

SOME REMARKS ON NAA IN GEOCHEMICAL RESEARCH

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INTRODUCTION

Next year will see the 50th anniversary of the first neutron activation analysis. In this relatively short time of only one or two generations of scientists this method has become a powerful analytical tool which can yield maximum outputs in various respects. Among the manifold fields of application, geology is one of the most important ones. This can be clearly seen by the fact that recently geological sections have been included in many conferences on activation analysis.

There are various reasons for this. One of them is of course the great number of possibilities inherent in activation analysis. Secondly, the development of geology itself has contributed greatly. The different neutron sources ranging from portable isotopic neutron sources with a source strength of some 10^6 n·s⁻¹ to nuclear reactors giving neutron fluxes of 10^{13} n·s⁻¹·cm⁻² and more are suitable for analysis for concentrations from the per cent range of geological macrocomponents up to ppb or sub-ppb levels of trace elements. Some elements, especially light ones, are analysed by fast neutrons of neutron generators, and for some time elements of the periodic table having a low neutron activation sensitivity have been analysed by high-energy gamma rays generated by linacs and microtrons.

Neutron activation analysis can be performed in geological bore holes, in ore dressing plants and on field exploration vans. But the neutron source used most widely for activation analysis, also for geological purposes, is the nuclear reactor and will continue to be so in future.

As far as the measuring aspect of NAA is concerned we do not find such a diversified picture. Equipment for geological analysis ranges from scintillation counters to multi-channel-analysers coupled semiconductor detectors.

It is not possible here to deal with geological NAA in all its various aspects. Rather I would like to restrict myself to reactor activation and make a few remarks on NAA in geochemical research without pretending to give a complete and comprehensive picture. For this purpose it might be first of all useful to have a look at the efficiency of NAA in geochemical conditions. Then it will be easier to define the position of NAA in geological research. Finally, the statements made will be illustrated by a few examples.

THE EFFICIENCY OF NAA

Sensitivity and detection limits are some of the most interesting parameters of an analytical method. Sensitivities of NAA are tabulated frequently. Analytical detection limits L_A containing counting detection limit L_C and sensitivity S as

$$L_A = L_C/S$$

are not of such general significance because the conditions of counting detection limit are mostly idealized and related to pure samples, and therefore they are not valid for the large field of instrumental NAA (INAA). For this reason we will first of all concentrate on sensitivity in our subsequent considerations.

If an analytical method is to be appraised relating to a special group of samples, i. e. geological ones, then sensitivities should be combined with the typical contents of these samples. This has been done in Fig. 1. Of course it is not so easy to define the typical geological sample. In our investigations a fictive sample was used for this purpose containing the lithospheric Clarke concentrations, that is the mean contents of the elements in the whole lithosphere. The lithosphere is generally assumed to contain 2 parts acidic and 1 part basic rock. These contents (in ppm) /1/ are multiplied by NAA sensitivities (counts per second and μ g element) taking into consideration the activation of 100 h or up to saturation in 10^{13} n·cm⁻²·s⁻¹, the intensity of the strongest gamma line and the detection efficiency of a medium size Ge(Li)-detector for this line. The product may be called Clarke sensitivity and gives the pulses per g of the fictive sample in the strongest line of the most active radionuclid of each element. These values are compiled in Fig. 1.

Three different symbols are used to represent these values depending on the NAA technique mainly employed to determine an element in geological samples: INAA either by short irradiation in a range of minutes or by longer irradiation of some hours, followed by measurement after some days or weeks, resp., or as a third way, radiochemical separation before measurement. As a result of this marking procedure, symbols contain indirectly half-life relations and con-

ditions in the gamma spectra.

Though Fig. 1 cannot give all details of NAA in geology, many facts of this field are immediately visible from it. Thus it shows very clearly the limitation of short irradiation INAA by Al and Mn and of long irradiation by Na and to a certain extent by La and Sm.

Here we have the favourable circumstance that more than 20 elements can be determined instrumentally in geological samples which is mainly due to the fact that so many Clarke sensitivities are concentrated in a relatively narrow belt in the middle of Fig. 1 without having long-lived ones on top. Elements needing radiochemical separation are placed in the lower part and include both NAA-sensitive ones, such as Ir and Au, and insensitive ones, such as Ni and Zr having, however, high Clarkes.

I would like to stress once more that the classification INAA - radiochemical NAA is purely empirical, and certain experimental conditions can lead to variations in borderline cases. Such modified techniques are i. e. epithermal neutron activation which has been increasingly used in routine work recently /2/, measuring of X-rays, or spectrometric coincidence measurements.

Diagrams such as Fig. 1 can also be arranged for other rock types with variations occurring only in some elements in most cases. Completely altered relations are obtained for ores or special minerals.

A second criterion for the assessment of an analytical method is the number of elements analyzed. More than 20 trace elements in geological samples is a remarkable result for INAA. Only mass spectroscopy seems to be superior to it. However, it should also be noted that NAA is doubtless a multielement method but without any survey character because sensitivity varies from element to element, and some important elements such as F or Pb are missing totally.

If we include radiochemical separation procedures more than 60 elements can be analysed by NAA. This now touches another aspect of analysis - effort and expense in terms of equipment and manpower.

NAA requires more specialized equipment than other methods as a nuclear reactor and conditions for radioactive working are necessary. Whereas in the beginning NAA was restricted to nuclear research centers only their irradiation

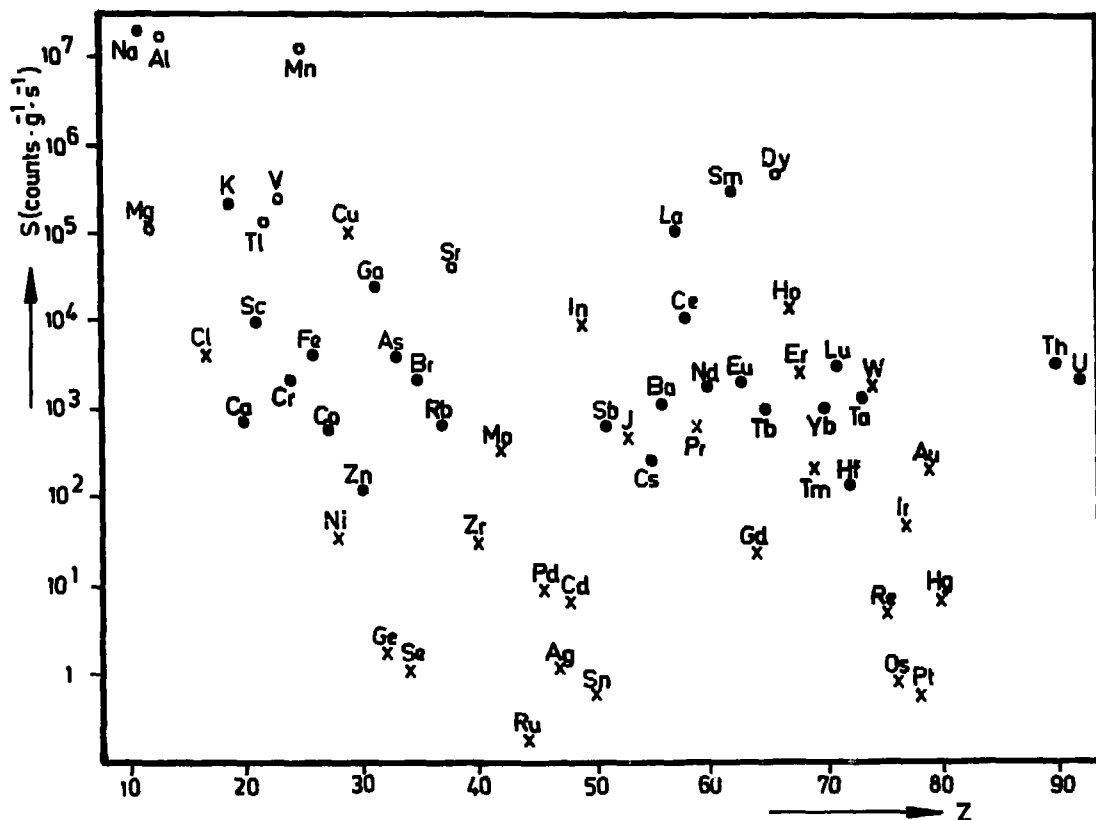


FIG. 1: NAA SENSITIVITIES FOR A GEOLOGICAL SAMPLE REPRESENTED BY LITHOSPHERIC CLARKE VALUES. (PULSES PER SECOND) AND GRAM SAMPLE IN THE STRONGEST LINE BY A MEDIUM-SIZE GE(LI) DETECTOR AFTER 100 H ACTIVATION (OR SATURATION) IN 10^{13} N/S*CM²)

service is often used today. The radioactive disadvantage is partly compensated at the very least in INAA by nondestructive handling of samples avoiding chemical dissolutions as necessary for atomic spectroscopical methods. Moreover gamma-spectroscopy has best conditions for automation and computer evaluation. Therefore today microcomputerbased systems accomplish INAA of geological samples fully automatically if they are supplied with activated samples. Such systems work in geological institutions too.

In fully automatic systems the number of samples analysed per year can be between 5000 and 10000. As a result of this efficient exploitation of equipment and low labour demand the cost per element determination can be in the same order or lower than that obtained with most other analytical techniques /2/. In this way INAA is able to compete with other methods also in terms of economy.

This is not possible if radiochemical separations are involved. But here other aspects have to be taken into consideration. Only radiochemical separation removing the Compton background under analytical lines can take full advantage of high NAA sensitivities and make it possible to attain detection limits for which other economically comparable methods do not exist. For instance it is hardly possible to obtain detection limits of 0.02 ppb Pd, 0.5 ppb Pt, and 0.002 ppb Ir /3/ in silicatic rocks by methods other than NAA.

In my opinion, radiochemical NAA should be used more intensely in future after its relative decrease during the last decade in which greater attention was paid to INAA. Despite improvements in competing methods - or may be even because of them - radiochemical NAA has its chance if used in the right place. Separation should be done up to a level pure enough for gamma-spectroscopical measurement but always under control of chemical yield for which the tools were enlarged by new tracer methods /4/.

Further analytical parameters are precision connected with random errors and accuracy connected with systematic ones. NAA is well-known for its excellent accuracy. This is valid for geochemical samples too. The reasons for this can be briefly characterized i. e. by no chemical influence on nuclear reactions, controllable interferences as neutron self-shielding or interfering reactions, selectivity by direct spectrometric identification in the measuring process and no contamination after activation. What is mostly practised in geological INAA is the application of reference materials as standards avoiding additional errors by standard preparation. Fortunately there are good geological standard reference materials.

All that is said about accuracy is rather theoretical. A confirmation by a practical example will be given below.

Whereas it is always necessary to aspire to highest accuracy the question of precision needed for geological samples is more delicate. Here the type of samples has to be taken into consideration. For instance a set of samples from a geological profile with a possible small variation of contents will require a better precision than samples for the investigation of a geological phenomenon from different regions for which perhaps only the order of magnitude is interesting. Such problems including sample representance and preparation should always be discussed together with geologists because too high demands for precision can cause inconveniently long measuring periods.

A coarse rule for trace analysis should be: as accurate as possible - as precise as necessary. Interactions between both terms can complicate the situation from case to case.

But the question is justified which precision is in general attainable. Two main factors influence precision in NAA. The first of them is reproducibility of all analytical conditions for all samples and standards during analysis. This includes neutron flux, counting geometry etc. Using an individual neutron flux monitor for each sample /5/, considering build-up correction etc. a reproducibility of 1-2 % rel. is obtainable. The second factor is counting statistics. In INAA, analysing more than 20 elements under the above mentioned conditions, precision for about only a third of them is limited by reproducibility. For the rest counting statistics is dominating and precision of some per cent rel. is typical. Here an improvement of precision requires a quadratic prolongation of measuring time.

THE POSITION OF NAA IN GEOCHEMISTRY

The main task of geological research is to help secure the country's raw material basis or - more exactly - to provide a scientific foundation of advantage for the mining industry. In some articles on geological basic research this connection does not seem to become too evident. But increasing difficulties in the exploration and exploitation of deposits make it necessary to carry out more basic research before special exploration can start. One example is the study of general regularities of deposit formation as a prerequisite for the formulation of exploration criteria. In this connection such basic geological questions as the old granite problem are raised once more.

In the old days activities oriented towards mining output began only at local exploration of deposits. Fundamental geological investigations were carried

STAGES OF GEOLOGICAL AND MINING ACTIVITIES	CONTENT OF THE ELEMENTS DETERMINED	NUMBER OF SAMPLES ANALYSED	NUMBER OF THE ELEMENTS DETERMINED	AVAILABLE TIME FOR ANALYSIS
-FUNDAMENTAL RESEARCH, BASIC PROBLEMS OF FORMATION OF DEPOSITS	CLARKE (PPM)	< 100	MANY	MONTHS
-VALUATION OF REGIONAL DEPOSIT PROBABILITY				
-EXPLORATION OF DEPOSITS (LOCAL)				
-DEPOSIT EVALUATION				
-MINING PROCESS CONTROL	...%	> 1000	1	< HOURS

FIG. 2: REQUIREMENTS FOR ANALYSIS IN SEVERAL STAGES OF GEOLOGICAL RESEARCH AND MINING

out nearly independently. Nowadays the chain from basic research to practical mining is longer and also more compact.

In Fig. 2 some steps of this chain are compiled together with different analytical requirements. Fundamental geological research mostly far away from concentrations where mining would be worthwhile is the main field of geological trace analysis. Typical concentrations are in Clarke levels. Up to the present day one can find many articles about this field in which sample numbers lower than 100 are analysed. These investigations are mostly of a relatively complex character and if no other methods are included at the very least many elements are determined. Usually there is no limitation in time available for carrying out the analysis. As far as the mining industry is concerned fundamental research is followed by evaluations relating to the possibility of deposits in larger regions before local explorations take place. The last step is controlling the mining process.

In this line concentrations increase up to those where mining is worthwhile which vary for different ores but can be in the per cent region. The number of samples to be analysed increases whereas the number of elements determined decreases. In exploration sometimes special indicating elements are used, and therefore not only the mining element is analysed. But at the face only the ore forming element is important. Looking at available analysis periods makes it clear: the nearer to the end of this chain the faster the results are needed.

The position of NAA will become obvious from these considerations. The parameters in the first line are the typical ones for reactor NAA. Multielement analysis in Clarke concentration level is its strong point as we have seen. In INAA decay periods up to one month till the last measurement are necessary. Therefore results cannot be obtained any faster.

With that the close connection between NAA and geochemical fundamental research which we all know has become a little more founded. But the new tendencies towards increasing sample numbers by full automation open at least the next two lines in Fig. 2 for INAA in special cases. After that competing methods predominate using bore hole logging techniques or portable instruments. Radiochemical NAA is mostly used in fundamental research only.

The share of trace analysis in geochemistry may be demonstrated by the following numbers. Only 8 macroelements account for more than 99 % of the lithosphere, the 8 next frequent ones for 0.9 % and all other elements together for less than 0.1 % /1/. We find much higher variations in trace elements than in macrocomponents especially in equal or similar rock types. Therefore trace elements can give information about more complex geological processes. On the other

hand we must not forget that in most cases we determine the trace content of the whole sample and not of individual mineral phases or even solve crystal structure problems for traces which all can be carried out for macroelements.

At the beginning when I was talking about the reasons in geology itself for the success of NAA I had the following in mind. During its development NAA encountered a geology changing from a more phenomenological and descriptive science to a measuring and calculating one. NAA stimulated this process in the same way as other methods. During this period of data collection geologists were and are interested in as many data as possible. All of us who work together with geologists know this tendency. It can be understood by the very complicated interpretation of geochemical or more general geological phenomena, always hoping that an element more could give a hint more.

Recently, the next step has been taken more frequently: instead of a more or less empirical interpretation attempts are made to advance to the fundamental processes forming the complex picture of geological occurrences. Because a satisfactory laboratory simulation is often not possible owing to extreme physical parameters geological processes have to be studied by their results in nature. This requires very complex investigation techniques including NAA among many other methods.

In our institute these are physical age determination, investigation of stable isotopes together with the study of liquid and gaseous inclusions. Most works are performed in close cooperation with geological institutions which contribute also their analytical methods.

In such complex systems it is important for the analyst to have good relations to all coworking institutions for optimizing analytical tasks and tracing the results in the final interpretation.

Although NAA offers a wide and manifold spectrum of possibilities in geochemistry some application fields stand out. Determination of rare earth elements (REE) should be mentioned in first place in my opinion. This first place results from the number of publications, the geological importance of REE and difficulties in determination by other methods. It is possible to determine more than the half the REE in most rocks by INAA together with many other elements. If INAA fails i. e. in ultrabasic rocks there are effective radiochemical procedures to separate the REE group before measurement and determine nearly all REE.

REE can provide information in connection with many geological problems. Their chemical behaviour is very similar through the whole group (except Ce and Eu) but the varying ionic radii can cause different conditions for incorporating them into the crystal lattice. The measured contents are usually normalized to the adequate contents in chondrites representing primary matter, or to other suitable samples. These REE patterns are interpreted, but unfortunately mostly in a qualitative manner only. This rather unsatisfactory situation results from the fact that the path of REE has not yet been explored quantitatively in many geological fundamental processes. Exceptions exist in an embryonic stage. Nevertheless or even because of this REE should stay in the foremost position.

A second main field is determination of very rare elements mostly in concentration levels in which NAA is superior to other methods by exhausting its whole sensitivity using radiochemical separation. Favoured objects here are gold, rhenium and the elements of the platinum group.

Contributions of NAA in establishing geochemical or similar standard reference materials should also be mentioned as a third field.

Let me underpin my rather theoretical statements by some small examples from these three fields.

EXAMPLES

REE IN GRANITES AND FLUORITES: In the western part of Erzgebirge (GDR) there are two large granitic intrusive complexes both including three intrusive phases. Their temporal order is established by geological facts and Rb/Sr age determinations /6/. The older complex (AG) is geochemically very similar to normal granites. The younger one (JG) is highly specialized for some elements and connected with Sn-deposits /7/.

More than 40 granites of these complexes were analysed for REE by INAA. Fig. 3 shows chondrite-normalized REE patterns of the three phases of the older complex (AG 1-3) as averages from several samples in each case. The slope of the patterns from La to Lu decreases through the phases 1-3. The Eu anomaly increases. There are the same tendencies through the phases of the younger complex. In a diagram Eu anomaly (E) via slope (S), as in Fig. 4, homogeneousness and development of the phases in both complexes are clearly demonstrated as well as the interposition of the intermediate granites ZG 1 and ZG 2. Increasing Eu anomaly in connection with other facts (low initial isotopic Sr-87/Sr-86-ratio) indicates increasing focal depth for younger granites.

This nearly empirical interpretation of REE patterns is successfully transferable to other granites of the southern part of the GDR.

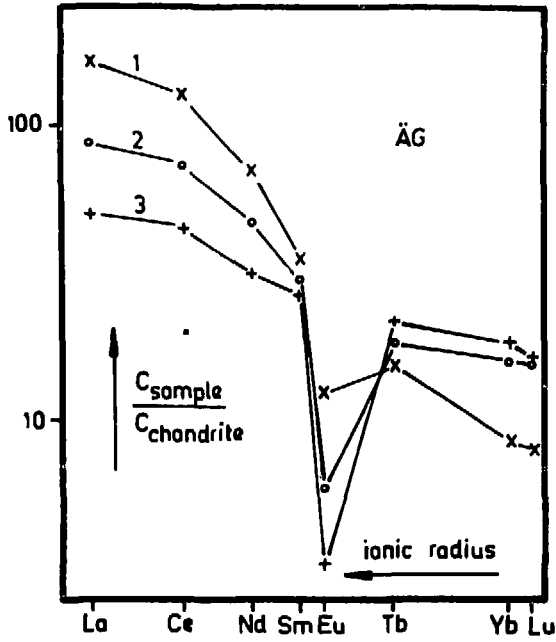


FIG. 3: REE IN GRANITES OF OLDER INTRUSIVE COMPLEX IN W-ERZGEBIRGE (GDR) (CHONDRITE-NORMALIZED)

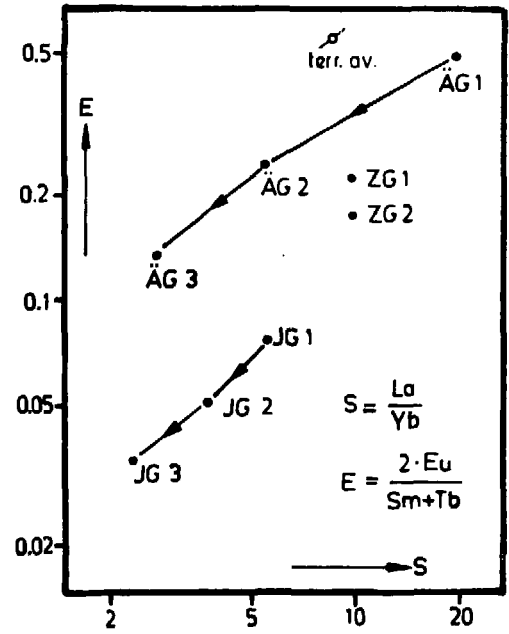


FIG. 4: DEVELOPMENT OF REE PATTERNS IN GRANITIC INTRUSIVE COMPLEXES IN W-ERZGEBIRGE (GDR)

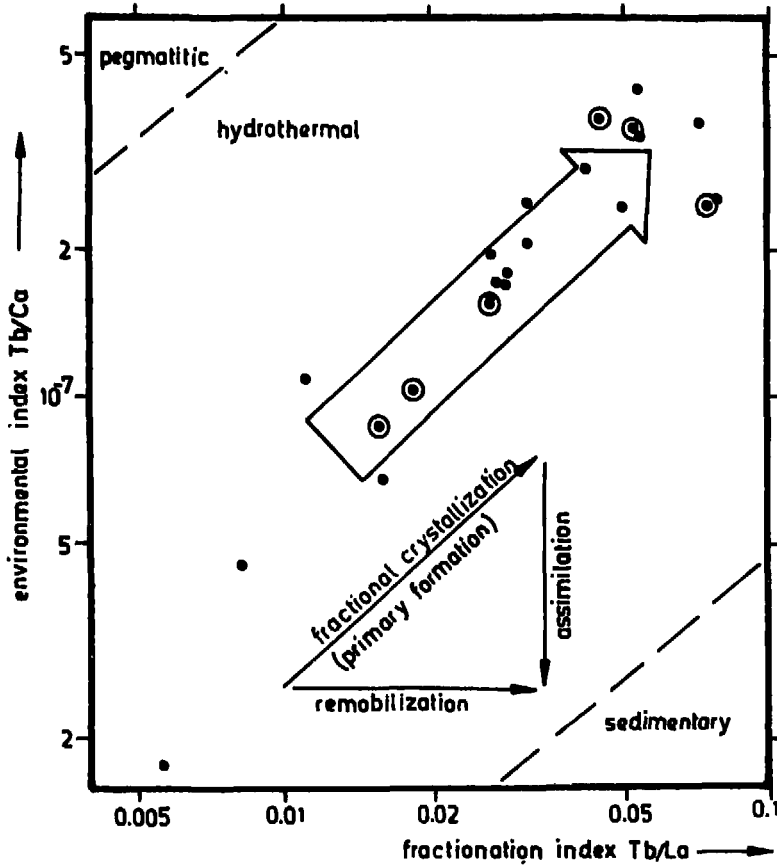


FIG. 5: TB/CA-TB/LA DIAGRAM OF FLUORITES FROM A PROFILE AT BOESENBRUNN, VOGTLAND (GDR)

Interpretation of REE in fluorite mineralization is theoretically better founded and considers geochemical fundamental processes.

We analysed many samples from a profile across a more than 2 m thick vein in a fluorite mine in the Vogtland region, GDR. We found very great variations in the REE patterns even over small distances in cm range. Some clarity could be provided by a diagram of the kind proposed by Möller et al. /8/ on the basis of theoretical considerations on fractional crystallization including REE complex formation. Fig. 5 shows this diagram. The direction of primary formation is dominating in distribution of measuring points. Considering their order in the profile it is possible to identify some cycles which were passed successively. The points of one cycle are especially marked in Fig. 5. These cycles were also confirmed by analysis of liquid inclusions (macroelement composition, isotopic ratios). On the basis of these facts in connection with the geothermal gradient determined by homogenisation measurements and by Na/Ca/K-temperatures of liquid inclusions a seismic pumping system is proposed as a model /9/.

DETERMINATION OF OSMIUM: Os may serve as an example for an element requiring chemical separation. An osmium geochemistry has not yet been worked out because there are too few data. But Os takes a part in Re/Os age determination. During previous preparation work for introducing this method in our institute our laboratory worked out a method for NAA determination of osmium in geological samples /10/. Separation is based on distillation of Os as osmiumtetroxide followed by extraction in chloroform. A detection limit of 0.01 ppb is attained.

In the case of Os a rarely appearing circumstance has to be considered in NAA. The isotope ratio in Os can be changed in Re rich geological samples by radioactive decay of Re-187 (half-life $4.3 \cdot 10^{10}$ y). NAA via activation of Os-190 yields only the non-radiogenic part of Os using a "normal" Os as NAA standard.

This analytical disadvantage can give additional geologically relevant information if the total Os content is determined by another method. This was realized by Merz and Herr /11/ as early as 1958 for molybdenites in higher concentration levels by spectrophotometry. First attempts in our laboratory by a catalytic total Os determination showed for instance ratios of radiogenic Os to non-radiogenic one in the order of 10:1 in samples connected with copper mining. Such combinations of NAA with other methods can give information in concentration levels below typical working concentrations of mass-spectrometric isotope ratio determinations.

NAA IN INTERCOMPARISONS: The best method and the only one under practical conditions to obtain information about accuracy of a trace analytical technique is comparing results of the same sample analysed by several laboratories using different analytical methods if possible. Such intercomparisons are organized by several institutions and participation can be highly recommended.

Participating laboratories are supplied with extensive and detailed data from the final reports. But these reports do not or only partly evaluate explicitly the quality of laboratories and methods. This is omitted because quality criteria must have some arbitrary character among other things. I carried out such evaluations for the last two intercomparisons in which our laboratory took part. They are SOIL-7 from the IAEA /12/ and fly coal ashes ECH, ENO and EOP from the Institute of Radioecology and Applied Nuclear Techniques Kosice (CSSR) /13/, both similar to geological samples.

I used the following evaluation. The accepted data of each element are roughly divided into three equal parts in order of increasing value of results. Laboratories or methods having a result in the middle part around the overall mean get a positive point. Outliers produce negative points. Taking into consideration

PLACE NO.	LAB. CODE NO.	ANALYTICAL METHODS	POINTS
1	56	NOT REPORTED	16
2	49	NAA	12
3	30	NAA	11
4	33	NAA	10
5	43	XRF	9
6-9	22	NAA	8
	26	NAA	8
	31	AAS	8
	45	NAA	8
.	.	.	.
.	.	.	.
.	.	.	.
52-53	24	XRF	-12
	32	AAS, AES	-12
54	41	AAS, ET. AL.	-16
55	42	AAS	-22
56	15	AAS	-28

FIG. 6: BEGINNING AND END OF LABORATORY PLACEMENT LIST IN INTERCOMPARISON SOIL 7

total numbers of positive points and outliers, one outlier gives about 2.5 negative points.

Fig. 6 shows beginning and end of the SOIL-7 laboratory placement list indicating a leading part of NAA. 56 laboratories participated in SOIL-7, 18 among them used NAA exclusively. But 8 NAA laboratories are placed among the 12 best ones. In the fly-ash intercomparison the respective figures are 34-10-7. But here laboratories in the two last places are also NAA ones. That indicates that NAA can also be performed in a wrong manner.

Disregarding laboratories and evaluating only methods in SOIL-7 the order is: 1. NAA, 2. AES, 3. XRF, 4. AAS. In the case of fly-ashes NAA also holds the first place with advantage. This indicates that for this statement the kind of evaluation criteria is not so important.

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