 to 5 or 1 ppm. Matrix effects are serious. Characteristic is the almost same level of detection limits for all elements, except the lighter ones.

The classical method is the wave length-dispersive XRF with an analyzing crystal. It works sequential and is more time consuming. The newer (since 1966) energy-dispersive XRF operates simultaneous and much faster. It is the main multi-element approach among XRF methods. Modern variations of energy-dispersive XRF include the total reflection method (TRXRF, since 1971), which allows detection limits of about 100 to even 1000 times smaller than classical XRF. The particle induced method (PIXE, since 1970) has found general application to solid samples with detection limits of a factor 100 lower than the classical method, down to the ppb-range. The synchrotron-radiation induced method (SRXRF, since 1981) also shows promising features for trace element analysis because of its lower background. Both PIXE and SXRF, can be applied as micro probes.

General advantages of XRF are (a) the extreme multi-element character for almost all elements above $Z > 10$ to 16, its (b) high selectivity, (c) pure instrumental and non-destructive character, (d) much smaller number of spectral lines compared with atomic emission methods, therefore (e) less spectral interferences with respect to wave length and qualitative element identification, (f) fairly uniform detection limits for all elements except the lighter ones with $Z < 10$ to 16, (g) peak energy, characteristic for element identification, follows the sequence of the periodic system (Moseleys rule) (h) most suitable for element contents from 100 % to ca. 5 to 10 ppm, (i) good precisions of 0,1 to 1 %, for trace levels ca. $> \pm 5$ %, (h) good speed, (l) ease of operation and (m) economy, (n) automated analysis of large numbers of similar samples with help of a sample changer, (o) almost independent from the molecular form of the element.

Main disadvantages are (a) the high self-absorption of the analytical signal because of the relatively low energy of the soft X-rays emitted, therefore (b) strong matrix effects and (c) limitation to analysis of thin filmes or to surface layers in case of bulk material, (d) restriction to detection limits above 5 to 10 ppm, (e) dependence on particle size in case of powder pellets and (f) heterogeneous element distribution. This needs (g) elaborate and sometimes complicated calibrations when applying XRF to unknown samples in daily chemical analysis, (h) affords often fusion or preparation of standard series in case of powder pellets, (i) rather expensive equipment, expecially in case of wave-length dispersive operation (ref. 24, 27, 40).

Some 10 000 WD-XRF and about 1.500 ED-XRF instruments are world-wide in use.

4.4.1 Wavelength dispersive X-ray fluorescence spectrometry (WD-XRF)

The classical experimental set up consists of a X-ray tube with thin window, sample, diffracting crystal, electrical detection by proportional or scintillation counting. It is a sequential technique of multi-element analysis (ref. 1, 26, 66).

General advantages are the high spectral resolution, little peak overlap, good qualitative analysis according to Moseley's rule, relatively low background intensity, simple peak evaluation, relatively good precision, advantageous detection limits also for lighter elements down to Na and even B, and wide range of almost all elements above $Z > 5$ to 13.

Main disadvantage is the time consuming sequential mode for the multi-element technique, which may cause heat and radiation damage of the sample with possible loss of volatile elements (ref. 24, 27, 29, 40, 4).

Detection limits for a modern instrument within our chemical analysis service at ZCH are for elements above $Z = 9$ between 1 and 10 ppm. The sample weight usually is about 1 g, but may go down to 10 mg. With powder-pellet technique in some soils in favourable cases up to 70 elements can be determined with 20 to 100 sec per element. Figure 10 gives as an example the multi-element analysis of about 22 elements in granite and soil.

4.2.2 Energy dispersive X-ray fluorescence spectrometry (ED-XRF)

The instrument consists of an X-ray tube, sample, Si(Li) or Ge detector crystal liquid nitrogen cooling, multichannel analyzer and electronical device for signal and data treatment (ref. 24, 27, 35, 36, 40).

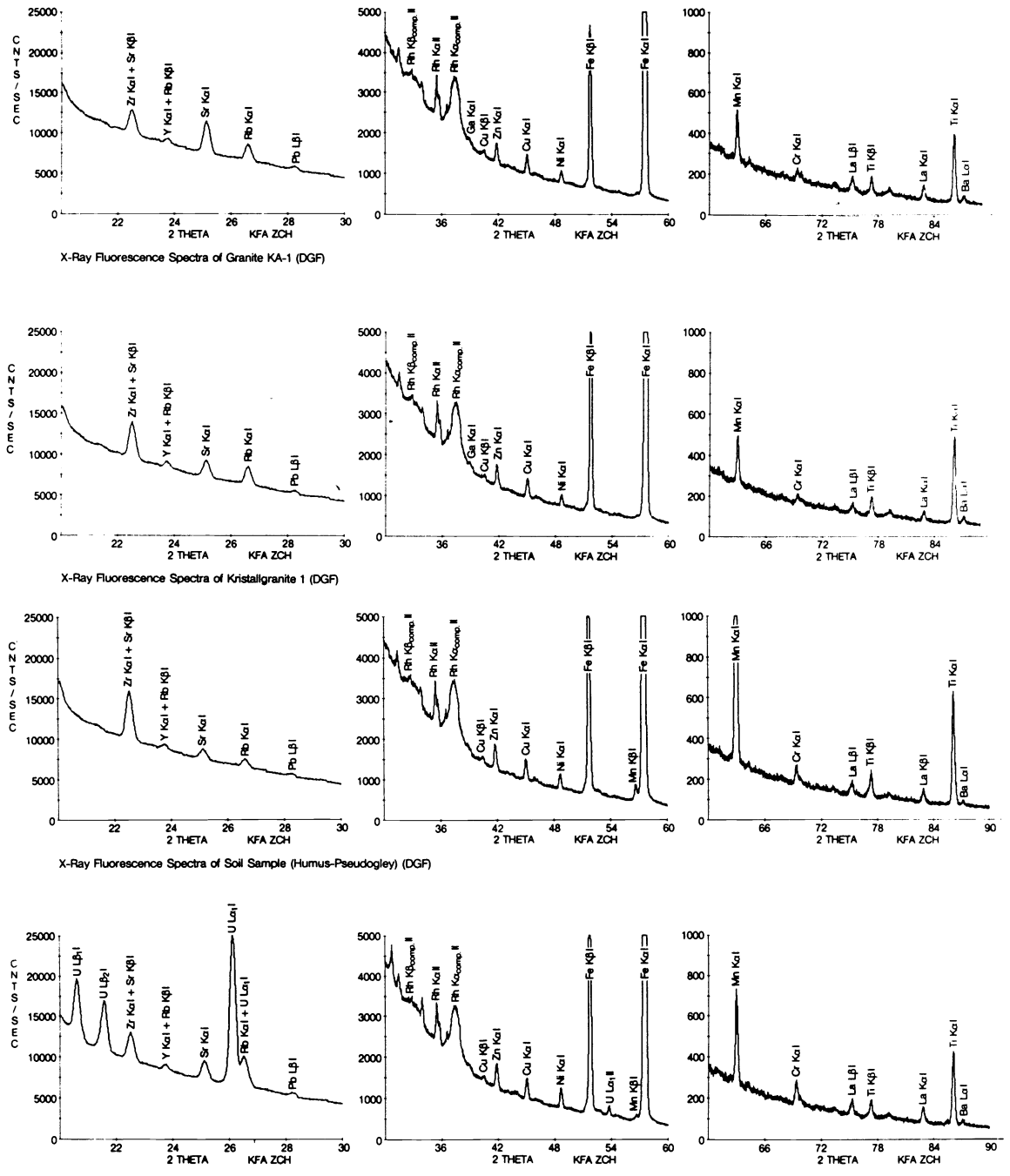
Advantages of ED-XRF are (a) the typical multi-element approach with (b) an order of magnitude smaller measuring time because of the simultaneous technique (c) fast survey analysis and qualitative analysis of unknown samples, (d) in-situ field analysis with portable instruments using a radionuclide X-ray source such as Cd-109, Am-241 or Co-57, (e) higher thermal and radiation stability for e.g. organic and biological material because of the much lower excitation power in ED-XRF (e.g. 50 W cf. 2500 W) compared with WD-XRF.

The main disadvantage is the limited energy-resolution of the common Si(Li) detector, which implies overlapping of X-ray peaks and a relatively larger background component in the spectra. By this reason, precision and accuracy are usually worse than for WD-XRF.

Accuracies between $\pm$ 5 to 10 % can be achieved for multi-element analysis, which is the main field of application.

4.4.3 Total reflection X-ray fluorescence spectrometry (TR-XRF)

This method is energy dispersive (ref. 17, 47, 75, 46). The experimental set up consists of X-ray tube, sample, Si(Li) detector, multichannel analyzer and electronic device for signal and data handling. The sample has to be prepared from a solution as a thin film on a polished quartz slice and irradiated in grazing incidence by a narrow collimator X-ray beam. At glancing angels below a few minutes of arc, total reflexion occurs on the surface. The scattered radiation from the sample support is virtually eliminated and the background of the spectrum is drastically reduced.



Wave-length dispersive, sequential X-ray spectrometer S/MAX 3 kW, Rigaku (Japan).
End-window: Rh-target with 125 µ Be window. Detector: NaJ(Tl). Crystal: LiF(200).
Step scan: $2\vartheta = 0.01°$, 4 sec counting time. Sample preparation: Glass disk 40 mm dia. and 4 mm thick; prepared by fusion of 1 g sample with 10 g of flux mixture (66 % $Li_2B_4O_7$ + 34 % $LiBo_2$).

Fig. 10: X-Ray Fluorescence Spectrometry

Granit KA-1 (DFG), Kristallgranit 1 (DFG), Soil (Humus-Pseudogley, DFG), Soil (containing uranium)

Multielement analysis of 17; 17; 17; 16 elements
Sequential, wave-length dispersive spectrometer S/MAX 3 KW, Rigaku
(According to A. Mannan, C. Freiburg, W. Reichert, B. Sansoni)

The sensitivity for trace elements is improved by a factor of 100 and up to 1000. Relative detection limits down to the pg-range have been observed. Further advantages are the small sample masses corresponding to 1 to 100 µl solution and the simple calibration procedure. The main disadvantage is the restriction to only a few sample types, such as e.g. aqueous solutions with lower salt contents, followed by the need for dissolution and the poor sensitivity for light elements.

Internal standards are necessary, which can be prepared by adding standard solutions to the dissolved sample. The solid film of the sample has only a few mm^2 diameter and a few µm thickness. This eliminates corrections for self absorption of elements with $Z > 16$.

As a result, TR-XRF offers an opportunity for multi-element trace analysis with detection limits a factor 100 to 1000 better than for normal ED-XRF.

4.4.4 Particle induced X-ray emission spectrometry (PIXE)

This method induces the emission of characteristic X-rays in the sample by the focussed beam of charged particles from an accelerator or synchrotron. Proton energies between 1 to 3 MeV are used, sometimes also α -particles. The proton beam is much more efficient in producing X-rays than the electron beam or cathode-rays in classical XRF. The K- and L-lines emitted are detected by a high-resolution Si(Li) detector (ref. 18, 24, 38, 40).

Main advantages of PIXE are the (a) multi-element analysis for all elements between Al and U with (b) rather uniform sensitivity. (c) Sensitivities of 0,1 to 1 ppm can be obtained in routine analysis of e.g. carbon or organic material as a matrix. (d) Typical accuracies of about $\pm$ 5 % and precisions of $\pm$ 2 % have been reported for geological samples. (e) An automated system allows to analyse up to 25-30 samples per hour. (f) This reduces the costs for a semi-commercial PIXE analysis of 10 to 20 elements at ppm levels to ca. 30 US-Dollar. (g) Sample weights are normally 1 mg, but may be reduced with microbeams to about 10 µg. PIXE, therefore, is a micro trace multi-element method. (h) With 5 min irradiation, about 20 elements can be determined.

It is a disadvantage, that a nuclear physics laboratory with accelerator or cyclotron is necessary. The sample has to be stable under vacuum, heat and radiation. Since the beam diameter is only a few mm^2, the sample has to be homogeneous. For heavy matrices PIXE seems to be less sensitive than WDXRF.

Sensitivity is limited by the bremsstrahlung from secondary electrons produced by the proton beam. Best sensitivities have been observed for elements between $Z = 25 - 80$, minimum sensitivities for the rare earths region. Because of the much smaller radiation background, detection limits are about 100 times smaller than for conventional ED-XRF. The optimal bombarding energy is rather low, therefore also smaller accelerators can be used.

PIXE can be used as a microprobe. Its advantages are the extreme sensitivity and relatively deep penetration. The costs for a high-resolution proton microprobe, on the other side, are very high. With beam diameters down to 10-50 µm the spatial resolution is similar to that for the electron microprobe. Good resolution can be obtained only for extremely thin films. Sensitivity is about 10 ppm compared with 1000 ppm for the electron micro probe.

4.4.5 Synchrotron radiation induced X-ray emission spectrometry (SR-XRF)

This method uses synchrotron radiation for inducing X-ray fluorescence of the element to be determined, instead of electron or proton beams (ref. 41, 68). Synchrotron radiation (SR) is emitted by relativistic electrons circulating in electron storage rings. Its continuous spectrum extends from radio frequency range to the high energetic X-ray region of about 100 KeV. The intensity of storage ring sources is many orders of magnitude larger than in case of bremsstrahlung from conventional X-ray tubes. Because of the high degree of polarization of the synchrotron radiation and its possiblility for total reflection on the sample holder, scattering effects can be minimized, which results in a very low background and high sensitivity.

The experimental set up is similar to that in the other ED-XRF methods.

General advantages are (a) better relative detection limits because of high linear polarization, which improves peak/background ratio by a factor of 10, (b) good absolute detection limits because of high radiation intensity, (c) high photon flux and collimation allow small irradiated sample areas and masses, the method therefore is a micro trace multi-element method. (d) The spectrum up to 35 keV is white and allows a more uniform excitation of all elements, which can be determined by their K-lines up to Z = 60. It shows a smaller dependence of the detection limits from atomic number. (e) A tunable monochromator can be used for complicated element mixtures, (f) the excitation source can be calculated, therefore an absolute method is possible; in practice, however, internal standard application is to be preferred.

Serious disadvantages are the high costs of the synchrotron. It is available only at a few sites. Therefore, SRXRF will be used mainly in cases, where other methods are not or only less suitable.

With SR continuum, detection limits down to a few hundred ppb have been achieved, with monochromatic SR even below. The absolute detection limits range from 0,01 pg to several pg for monochromatic excitation. The wavelength dispersive technique has better energy resolution and lower detection limits down to 10 ppb range. In general, the relative detection limits are 10 times better than the ones with conventional XRF beams, because of the lower matrix influence.

Transmission SR-XRF with white excitation affords thin samples with < 1 mg/cm^2 sample mass. For this case, detection limits between 0,05 and 1 ppm are reported. Because of high intensity and collimation, absolute detection limits down to the pg-range have been observed.

4.5 Atomic emission spectrometry (AES)

In optical atomic emission spectrometry (ref. 1, 7, 6, 11, 73), the ultraviolet and visible light to be measured is emitted in the outer electron shell of the atom. By absorbing external energy, one or more electrons are excited to higher energy levels. During spontaneous returning to the ground state, each energy transition emits one spectral line. The energies or wavelengths of the resulting spectral line system are characteristic for the type of the electron shell and, therefore, the type of the element. Its intensity is more or less proportional to the number of atoms per sample unit. The heavier the elements, the larger the number of electrons in the shell system, the much larger is the number of possible energy transitions. Systems with up to 90 electrons allow thousands of possible energy transitions and, therefore, spectral lines. Fig. 11 gives an example for the UV-region of a d.c. arc atomic emission spectrum of iron standard (above) and an uranium containing soil (below).

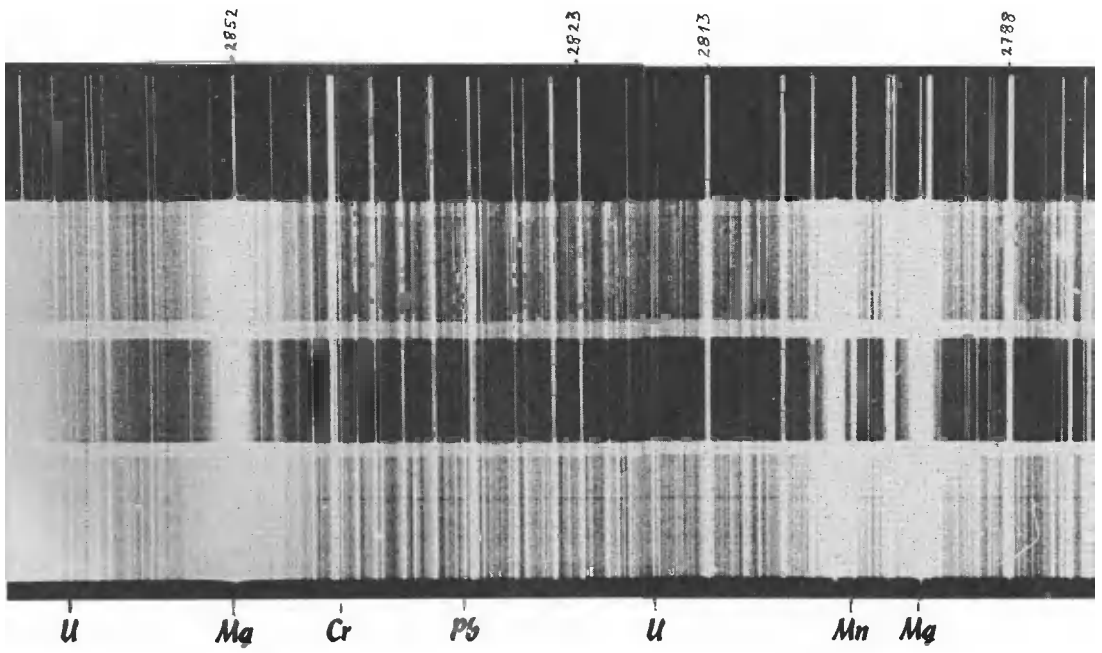


Fig. 11: DC Arc Atomic Emission Spectrometry of Uranium Containing Soil [1,5 m Spectrograph Jarrell-Ash, type Wadsworth; grating with 600 lines per mm; graphite electrodes, 230 V, 20 A; 1 to 3 mg sample weight. W. Hilgers, G. Wolff, 1980]

By this reason, characteristic for AES is its pronounced multi-element capability on one side and lack of selectivity and accuracy because of manyfold spectral interferences on the other. The latter implies a chance for many elements, to find characteristic and optimal spectral lines, but also the danger to find fictitious elements, which are not present in the sample below detection limits and to take lines not optimal for e.g. quantitative determination.

The experimental set up for AES (ref. 1) includes an atomization and excitation source, sample, analyser of the emitted light, detector and electronic device. The source might be a flame, better a d.c. arc, a.c. or high frequency spark, glow discharge, high frequency plasma or laser. The analyser in case of multi-element analysis has to have high resolution. It can be a quartz prism, grating and especially echelle grating or an interferometer. Detection can be performed by photoplate, photo cell, photomultiplier or phototransistor. Since AES needs free atoms or elements, as a gas or vapour, the excitation source first has to volatilize the solid sample.

Selectivity of AES (ref. 7, 6) can be improved by improving spectral resolution, choice of optimal excitation conditions in the source, selection of appropriate analysis lines and background corrections. Selection of the most sensitive and prominent lines for a given element and excitation source is based on detection limit and sensitivity. This depends to a large extent on the experience of the analyst. Background correction also is difficult. Main types of background are the simple flat, the sloping background and direct or complex line overlapping. Multi-element analysis especially needs high resolution. For this purpose, spectrometers with external order sorter, echelle spectrometer with crossed or parallel dispersion and classical grating monochromators have to be considered.

The d.c. arc can be used mainly for qualitative to semiquantitative, the a.c. spark for semiquantitative to quantitative analysis of solids and solutions. Their main disadvantages, however, are the relatively high detection limits and low precision and accuracy. The latter is mainly due to the serious spectral and chemical interferences. High frequency plasma, especially the inductively coupled plasma (ICP) because of its extremely high temperature of about up to 8000^{o}C have almost no chemical interferences, but spectral ones. Because of the high energy of the plasma, the intensity of the emitted lines and, therefore, the sensitivity is much better than with arc and sparc source. Mainly because of lack of chemical interferences, the precision and accuracy is also remarkably better.

The old flame AES with bunsen burner allowed to analyse about 12 elements, mainly alkali and alkaline earth elements. The hot flames introduced by Lundegaard allowed to determine about 35 elements (ref. 1).

About 20 elements, which cannot or not sufficiently be analysed by AES are mainly C, O, S, N, Cl, Br, (J); He, Ne, Ar, Kr, Xe, Rn; Fr, Ra, Tc, Pm, Po, At, Ac, Pa.

For multi-element analysis, the most sensitive lines for the ionized atoms in arc or spark AES are in the UV region between 200 to 450 nm (Figure 11). Above 450 nm are emitting almost only Sr, Ba, alkaline metals, In, Tl, Ti, Zr.

4.5.1 DC arc atomic emission spectrometry

According to Ahrens and Taylor (ref. 1), under optimal conditions, about 70 elements can be determined with detection limits between 0,5 and 500 ppm in the spectral range from 220 to 900 nm. Under optimal conditions with 0,1 to 1 ppm the elements Li, Na, Cu, Ag; with 1 to 10 ppm Cr, Rb, In, Tl; Mg, Al, K, Ca, Sc, Cs; Zn, Ga; V, Fe, Ge, Sr, Mo, Ba, Pb; Be, B, Ti, Mn, Co, Y, Zr, Ru, Rh, Pd, Cd, Sn, La, Ag, Pr, Nd, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu; with 10 to 100 ppm Si, Sb, W, Bi; Os, Ir, Pt; F, P, As, Re, Hg, Th, U; with 100 - 1000 ppm Te, Gd, Ce, Sm. In general, 1 to 5 mg powdered solid are sufficient. Precision is not better than $\pm$ 5 to 10 %, for a.c. spark however down to $\pm$ 2 to 3 %. Systematical errors due to matrix interference can be as high as $\pm$ 100 % and more.

By these reasons the d.c. arc today mainly is used for fast qualitative or semiquantitative multi-element surveys.

4.5.2 ICP atomic emission spectrometry

This method (ref. 16, 26, 46, 66) is able to analyse up to about 50 elements or more from solution. The mode of operation is either simultaneous or sequential. Precision in general is between + 0,2 to 5 %. Because of the high temperature of the plasma with up to about 8000°C, the method shows no or not much chemical interferences, but similar spectral interferences as arc and spark source and additional ones because of higher ionization stages of the volatilized atoms. The simultaneous technique for 40 to 50 elements needs only 2 to 5 ml of solution and about 5 minutes for complete analysis with print-out of the report. Important, however, is the sample preparation of the solutions and standardizing.

Under the conditions of our chemical analysis service at ZCH, with an ARL 34.000 spectrometer with Ar/Ar-ICP plasma the following detection limits for 46 elements simultaneously can be obtained (G. Wolff). Between 30 to 100 ppt: Be, Ca; 0,1 to 1 ppb: Mg, Sr, Ba; Mn; 1 to 10 ppb: Zn, Zr, Cd; Li, Cu, Ti, V, Co, Mo, Ag, La; Nb, Gd; B, Si, Ru; 10 to 100 ppb: Cr, Ni, Sn, Ta, Bi, Th; Na, Al, Fe, Sb, Te; W, Ce; Hg, C, P, As; S, K, Tl, U; Se; Pb. These detection limits for pure aqueous solutions are by far much better than for d.c. arc or a.c. spark emission (G. Wolff, H. Heckner).

4.5.3 Further AES methods

Further multi-element methods based on AES are using a hollow-cathode graphite electrode, which is a micro trace element method for down to 10 - 50 µg sample only and the glow-discharge AES.

4.6 ICP atomic fluorescence spectrometry (ICP-AFS)

Atomic fluorescence spectrometry (ref. 71) is based upon the absorption of radiation of a certain wavelength by an atomic vapour and subsequent radiational deactivation of the excited atoms. Absorption and measured atomic emission, the fluorescence, occur at resonance wavelengths, which are characteristic of the atomic species present. This resonance lines are almost the same for atomic absorption and atomic fluorescence. As excitation source, normal hollow cathode lamps from AAS as well as flames have been used.

Radiation of a primary light source strikes a cloud of free atoms. Part of it is absorbed and subsequentially re-emitted in all directions as fluorescence radiation.

Knowledge of fluorescence of atomic vapour in flames goes back as far as to the late 19th and early 20th century. Analytical atomic fluorescence spectrometry, however, was proposed by Winefordner and Vickar in 1964. In 1970/71 D.R. Demers (13) described multielement-AFS using an ICP-plasma for atomizing and up to 12 hollow-cathode lamps around it for excitation. The latter are pulsed, one after the other, in sequential order. The sample solution is introduced into the plasma by a nebulizer.

The following detection limits have been reported (ref. 13): around 1 ppb: Li, Se, Zn; Ca, Cd, Mg, Be; 1 to 10 ppb: Ag, As, Na, Cu, Si, Mn, Cr, K, Rh, Ni, Co, Pd; 10 to 100 ppb: Fe, Al; Au, Ba, Mo, Pb; 0,1 to 1 ppm: Sn. In this laboratory, the following realistic detection limits have been obtained: 1 ppb for Na, K, Mg; 2 to 3 ppb Li, Ca; 3 to 5 ppb Zn, Mn, Cu; 5 to 10 ppb Cd, Cr; 10 to 15 ppb Fe, Co (W. Brunner, M. Plum, B. Sansoni).

Main advantages of the ICP-AFS are the fast sequential mode of operation for 12 elements in less than 5 minutes, relatively high sensitivity comparable to AAS, small spectral interferences because of extremely simple spectra, use of the same hollow cathode lamps as for AAS.

Disadvantages are sometimes occurring quenching effects, limitations of hollow cathode, excitation with respect to sensitivity. Commercially available is only one instrument, almost from the first generation (Baird).

Use of tunable UV-laser beams might lead to a break through in detection limits of two to three orders of magnitude lower.

4.7 Coherent forward scattering spectrometry (CFS)

Whereas the fundamental magneto-optical effect is known since 1912, its application as coherent forward scattering spectrometry for analytical determinations has been introduced 1974. Until now, no instrument is commercially available.

CFS is based on the magneto-optic rotation produced by the Faraday or Voigt configuration in an atomized vapour. Rotation of the plane of polarization is observed, when plane polarized resonance radiation passed through an atomized vapour of the sample, located within the magnetic field. At low atomic density, intensity of forward scattering radiation is proportional to the square of the atomic number density and high sensitivity can be expected. On the contrary, the signal drops very rapidly with the concentration near the detection limit, resulting in degrading sensitivity at low concentrations.

Atomizer is a graphite furnace, radiation source in case of single-element analysis a hollow cathode lamp and in case of multi-element analysis a xenon lamp.

Detection limits have been reported for 20 elements between 0,002 and 3 ppm, for additional 5 elements between 20 and 300 ppm. Detection limits for some elements are similar to AAS, for others one order of magnitude higher.

Advantages are (a) the simple instrumentation, (b) possibility for simultaneous multi-element trace analysis, (c) lower background interferences compared with the absorption methods (AAS), (d) advantages over Zeeman-AAS, (e) nitric acid suitable for preparing solutions, (f) high sensitivity to be expected because of forward scattering is proportional to the square of the atomic number density.

Disadvantages are (a) the rapid decrease of scatter signals at concentration ranges near the detection limits, (b) self-absorption effects at higher concentration ranges responsible for an only small dynamic range, which affords more than one calibration curve for the same element, (c) difficulty to find an optimal continuum light source at the UV-region below 250 nm for multi-element analysis. Whereas the spectral interferences by molecular vapour are relatively small, (d) the influence of matrix elements or atomizing modifiers etc. has still to be considered, (e) very weak spectral radiance of a xenon lamp below 250 nm results in low sensitivity for elements which have their resonance lines in this range (ref. 12, 32).

4.8 Voltammetry (polarography)

Voltammetry (ref. 51, 76, 78) is based on the electrochemical reduction or oxidation of a species to be determiend in an electrolyte solution between a working and reference electrode. Between both, the potential (voltage) is increased and the corresponding current measured. These current-voltage curves show characteristic peaks for each species reduced or oxidized at a constant normal redox potential. The voltage of the peak corresponds to this redox-potential, the peak hight according to Farrday's law to the concentration. In case of a hanging mercury drop electrode as working electrode, this "polarography" is a special case of voltammetry. The fundamental quality is the normal redox-potential of solvated cations or anions in an electrolyte solution.

Polarography and voltammetry are oligo-element methods, which according to Fig. 12 allow to determine simultaneously (fast sequentially) a maximum of 5 to 6 elements or species. Most important are the differential-pulse-polarography (DPP) and anodic stripping voltammetry (ASV).

4.8.1 Differential-pulse polarography (DPP)

About 25 elements can be analysed by this method, however not simultaneously or sequentially, but in different batches of 1 to 5 elements: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Mo, Cd, In, Sn, Sb, W, Tl, Pb, Bi, V, Pr. Detection limits are in general between $\pm$ 0,1 and 10 ppm and precisions around $\pm$ 3 % can be obtained (ref. 76, 78).

4.8.2 Anodic stripping voltammetry (ASV)

Anodic stripping voltammetry (inverse voltammetry) (ref. 51, 76, 77) uses a preconcentration step prior to polarography within the same experimental arrangement. The elements to be determined are concentrated by cathodic electrolytical deposition into the hanging mercury drop. Afterwards anodic stripping polarography with DPP is used for determination. This combination is the most sensitive

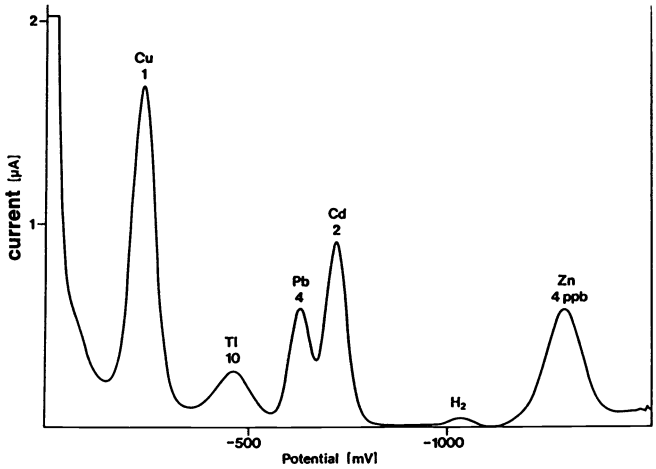


Fig. 12: Differential Pulse Polarography with Hanging Mercury Drop Electrode
Polarograph PAR, type 174; concentrations in µg/l (ppb); 2m K_2CO_3 solution [M. Michulitz, H. Heckner, 1984]

trace element method for several heavier elements such as Ni, Co with detection limits of 50 to 100 ppt and 0,1 to 1 ppb for Zn, Cd, Pb, Bi, Cu, Sn, Tl; As, Se. According to (ref. 51, 77), up to about 30 elements can be determined by stripping voltammetry. Precisions in pure aqueous solution of about ± 5 to 10 % have been obtained in our chemical analysis service. This methods are especially useful for trace analysis of toxic heavy metals, but also for solutions with high matrix concentration.

Main advantages of DPASV are the (a) highest sensitivity from most other instrumental trace element analysis methods for a larger group of electrochemical active elements with environmental importance down to detection limits of about 0,1 to 1 ppb, (b) independence to even high concentrations of electrochemical inactive neutral salts, contrary to atomic emission spectrometry, (c) the at least oligo-element character of the method.

Disadvantages are (a) restriction to only a group and not to all elements, (b) interference of even traces of organic molecules in the solution, e.g. residues from wet ashing, which (c) affords wet ashing with $HNO_3/HClO_4$, (d) relatively long analysis time and (e) difficulties until now with complete automatic analysis of large sample series.

4.9 Other methods

4.9.1 Ion chromatography (IC) and gas chromatography (GC)

Since about ten years, ion chromatrography (IC) of aqueous solutions of non-metallic anions or metal cations and since about fifteen years gas chromatography (GC) of volatile mixtures of metal chelates has been used for oligo-element or oligo-anion analysis down to the range of 5 to 0,5 or 0,1 to 0,01 ng level, resp.. Both techniques apply powerful separation techniques in combination with unspecific detections. They are methods for molecule analysis (Fig. 2) applied to element analysis. The number of constituents to be separated and determined is around ten or less.

IC (ref. 67) according to Small, Stevens, Baumann (1975) combines an ion exchanger column for chromatographic separation with a suppressor column with H^+- or OH^--ion exchanger for neutralizing the electrolyte in the effluent, followed by electrical conductivity detection. Today the term ion chromatography covers all liquid chromatography methods for separation of cations or anions without derivatization, in different chromatographical systems and any detection method. Simultaneous anion chromatography of 6 to 9 anions with detection limits below 1 ppm e.g. for drinking water analysis, have been performed in 10 to 20 minutes.

GC (ref. 50) can be applied to such mixtures of elements, which previous to separation can be derivated into volatile metal chelates, volatile and stable enough to be separated by gas chromatography. As an example, Bi, Pb, Fe, Co, Hg, Cd, Ni, Co, Zn as di- and tri-fluoroethylenedithiocarbaminates have been separated within 40 minutes.

4.9.2 Micro trace element analysis of surfaces by ion micro probe (SIMS)

Within the last decade, multi trace element analysis of surface layers, thin films and small domains in surfaces has become important in several fields (ref. 19, 20, 21). Among these methods, the ion micro probe based on the SIMS principle has the unique advantage of (a) extreme multi-isotope character for up to ca. 80 elements, combined with (b) detection limits down to the ppm level, (c) micro analysis of micro domains in the surface of about 0,2 to 400 µm in diameter, (d) horizontal and vertical element content mapping for the upper two to three atom layers. (e) Using depth profiling, even micro-bulk analysis in surface layers is possible. Ion microprobe, as SIMS, allows to analyze isotopes, and only indirectly, elements.

Fig. 13 gives as an example from this laboratory (L. Radermacher, J. Schilling, H. Beske, H. Holzbrecher, 1984) of an ion micro probe isotope distribution picture within a micro domain of incoloy 800 H.

4.10 Applications

A review about special applications of multi-element analysis methods to environment- (ref. 69), geo- (ref. 1, 66, 73), life- (ref. 11, 52, 63, 62), material- (ref. 42) and food science, as well as information (ref. 48) and nuclear technology is outside of the scope of this lecture and can be found in (ref. 58). Comparison of different instrumental multi-element methods for several types of matrices is presented in (ref. 9, 11, 16, 42, 45, 46, 48, 52, 59, 66, 73).

5. FUTURE TRENDS

At the end of this lecture, some future aspects of instrumental multi-element analysis in general will be summarized (ref. 59. 58. 61).

5.1 Multi-element approach

Within a chemical analysis service, multi-element analysis methods allow to analyse more elements than ordered in the same sample in all cases, where it is not too expensive and time-consuming. Therefore revision of the original research programme of the scientist or employer in analysis service and including the additional elements obtained by simple multi-element approach, are to be proposed where it is useful. This in future needs closer co-operation between the research scientist and the analyst.

Careful optimization of the mean experimental conditions for simultaneous analysis of as many elements as possible is necessary in order to improve the often smaller accuracies compared with mono-element methods.

Therefore, the range of detection limits of individual chemical elements throughout the periodic system, precision, dynamic range and accuracy for each multi-element analysis problem shall be evaluated carefully.

Lowering of detection limits for many elements by one or even two orders of magnitude compared with current ICP atomic emission spectrometry is desired.
Large dynamic concentration ranges for each method and element are a main prerequisite for applying the multi-element analysis concept successfully. Much more carefully prepared and certified reference standards (ref. 70) with special consideration of multi-element analysis is still more important in future.

Each instrumental multi-element method has a different range of optimal application and of failure. When considering multi-element survey over the whole range of the periodical table, as e.g. in geochemistry, it becomes obvious, that a combination of more than one multi-element method applied to the same sample is highly to be recommended. As an example, Fig. 14 gives the result of the multi-element analysis of an uranium containing soil by instrumental neutron activation analysis, spark source mass spectrometry, atomic emission spectrometry (d.c. arc), X-ray fluorescence spectrometry, supplemented by atomic absorption spectrometry.

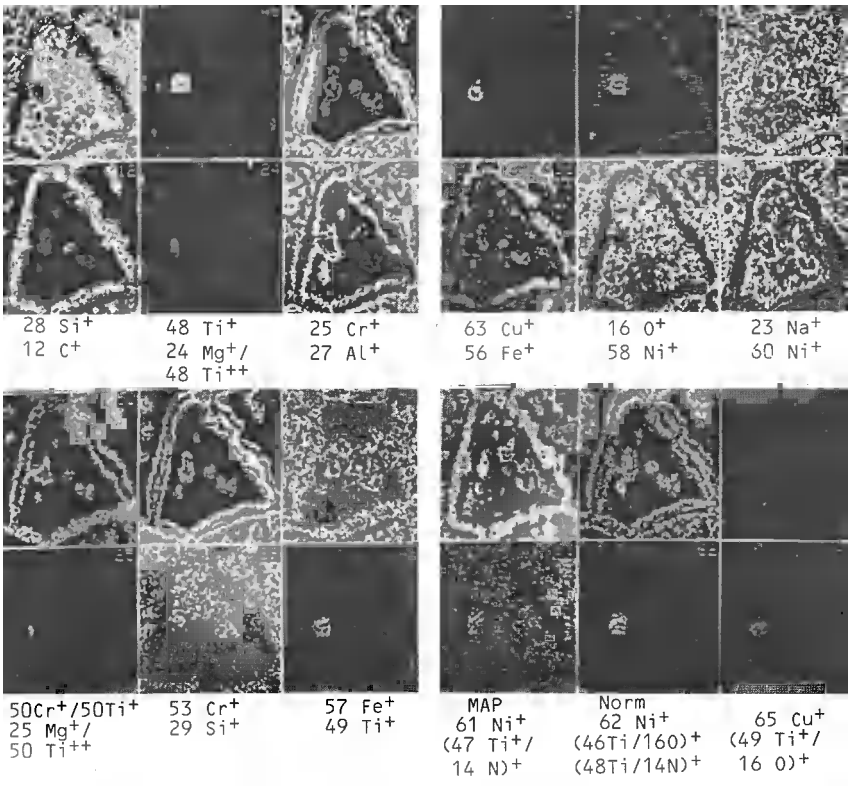


Fig. 13: Trace Element Distribution in Incoloy 800H by Ion Micro Probe (SIMS)

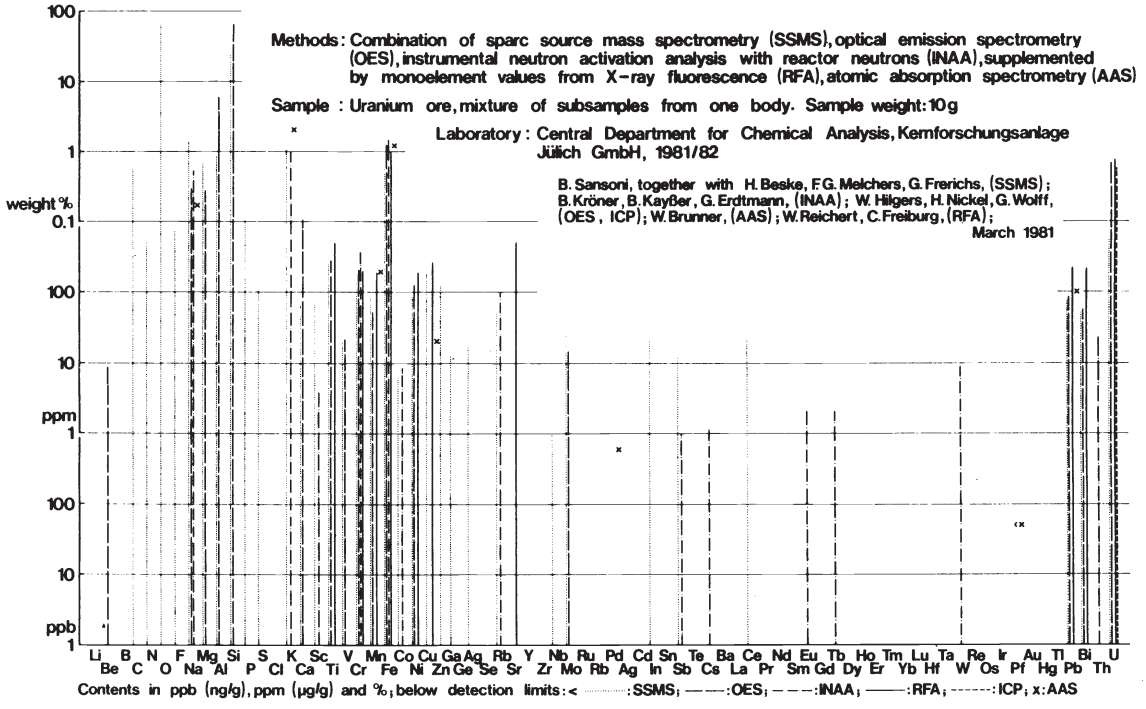


Fig. 14: Application of more than one instrumental method for multi-element analysis of major, minor and trace element constitutents in one sample

Survey of all elements of the periodical table above detection limits, uranium containing soil as an example. According to (ref. 59,61)

5.2 Automation

Within a given research project, now a much larger number of samples can be analysed than before if (a) they have the same or at least similar matrix, (b) element composition and (c) concentration range. This again has a strong influence on the planning of a research project using chemical element analysis.

Further advantages are the improved precision by eliminating the human error and avoidance of time-consuming and erroneous wet-chemical methods by preferring purely instrumental methods.

On the other hand, however, increased quality control of the results is still more necessary than before in order to guarantee accuracy of the much larger number of results. Furthermore, a large dynamic range of element concentrations is a prerequisite also for automation.

5.3 Computerization

Computerization supports and improves the automation of instrumental methods, allows data concentration and evaluation on-line by statistical and chemometric methods, graphical data presentation and documentation of the results.

5.4 Chemical methods

The dominance of the classical chemical methods in research and especially services for detection and determination of elements is shifting to sample preparation, including disintegration, ashing, dissolution, pre-concentration and separation.
They are still to be preferred in cases where high precision and accuracy are necessary, e.g. for standardizing methods and reference materials or determination of stoichiometry of compounds. They are, however, not usable in the case of small trace concentrations.
If necessary, those chemical methods in solution will be preferred which can be easily automated, e.g. by robot application or column operation to ion exchange or chromatographic procedures.

As a summary, multi-element analysis methods in future will give much more information about multi-element composition of the environment and materials in general. However, one has to be aware that because of the leveling to mean experimental conditions, the precision, accuracy and detection limits cannot be optimal for each element by principle. In any case, however, the multi-element approach gives at least a semiquantitative overview of the element composition in a given sample. One should keep in mind that the statement "content below detection limit" is also equivalent to a numerical analytical result. The sometimes enormous increase of the number of element contents and concentrations obtained by automated instrumental multi-element analysis has the consequence, that sometimes data handling and data evaluation may determine the speed of analysis more than the measurement of the analytical signal itself. Therefore, computerization of the measurement as well as extended and also on-line data evaluation cannot be avoided in future. Last but not least, attention has to be drawn to representative sampling as well as contamination and loss free sample preparation prior to measurement.

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