

## ACTIVATION ANALYSIS OF ORES AND MINERALS

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**Abstract** - This review deals with applications of activation analysis to geological samples: ores, minerals and rocks. The various activation sources suitable for this purpose are discussed. Applications using isotopic neutron sources are reviewed in some detail, those using neutron generators are discussed on a more general basis. Present trends in instrumental neutron-activation techniques are briefly indicated, in particular Ge(Li) gamma-ray spectrometry, coincidence counting, delayed neutron counting, prompt gamma counting and observation of nuclear tracks. The application of photon and charged particle activation to geological samples is also considered.

### INTRODUCTION

It is the task of the geochemist to determine the abundance and the distribution of the chemical elements in the earth and in earth-related materials, including meteorites, tektites and lunar rocks and soil. For convenience the chemical elements have been grouped into major (> 1%), minor (0.01 - 0.1 %) and trace elements (< 0.01 % or < 100 ppm). In the case of extremely low concentrations, such as for iridium in many terrestrial silicate rocks (0.0X ppb) it is perhaps appropriate to talk about ultra trace elements (Ref. 1).

Activation analysis has predominantly had its use as an ultrasensitive method of trace analysis. The more recently developed instrumental neutron activation analysis (INAA) using semiconductor detectors and on- or off-line computers has made activation analysis a promising tool not only for chemists and specialized geochemists, but also for geologists in general. It is a fact that emission spectrography, X-ray fluorescence, atomic absorption and even mass spectrometry have gained greater acceptance and are more common in geology and geochemistry departments and mining institutes than activation analysis is. An increased emphasis on activation analysis as a tool in geochemistry in the years to come is, however, to be expected (Ref. 2).

Indeed, in reviewing the results obtained by various groups, selected by NASA, on the powdered, reasonably homogeneous lunar fines from Apollo 11 (Ref. 3), Smales (4) pointed out that activation analysis was clearly the most frequently used analytical method, not only for trace elements, but even for major elements.

Some recent conferences have revealed a tendency to use activation analysis for determining major elements, indeed, and to place emphasis more on precision and accuracy than on ultimate sensitivity. Fast, automated "non-destructive" analyses are possible in a number of cases with a modest isotopic neutron source (Ref. 5), which is very attractive for a variety of routine applications.

The literature on activation analysis applied to geological materials is already quite impressive (Ref. 6). It can be studied on the basis of the application (e.g. terrestrial, meteoritic and lunar studies), or on the basis of the concentration range of the element determined (major, minor, trace), for instance. We consider it more convenient to discuss the analytical possibilities of various activation sources: isotopic neutron sources, neutron generators, and nuclear reactors. Bremsstrahlung and charged particle sources will also briefly be considered. It is hoped that the general applicability of activation analysis will be realized through the discussion of a few specific applications and the presentation of some synoptic tables.

### THE CHOICE OF A NEUTRON SOURCE

The choice of a neutron source depends on the problem to be solved. It is obvious that a research reactor or even a high-flux reactor is recommended when a very high sensitivity is required or desirable, e.g. for determining p.p.b. concentrations of rhenium in minerals or flue dusts. If oxygen must be determined, a 14 MeV neutron generator is most suitable because of the high threshold energy ( $\sim 9$  MeV) of the most useful nuclear reaction  $^{16}\text{O}(n,p)^{16}\text{N}$ .

An unmoderated isotopic neutron source (e.g.  $^{241}\text{Am}/\text{Be}$ ) is perhaps the best choice for determining the fluorine content of fluorine ores and concentrates via the reaction  $^{19}\text{F}(n,\alpha)^{16}\text{N}$  (threshold energy  $\sim 2$  MeV), without interference from the  $^{16}\text{O}(n,p)^{16}\text{N}$  reaction. For the precise instrumental determination of manganese in pyrolusite ores, via the sensitive reaction  $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$ , a relatively modest isotopic source of moderated neutrons is ideally suited. Nuclear reactors, accelerators and isotopic neutron sources are so different in neutron production and neutron energy, that only for some applications they can be considered competitors.

Other criteria to be considered are, of course, cost of the neutron source, possibility for transportation, dimension of source plus shielding, the necessity of having highly specialized personnel, etc. In mobile installations, for geophysical prospecting, radioisotope sources with yields of less than  $10^8\text{n/s}$ , with or without moderator, have mostly been used, mainly in the U.S.S.R. (Ref. 7). The neutron flux in the irradiation zone with the above source strength is usually not more than  $10^5\text{n.cm}^{-2}\text{s}^{-1}$ , depending upon the design. Experiments in the U.S.A. and in the U.S.S.R. have shown that deuteron accelerators, (pumped and sealed tube), producing 14 MeV, 3 MeV or moderated neutrons are also transportable (Ref. 7-14).

In stationary conditions, heavier shielding is only a cost, not a transportation problem, hence more powerful neutron sources can be used than in field conditions (i.e. isotopic neutron sources of greater strength; laboratory neutron generators and so-called neutron multipliers).

Reactor neutron activation analysis, charged particle and gamma activation analysis (Bremsstrahlung of varying energy, 3-40 MeV, obtained from electrostatic, linear wave-guide and cyclic electron accelerators: betatron and synchrotrons) is practically restricted to stationary applications. The main trends of the use of various neutron and Bremsstrahlung sources for the study of rocks and ores have been described by Savosin *et al.* (15).

#### APPLICATIONS USING ISOTOPIC NEUTRON SOURCES AND NEUTRON MULTIPLIERS.

The use of isotopic neutron sources and neutron multipliers in ore and rock analysis has been discussed in some detail by Gijbels (16). One can use the original neutron spectrum with neutron energies up to 4 MeV, or thermalized neutrons, or a combination of both. The fast neutrons have frequently been used for determining fluorine by the  $^{19}\text{F}(n,\alpha)^{16}\text{N}$  reaction; the thermalized neutrons have often been used for determining manganese, copper and tungsten by  $(n,\gamma)$  reactions; silicon and aluminium can be determined by irradiating the sample subsequently with fast and moderated neutrons, the relevant nuclear reactions being  $^{28}\text{Si}(n,p)^{28}\text{Al}$  and  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ .

Russian workers have mostly used  $^{210}\text{Po}/\text{Be}$  and  $^{239}\text{Pu}/\text{Be}$  sources, up to 10 Curie. For Western countries, a number of papers deal with the application of  $^{241}\text{Am}/\text{Be}$  (typically 5 Curie) and  $^{252}\text{Cf}$  (typically 100  $\mu\text{g}$ ) in neutron activation analysis of geological materials.  $^{228}\text{Th}/\text{Be}$  and  $^{226}\text{Ra}/\text{Be}$  have not been utilized so often, because of their high gamma dose rate; the same is true for  $^{124}\text{Sb}/\text{Be}$ . A source that is quite promising both in investment and replenishment costs is  $^{227}\text{Ac}/\text{Be}$  ( $T_{1/2} = 21.8$  y).

Table 1 lists a number of typical fast, instrumental major element determinations in geological material by isotopic neutron source activation analysis. In addition, the A.F.C.L. (Canada) has investigated the feasibility of determining a number of economically interesting elements in various minerals, using a 6000 Curie  $^{124}\text{Sb}/\text{Be}$  source (Ref. 17): Al in bauxite, Ag in friebertite, As in skutterudite, Au in auriferous quartz, Ba in barite, Ca in limestone, Co in skutterudite and in Cu-Ni ore, Cr in chromite, Cu in chalcopyrite, in Cu-Ni ore, in Cu-Zn-Pb ore and in malachite, Dy in apatite, F in fluorite, In in sphalerite, Mg in dolomite and in brucite, Mn in manganese ore, Mo in molybdenite, Ni in pentlandite, rare earths and Th in monazite, Sb in stibnite, Se in Cu-Zn ore, Sn in cassiterite, Ti in ilmenite, W in wolframite, U in uraninite and carnotite, V in carnotite, Zn in sphalerite and Zr in zircon. This mobile system is built around an  $^{124}\text{Sb}/\text{Be}$  source and allows thermal fluxes of  $10^8\text{n.cm}^{-2}\text{s}^{-1}$ . The whole can be placed on a 12-m long trailer.

Isotopic neutron source activation can also be applied to common rocks. Janghorbani *et al.* (18), for instance, used a 1.25 mg  $^{252}\text{Cf}$  source for determining Mn, Al, Na and Ti in lunar rocks. The induced activities were, however, rather low in the 0.5 to 1 g samples available.

Usually the method is optimized for determining one single element of (economic) interest, although sometimes more elements are sought for, e.g. Al, Cr and Si in chrome ores. Countings are usually performed with NaI(Tl) detectors coupled to single-channel analyzers. In special cases, such as the prompt gamma counting from nickel ores (Ref. 19), or the rhenium assay in molybdenite concentrates (Ref. 20), Ge(Li) detectors have been preferred.

TABLE 1. Neutron activation analysis of ores using isotopic neutron sources.

| Element determined       | Activation reaction                                | Half-life                    | Type of ore analyzed   | Ref.     |
|--------------------------|--|------------------------------|--|----------|
| A. Unmoderated neutrons. |  |                              |  |          |
| Aluminium                | $^{27}\text{Al}(n,p)^{27}\text{Mg}$                | 9.46 m                       | chrome ores and concentrates   | 26-28    |
| Chromium                 | $^{52}\text{Cr}(n,p)^{52}\text{V}$                 | 3.75 m                       | chrome ores, concentrates and tailings   | 26-28    |
| Fluorine                 | $^{19}\text{F}(n,\alpha)^{16}\text{N}$             | 7.14 s                       | fluorite ores and concentrates, apatite  | 29-37    |
| Iron                     | $^{56}\text{Fe}(n,n'\gamma)$                       | inelastic neutron scattering | iron ores, concentrates and filings, manganese ores  | 38       |
| Silicon $\star\star$     | $^{56}\text{Fe}(n,p)^{56}\text{Mn}$                | 155 m                        | taconite ore   | 39       |
|                          | $^{28}\text{Si}(n,p)^{28}\text{Al}$                | 2.24 m                       | chrome ores, concentrates and tailings, pyrite, pyrite smelter slag, nickel smelter slag, taconite ore   | 26-28,39 |
| Uranium $\star$          | $^{238}\text{U}(n,\gamma)^{239}\text{U}$           | 23.5 m                       | uranium ore (equilibrated and not)   | 40,41    |
| B. Moderated neutrons.   |  |                              |  |          |
| Aluminium $\star\star$   | $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$           | 2.24 m                       | alumino-silicates, sedimentary rocks, marine sediments, aluminium ores and dressing products   | 42,43,61 |
| Copper                   | $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$           | 5.1 m                        | copper ores  | 42       |
|                          | $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$           | 12.8 h                       | copper-bearing drill core and other copper-bearing products  | 44-46    |
| Dysprosium               | $\text{Cu}(n,\gamma)$                              | prompt $\gamma$              | porphyry copper deposits   | 47       |
|                          | $^{164}\text{Dy}(n,\gamma)^{165}\text{Dy}$         | 139 m                        | phosphorite ore  | 48       |
| Gold                     | $^{197}\text{Au}(n,\gamma)$                        | prompt $\gamma$              | gold ore   | 49       |
| Indium                   | $^{115}\text{In}(n,\gamma)^{116\text{m}}\text{In}$ | 53.7 m                       | multimetallic ores and concentrates, sphalerite  | 50,51    |
| Iron                     | $^{56}\text{Fe}(n,\gamma)$                         | prompt $\gamma$              | iron ores, concentrates and filings  | 38,52,53 |
| Manganese                | $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$           | 155 m                        | manganese ores (pyrolusite) sedimentary rocks and soils, wolframite, hibnerite-bearing rock, multimetallic ores, ferromanganese, marine sediments                | 54-61    |
| Nickel                   | $\text{Ni}(n,\gamma)$                              | prompt $\gamma$              | low-grade nickel ore (> 0.1 %), nickel laterites   | 19,47    |
| Rhenium                  | $^{187}\text{Re}(n,\gamma)^{188}\text{Re}$         | 16.8 h                       | molybdenite concentrates   | 20,62    |
| Silver                   | $^{107}\text{Ag}(n,\gamma)^{108}\text{Ag}$         | 145 s                        | silver ore   |          |
|                          | $^{109}\text{Ag}(n,\gamma)^{110}\text{Ag}$         | 24.4 s                       | phosphorite ore  | 48       |
| Tungsten                 | $^{186}\text{W}(n,\gamma)^{187}\text{W}$           | 23.9 h                       | wolframite, hibnerite-bearing rock, tungsten concentrates, mixtures of scheelite + fluorite, hibnerite, ferberite, Mo-containing scheelite ores and concentrates | 60,63-65 |

|          |  |        |  |       |
|----------|--|--------|--|-------|
| Vanadium | $^{51}\text{V}_{(n,\gamma)}\text{}^{52}\text{V}$ | 3.75 m | titanium-magnetite ores,<br>limonite, marine sediments | 50,61 |
|----------|--|--------|--|-------|

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C. Combination of fast and moderated neutrons

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|                             |   |                  |   |             |
|-----------------------------|---|------------------|---|-------------|
| Aluminium<br>and<br>Silicon | $^{27}\text{Al}_{(n,\gamma)}\text{}^{28}\text{Al}$<br>$^{28}\text{Si}_{(n,p)}\text{}^{28}\text{Al}$ | 2.24 m<br>2.24 m | bauxite, nepheline, clay,<br>kaolin,<br>manganesian rocks | 50,58,66-70 |
|-----------------------------|---|------------------|---|-------------|

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\* minimum of moderator used; activation essentially with epithermal neutrons

\*\* see also Table 1, C.

Sample sizes are usually rather large, at least 10 grams, sometimes a few hundreds of grams, or even kilogram amounts. This requires careful standardization, e.g. study of thermal neutron attenuation (especially in Mn, Cu and W ores) and gamma attenuation, if reliable results are to be obtained. It has been shown that a reproducibility of  $\pm 0.5\%$  relative can be obtained for the Mn assay in pyrolusite; the results are of the same quality as titration methods (pyrophosphate or bismuthate method), with the advantage of not requiring the dissolution of the sample (Ref. 54).

For details on the determination of other elements, the original literature should be consulted, or a recent review article (Ref. 16). We finally note that a number of commercial systems are offered by American, French, Finnish, Russian and Hungarian companies or organizations (Ref. 21-25).

#### APPLICATIONS USING A NEUTRON GENERATOR

The voluminous literature on 14 MeV neutron activation analysis (more than 800 references) has been abstracted in a recent annotated bibliography (Ref. 71). The state of the art of this technique is well described in a recent monograph (Ref. 72). About 120 papers deal with the analysis of geological samples, and it would be impractical to discuss even a part of them here, for more details and references, see (Ref. 16).

TABLE 2. - Neutron activation analysis of geological samples with the aid of a neutron generator.

| Material analyzed (*)   | Elements determined (**)  |
|---|---------------------------|
| Apatite, phosphorite, phosphate rock  | P, Al, Si, F, Fe, Sr      |
| Bauxite   | Al, Si, Fe, O             |
| Coal, coal ash  | O, Al, Si, C, Fe          |
| Copper ore, concentrates and tailings   | Cu, Si, Al, O, Fe, Mn, P  |
| Copper-nickel ores, Cu-Ni-Te mixtures   | Se                        |
| Copper-zinc flotation products  | Cu, Zn, Fe, Si            |
| Fluorite, fluorspar   | P, Si, Ba                 |
| Gold-bearing ores and solutions   | Au                        |
| Iron ores, minerals and slags   | Fe, Si, Al, O, Mg         |
| Manganese ore   | Mn                        |
| Mica  | F                         |
| Nepheline   | Al, Si, Fe                |
| Polymetallic ores   | Pb, Cu, Zn                |
| Rare earth element ores, gadolinite, monazite   | Ce, Pr, Y                 |
| Rare earth element concentrates   | Y, Ce, Pr, Nd, Sm, Tb, Er |
| Taconite and concentrates   | Si, Fe, Al, O             |
| Tar sand  | Al, Si                    |
| Zirconium concentrates  | Hf                        |
| Rocks (igneous, sedimentary, metamorphic), rock-forming minerals, soils, meteorites and lunar rocks and soils | O, Si, Al, Fe, Mg         |

\* Including ore concentrates and other materials of industrial interest

\*\* References to the original literature can be found in Ref. 71 and 16.

Table 2 gives a survey of the elements that have been determined so far in ores and minerals using 14 MeV neutron activation; most applications deal with the determination of silicon, oxygen, aluminium, fluorine, iron, copper and phosphorus. In the bibliography referred to above one finds, for igneous, sedimentary and metamorphic rocks, rockforming minerals, sediments and soils, 53 papers on the determination of silicon, 37 on oxygen, 34 on aluminium, 16 on iron, 15 on magnesium, and a few on the determination of fluorine, potassium, silver, sodium, zinc and gold.

The most frequently employed nuclear reactions in 14 MeV neutron activation analysis of ores, minerals and rocks are shown in Table 3.

TABLE 3. - Nuclear reactions most frequently employed in 14 MeV neutron activation analysis of ores, minerals and rocks.

| Element    | Nuclear reaction                         | Threshold energy (MeV) | Isotopic cross section ( $10^{-27}$ cm <sup>2</sup> ) | Half-life produced | Main gamma-ray transition energies (MeV) |
|------------|--|------------------------|---|--------------------|--|
| Oxygen     | $^{16}\text{O}(n,p)^{16}\text{N}$        | 10.3                   | 40  | 7.12 s             | 6.130; 7.112                             |
| Fluorine   | $^{19}\text{F}(n,p)^{19}\text{O}$        | 4.2                    | 15  | 29.1 s             | 0.197; $1_{,356}^+$                      |
|            | $^{19}\text{F}(n,2n)^{18}\text{F}$       | 11.0                   | 60  | 109.7 m            | 0.511 ( $\beta^+$ )                      |
|            | $^{16}\text{F}(n,\alpha)^{16}\text{N}$   | 1.6                    | 57  | 7.12 s             | 6.130; 7.112                             |
| Magnesium  | $^{24}\text{Mg}(n,p)^{24}\text{Na}$      | 4.9                    | 200   | 15.0 h             | 1.368; 2.754                             |
| Aluminium  | $^{27}\text{Al}(n,p)^{27}\text{Mg}$      | 1.9                    | 80  | 9.46 m             | 0.844; 1.015                             |
|            | $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$ | 3.3                    | 120   | 15.0 h             | 1.368; 2.754                             |
| Silicon    | $^{28}\text{Si}(n,p)^{28}\text{Al}$      | 4.0                    | 250   | 2.24 m             | 1.779                                    |
| Phosphorus | $^{31}\text{P}(n,\alpha)^{28}\text{Al}$  | 2.0                    | 140   | 2.24 m             | 1.779                                    |
|            | $^{31}\text{P}(n,2n)^{30}\text{P}$       | 12.8                   | 10  | 2.5 m              | 0.511 ( $\beta^+$ ); 2.24                |
| Iron       | $^{56}\text{Fe}(n,p)^{56}\text{Mn}$      | 3.0                    | 115   | 155 m              | 0.847; 1.811; 2.113                      |
| Copper     | $^{63}\text{Cu}(n,2n)^{62}\text{Cu}$     | 10.7                   | 500   | 9.9 m              | 0.511 ( $\beta^+$ )                      |
| Zinc       | $^{64}\text{Zn}(n,2n)^{63}\text{Zn}$     | 12.0                   | 100   | 28.1 m             | 0.511 ( $\beta^+$ )                      |

#### Analysis of common rocks.

Fourteen-MeV neutron activation analysis is probably the most suitable analytical technique available for oxygen determination. The measurement of  $^{16}\text{N}$  can easily be performed in the presence of many other radionuclides because of its hard gamma-rays. Interfering reactions occur practically only in the presence of fluorine,  $^{19}\text{F}(n,\alpha)^{16}\text{N}$ , boron,  $^{11}\text{B}(n,p)^{11}\text{Be}$  ( $T_{1/2} = 13.6$  s, high energy beta and gamma radiation), and perhaps uranium (fission products having a wide range of beta and gamma energies).

For silicon determinations the method is also extremely useful, and excellent results, comparable with gravimetry, can be obtained within a few minutes, by counting the 1.779 MeV gamma-rays of 2.24 min  $^{28}\text{Al}$ . Nuclear interference arises from the presence of phosphorus due to the  $^{31}\text{P}(n,\alpha)^{28}\text{Al}$  reaction; this will only be important in phosphate rocks, and the like. Interference from  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$  is usually negligible when irradiating with unmoderated 14 MeV neutrons. A common gamma-spectrometric problem is the presence of  $^{56}\text{Mn}$  activity produced by the  $^{56}\text{Fe}(n,p)^{56}\text{Mn}$  reaction, because its 1.811 MeV gamma-ray cannot be resolved from that at 1.779 MeV when using a NaI(Tl) detector. A correction is, however, possible by simultaneously measuring another  $^{56}\text{Mn}$  gamma-ray, e.g. at 0.847 or 2.113 MeV; the 2.56 h  $^{56}\text{Mn}$  contribution can also be established by a second counting, after decay of  $^{28}\text{Al}$  (after ca. 20 minutes). A correction can also be calculated if the iron content is known from an independent analysis. When a Ge(Li) is being used, the two peaks at 1.779 and 1.811 MeV are resolved.

Aluminium and iron can also be determined, via  $^{27}\text{Mg}$  and  $^{56}\text{Mn}$ , respectively. The 0.844 and 0.847 MeV photopeaks are, of course, not resolved and present a gamma spectrometric interference; the radionuclides have, however, very different half-lives, allowing the problem to be solved. Alternatively, the  $^{27}\text{Mg}$  activity can be measured using the (less intense) 1.015 MeV photopeak. For magnesium the method is less suited (usually low Mg content and interference from aluminium!) except for ultrabasic rocks.

Fourteen-MeV neutron activation analysis of rocks and meteorites has been reviewed by Morgan and Ehmann (73) and is also discussed by Gijbels (16). In most of the published papers the concern has been mainly analytical. The techniques are now at a point where the precision and accuracy are satisfactory, especially for oxygen and silicon in rocks, and these methods should be thoughtfully applied to actual problems. The direct determination of oxygen may indeed be useful in studying various kinds of metamorphism, for instance, or simply as a check of the classical rock analysis. The strange situation exists where there are probably as many good oxygen analyses available for lunar rocks and meteorites as for terrestrial rocks.

#### Analysis of ores and minerals.

The basic ideas underlying the 14 MeV neutron activation analysis of ores and minerals can be summarized as follows :

##### (a) Aluminium, silicon and iron.

The determination of these elements in various ores and minerals, such as bauxites, nephelins, and iron ores poses basically the same problem as for common rocks. Again the reactions  $^{27}\text{Al}(n,p)^{27}\text{Mg}$ ,  $^{28}\text{Si}(n,p)^{28}\text{Al}$  and  $^{56}\text{Fe}(n,p)^{56}\text{Mn}$  are usually employed. The gamma spectrometric interferences  $^{28}\text{Al}-^{56}\text{Mn}$  and  $^{27}\text{Mg}-^{56}\text{Mn}$  can be solved as discussed above. Ivanov *et al.* (66) have analyzed bauxites and nephelins and concluded that activation with a sufficiently intense isotopic neutron source is recommended because of its simplicity, if only Al and Si are to be determined. If the iron content was also wanted, these authors used a neutron generator.

##### (b) Phosphorus.

Toon (74) has determined phosphorus in phosphate rocks (4-13 %P) via the reaction  $^{31}\text{P}(n,\alpha)^{28}\text{Al}$ . The interference from  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$  appeared to be negligible, whereas the nuclear interference from silicon,  $^{28}\text{Si}(n,p)^{28}\text{Al}$  was avoided by treating the sample first with HF ( $\text{SiF}_4$ ) and  $\text{HClO}_4$  ( $\text{HF}^+$ ).

Several papers appeared in the Russian literature dealing with the determination of phosphorus in apatite, phosphorite and phosphoric raw material, all utilizing mobile neutron activation equipment (Ref. 9-12). There is a tendency of using large sample sizes : up to 50 kg. The reaction  $^{31}\text{P}(n,2n)^{30}\text{P}$  was used (Ref. 10) and the  $\beta^+$  annihilation radiation counted with a  $\gamma\gamma$  coincidence array. Correction for pair production by hard gamma emitters (in particular from  $^{28}\text{Al}$  : 1.779 MeV) was required. Since apatite contains fluorine, interference from the reaction  $^{19}\text{F}(n,2n)^{18}\text{F}$  can be expected; the positron emitter  $^{18}\text{F}$  has, however, a much longer half-life (109.7 min against 2.5 min for  $^{30}\text{P}$ ) so that a correction can easily be applied. Interference from other  $\beta^+$  emitters is possible, e.g.  $^{54}\text{Fe}(n,2n)^{53}\text{Fe}$  ( $T_{1/2} = 8.5$  min). Kasatchin *et al.* (10) reported an accuracy of  $\pm 3$  to 5 % relative for  $\text{P}_2\text{O}_5$  contents of 15 % and a sensitivity of ca. 0.5 %  $\text{P}_2\text{O}_5$  when using a sealed neutron tube with a yield of 1 to  $3 \times 10^8 \text{ n.s}^{-1}$ .

##### (c) Fluorine.

The use of a 14 MeV neutron generator permits the production of both  $^{19}\text{O}$  and  $^{18}\text{F}$  for the determination of fluorine, and has been applied to fluorspar ores, apatite and mica. Knight *et al.* (75), Bartošek *et al.* (76) and Weber and Guillaume (77) used 29.1 s  $^{19}\text{O}$ , Jeffery and Bakes (78), Nargolwalla *et al.* (79), Strain *et al.* (80) and Botvina *et al.* (81) used 109.7 m  $^{18}\text{F}$ . Dibbs and Mc Mahon (82) measured both isotopes.

A disadvantage of  $^{19}\text{O}$  is its low-energy gamma radiation (mainly 0.197 MeV) which gives rise to gamma absorption in large samples. The high background from Compton scattering worsens the counting statistics, and the presence of a backscatter peak can give rise to positive errors. The use of 109.7 m  $^{18}\text{F}$  invariably requires longer analysis times, and since this radionuclide is a  $\beta^+$  emitter it lacks specificity.

The reaction  $^{19}\text{F}(n,\alpha)^{16}\text{N}$  cannot readily be used with a 14 MeV neutron generator, since the high energy neutrons also produce  $^{16}\text{N}$  from the reaction  $^{16}\text{O}(n,p)^{16}\text{N}$ ; this is not the case with unmoderated isotopic source neutrons (Ref. 83).

##### (d) Copper, zinc.

In all cases 9.9 min  $^{62}\text{Cu}$  is counted, formed by the sensitive  $^{63}\text{Cu}(n,2n)^{62}\text{Cu}$  reaction;  $^{62}\text{Cu}$  is a positron emitter, allowing one to count the annihilation gamma rays with a coincidence array (Ref. 84, 85, 10). This results in a more favorable signal-to-background ratio and is especially useful for low copper contents (< 1 %). Soviet workers have employed a portable neutron generator (sealed neutron tube, 1 to  $3 \times 10^8 \text{ n.s}^{-1}$ ) for the determination of copper in ores under field conditions (Ref. 9-11), e.g. at the Kounradskij deposits in Kazakhstan, and reported a sensitivity of 0.01 to 0.05 % Cu.

Gorski *et al.* (84) have determined copper in lower Silesian deposits (0.01 to 12 % Cu) with a coefficient of variation of ca. 2 %. Interfering radionuclides formed from K, Zn, Ag, Mo and Sb, gave an apparent copper content of ca. 0.05 %.

Pradzynski (86) examined fast neutron and photonuclear activation with a betatron for the analysis of copper in ores, tailings and concentrates, via the reactions  $^{63}\text{Cu}(n,2n)^{62}\text{Cu}$  and  $^{63}\text{Cu}(\gamma,n)^{62}\text{Cu}$ , respectively. Satisfactory results were obtained with both methods, although photon activation was preferred because of the somewhat better precision and because of the possibility of changing the photon energy, allowing to exclude some interfering reactions.

When zinc is present, interference from the reaction  $^{64}\text{Zn}(n,2n)^{63}\text{Zn}$  occurs with 14 MeV neutrons, since  $^{63}\text{Zn}$  is also a positron emitter. Correction is, however, possible because of its longer half-life (28.1 m). In fact, both elements can be determined in this way. Navalikhin *et al.* (87) determined down to 0.08 % copper and zinc in polymetallic ores by 0.511 - 0.511 MeV coincidence counting after two cooling periods : ca. 8 min and ca. 35 min.

#### APPLICATIONS USING REACTOR NEUTRONS.

Reactor neutron activation via  $(n,\gamma)$  reactions is particularly suitable for trace analysis, or when dealing with small samples, such as lunar specimens and meteorites. Trace element analysis may be of interest for studying origin, genesis and paragenesis of minerals, and other geochemical problems. Data for trace elements such as uranium, gold, rhenium, selenium, tantalum, lanthanides, etc. may, however, also be of technological interest. There exists an impressive literature on reactor neutron activation analysis of geological samples, some 400 papers according to Lutz *et al.* (6).

#### Radiochemical neutron activation analysis.

Earlier work was mainly by radiochemical separation of the elements of interest. Procedures for many elements can be found in the literature, and reference is made to bibliographic surveys such as those from De Soete *et al.* (88) and Lutz *et al.* (6), and systematic treatments such as those from Bowen and Gibbons (89), the ORNL "Master Manual", or the series "Radiochemistry of the Elements". Even today, many elements can only be determined after radiochemical separation, if they are present in too low concentrations, or if their spectra are masked by dominant activities from other species. Radiochemical neutron activation analysis (RNAA) can go down very far without preconcentrations. It should be emphasized that blank problems are virtually non-existent, contrary to other analytical techniques.

R.N.A.A. can lead to quite accurate results if the analyst is aware of the underlying principles and limitations of the technique. To give an idea of the sensitivity which can be obtained, we cite the determination of iridium in U.S.G.S. standard silicate rocks, at concentrations down to 0.005 parts per billion (Ref. 90,91).

#### Instrumental neutron activation analysis (INAA).

There is a definite tendency in recent years to use purely instrumental techniques, especially gamma-ray spectrometry of the irradiated sample, without chemical separation, or with simple group separations only.

##### (a) Scintillation gamma-ray spectrometry.

Analytical applications of direct scintillation gamma-ray spectrometry are very limited owing to the inferior resolution of NaI(Tl) detectors. In some cases, however, the spectra are sufficiently simple to use this technique, e.g. for determining Sc and Cr in pyrope, Ta in rutile and columbite, Na, Sc and Co in rocks, Hf in zircon, Ag and Sb in galena, V in magnetite, Sc and Ta in greisen, etc.

##### (b) High-resolution gamma-ray spectrometry.

Since the advent of high-resolution Ge(Li) detectors, more complex spectra can be tackled. Lamb *et al.* (92) determined Mn, In, Ga, Zn, As, Sb, Cu, Na, Fe and Au in a sulfide ore. Cobb (93) determined the abundance of Mn, Sc, Th and seven lanthanides (La, Ce, Sm, Eu, Dy, Yb, and Lu) in granites, basalts, limestone and one garnet sample.

For full details on the activation procedures, the detection systems, treatment of the data, gamma-ray energies of interest, and interferences in the instrumental neutron activation analysis of silicate rocks, reference is made to the comprehensive paper of Gordon *et al.* (94). Abundances were determined in six U.S.G.S. standard rocks, a subalkaline basalt and a rhyolite for 23 elements : Na, K, Rb, Cs, Ba, La, Ce, Sm, Eu, Tb, Tm, Yb, Lu, Th, Zr, Hf, Ta, Mn, Co, Fe, Sc, Cr and Sb. Some relevant data are summarized by Gijbels (95).

The method can also be extended to short-lived radionuclides. A few minutes after irradiation, the following activities can be observed in silicates :  $^{28}\text{Al}$ ,  $^{56}\text{Mn}$ ,  $^{27}\text{Mg}$ ,  $^{24}\text{Na}$ ,  $^{165}\text{Dy}$  and  $^{52}\text{V}$ , and sometimes  $^{139}\text{Ba}$ ,  $^{60}\text{Co}$  and  $^{51}\text{Ti}$ . The  $^{27}\text{Mg}$  844 KeV photopeak contains such a large contribution from the 2.58 hr  $^{56}\text{Mn}$  847 KeV peak that it is necessary to use the 1014 KeV peak instead. In practice, however, Mg determinations are restricted to ultramafic rocks and stony meteorites, which contain more than 10 % of Mg (Ref. 96). Gamma-ray spectrometry of short-lived species poses several problems, such as a decreasing fractional dead-time during the measurement, and also changes in the average dead-time per pulse. In addition, pulse pile-up problems may arise. These topics are discussed by Hertogen and Adams (97).

Similar methods have been developed and/or applied to terrestrial, meteoritic and lunar samples by others, as appears from a recent review (Ref. 95).

The precision and accuracy of INAA can be greatly enhanced by using a planar Ge(Li) or Ge detector, which exhibits an improved resolution as compared to "conventional" coaxial detectors. These so-called "low energy photon detectors" (LEPD) are especially useful for measuring low-energy photons, i.e. gamma and X-rays: this is of special interest for determining the rare earth elements, U and Th, as shown by Hertogen and Gijbels (98). Mantel and Amiel (99) applied X-ray spectrometry with a Si(Li) detector for the determination of the lanthanides in neutron-activated samples of xenotime and monazite. By combining short- and long-lived radionuclides, and counting with both a coaxial and a planar Ge(Li) detector, the following elements can be determined in basaltic rocks: Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Rb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb, Lu, Hf, Ta, Th and U. In more acid rocks, an additional number of elements can be determined, such as Zn, Sr and Zr, but in ultrabasic rocks the situation is less favorable. In addition to the above elements, one can also determine silicon via the reaction  $^{29}\text{Si}(n,p)^{29}\text{Al}$  if the neutron flux is not too well thermalized. Phosphorus can be determined in silicate rocks by  $\beta$ -counting, using a 210 mg/cm<sup>2</sup> Al absorber (100, 101).

INAA is obviously also applicable to ores and concentrates. De Lange *et al.* (102) determined Au and U in Witwatersrand ores, Turkstra *et al.* (103) determined Pd, Ir, Pt and Au in ores, matte and lead assay beads, whereas Schroeder *et al.* (104) determined Ag in minerals and ores. Steinnes and Mukherjee (105) analyzed samples of pyritic lead-zinc ore for Sc, Cr, Co, Zn, As, Se, Ag, Sb, Ir, Au and Th using thermal neutron activation; activation with epithermal neutrons (see further) improved conditions for the determination of As, Sb, Se, Ag, Au and Th. Monomineralic sulphide fractions (pyrite, pyrrhotite, arsenopyrite, and galena) from kimberlites and other rocks were analyzed for Fe, Co, Sb, Se, Ag, Zn and Cr by Leipunskaia and Savosin (106). Generally the analytical possibilities of INAA with a Ge(Li) detector are determined by the composition of the sample, i.e. by the major elements (e.g. Fe), but also by the minor or trace elements, such as Mn, Na, La, Sc, Co, Cs, Eu, Ta, ... which may give rise to dominant peaks and corresponding Compton continuums in the gamma-ray spectrum of the activated sample. A systematic survey for a number of ores and minerals was conducted by Vobecký *et al.* (107). They found that a number of elements (not including those giving rise to short-lived radioisotopes) can easily be determined by INAA of minerals, such as, Na, K, Sr, Mn, Ba, La, Sm, Eu, Dy and Au in diamond, Ag and Sb in galena, Zn, Ag and Sb in sphalerite, Fe, Co, Zn, Se and Ag in chalcopyrite, Co, Zn and Se in pyrite, Sc, Cr, Se, Cs, Hf, Ta, W and Re in molybdenite, La, Ce, Nd, Sm, Eu, Tb, Yb and Lu in fluorite, Sc, Co, Cs, Ce, Eu, Tb, Yb and Hf in limestone, Sc, Fe, Ce, Eu and Yb in magnesite, Sc, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Th and U in monazite, Cr, Sr, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, and Th in apatite, Sc, Cr, Fe and Co in garnet (pyrope), Sc, Fe, Ce, Tb, Yb, Ta and Th in tourmaline, Sc, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Th in orthite, Sc, Fe, Zn, Rb, Sb, Ca, Ta and Th in cinvaldite, Sc, Cr, Fe, Co in serpentine, Sc, Ta and Th in wolframite and cassiterite, Sc, Cr, Fe, Co, Cs, Ce, Eu, Hf, Ta and Th in coal and brown coal. A number of elements could also be instrumentally determined in separated rock-forming minerals: Na, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Tm, Yb, Lu, Hf, Th in feldspars (108, 109), Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zr, (Ba), La, (Ce), Sm, Eu, (Tb), Dy, Ho, (Tm), Yb, Lu, Hf, (Ta), W, (Au), in (clino-)pyroxene (109), etc.

#### (c) Coincidence counting.

Instead of Ge(Li) gamma-ray spectrometry, other counting techniques can, of course, be used, especially if the analysis is aimed at a particular element. Iridium can, for instance, be determined in various materials on a purely instrumental basis by using triple gamma coincidence counting of  $^{192}\text{Ir}$ . For slags from copper-lead production, the sensitivity is 20 ppb ( $2 \times 10^{-6} \%$ ), for silicate rocks ca. 1 ppb, and for plagioclase feldspars even less (Ref. 90, 91, 110). Applications of coincidence counting to geological samples have been reviewed by Ehrmann *et al.* (111), with special emphasis on meteoritic studies.

#### Group separations.

The applicability of NAA can be substantially improved by introducing some rather simple group separations, followed by Ge(Li) gamma-ray spectrometry. Several approaches for geological samples appear in the literature, such as the group separation system of Morrison *et al.* (112), where the sample is dissolved in  $\text{H}_2\text{SO}_4$  and HF, the volatiles are trapped in concentrated NaOH and the residue dissolved in 8N HCl. Na and Ta are absorbed on hydrated antimony pentoxide (HAP) and the effluent of the HAP column is passed through a Dowex 1 x 8 column. The effluent and wash (8N HCl) are extracted with TBP: Sc, Zr, Hf and Pa appear in the organic phase, whereas the aqueous phase contains the rare earths, Cr, Ca, Ba, Sr, K, Rb and Cs. The anion exchange column is eluted with 0.5 N HCl. The eluate contains Fe, Co, Cu, Ni, Ga, W, Mo and Np. Zn, Cd, Sb, Re, In, Hg and Au are counted on the resin. This method was applied to lunar rocks, soils and fines.



Another group separation system is described by Iaul *et al.* (134, 135), and allows the determination of Au, Ga, Ge, Mo, Sb, Te, Tl, As, Hg, Re, Sb, Se, Os, Bi, Co, Sc, Zn and Cs. Allen *et al.* (115) have described a procedure for NAA of 39 elements in geological samples. The elements are separated into 12 chemical groups (4 of which are single elements), the order of separation being dictated by the short half-lives of some of the radionuclides of interest: group 1 (Ag, Cl, Br), group 3 (Mn), group 2 (Au, Ba, Pt, Ta), group 4 (In), group 5 (Cu, As, Se, Sb, Pd), group 6 (Fe), group 7 (lanthanides), group 8 (Cr, Hf, Sc), group 9 (Ni), group 10 (Co, Ga, Zn), group 11 (Ca, Sr) and group 12 (K, Rb, Cs). The twelfth group is separated and ready for radioassay within seven hours after the end of irradiation, when work is done by 3 persons. Chemical yields are typically between 50 and 90 % and are determined by reactivation, except for Fe and Ni.

Several authors have described the determination of the lanthanides, after separation as a group. The sample is first dissolved by an alkaline fusion, and the rare earths separated by hydroxide and oxalate or fluoride precipitations. Chemical yields are determined by reactivation (Ref. 116-120). Brunfelt and Steinnes (121) irradiate the samples with epithermal neutrons instead of reactor neutrons.

#### Selective activation by means of resonance neutrons.

A quantitative treatment of the advantage of applying epithermal neutrons in activation analysis of geological materials has been given by Steinnes (122). The resonance effect (i.e. resonance peak in the  $\sigma(E)$  curve) is utilized to some extent after removing thermal neutrons (below about 0.4 eV) by means of a thin cadmium shield surrounding the sample. It is obvious that the determination of an element is easier to perform, if the element of interest has a nuclide with a prominent resonance activation peak, whereas the interfering nuclides have not. One can define an advantage factor (Ref. 123):

$$F = (\sigma_0/I)_i / (\sigma_0/I)_d$$

where d refers to the nuclide to be determined and i to the interfering nuclides;  $\sigma_0$  is the thermal neutron activation cross section and I the resonance activation integral. Relevant cross section data and F values are tabulated by Steinnes (122). A recent compilation of  $\sigma_0/I$  values is given by Van der Linden *et al.* (124-125).

The applications of epithermal neutron activation analysis (ENAA) to geological material may be divided into 3 or 4 groups:

#### (a) Improvement of precision and sensitivity in INAA.

Advantages are obvious for determining Rb, Sr, Sb, Cs, Ba, Tb, Hf, Ta, Th and U in silicate rocks; in some cases it is even possible to determine Au at the ppb level. The dominant interfering  $^{46}\text{Sc}$ ,  $^{59}\text{Fe}$ ,  $^{60}\text{Co}$  and  $^{51}\text{Cr}$  activities in basic rocks are much reduced with ENAA, allowing a number of trace elements to be determined with a better precision and sensitivity, particularly when combined with a simple group separation (Ref. 126).

#### (b) Reduction of high activity levels.

In geological samples,  $^{56}\text{Mn}$  and  $^{24}\text{Na}$  most often represent problems of this kind. As both these nuclides have low relative resonance activation rates, the high-activity problem can be considerably reduced by ENAA. Another example is  $^{32}\text{P}$  formed in phosphate rocks.

#### (c) Reduction of fission interference.

Steinnes (122) has shown that the interfering reaction  $^{235}\text{U}(n,f)^{99}\text{Mo}$  can be minimized by ENAA, thus improving the accuracy of the Mo determination in rocks. Some sources of error, such as resonance absorption of neutrons within the sample, are discussed by Steinnes (122). The epithermal neutron activation analysis of sulphide ores and some ore beneficiation products by Steinnes and Mukherjee (105) has already been discussed in the section "High-resolution gamma-ray spectrometry". Randa (127) discusses the analytical possibilities of this technique in routine INAA of mineral materials.

### MISCELLANEOUS TECHNIQUES IN NEUTRON ACTIVATION

#### Neutron capture gamma-ray analysis.

In theory this technique offers a greater sensitivity than activation analysis, but in practice this sensitivity cannot be achieved due to the difficulties of operating gamma-ray detectors in regions of high neutron flux. However, capture gamma-ray analysis can complement INAA for the determination of a few elements which cannot be determined by the latter method because their isotope products are too short-lived, stable, or pure beta emitters. With the neutron fluxes available in reactor beam tubes, the technique is suitable for determining boron and selected rare earths at trace levels, and of hydrogen in the percentage range.

Whitley *et al.* (128) utilized this technique for determining boron in peralkaline lavas from the Main Ethiopian Rift. On irradiation with thermal neutrons,  $^{10}\text{B}$  is converted to  $^7\text{Li}$  by an  $(n,\alpha)$  reaction, for which the isotopic cross section is 4000 barns. The  $^7\text{Li}$  is in an excited state and decays with the emission of a 477 KeV gamma-ray. Potential sources of interference are sodium (472 KeV), chlorine (518 KeV) and background radiation (511 KeV). With a Ge(Li) detector the peak of interest is well separated from the 511 KeV peak but its lower sensitivity necessitates larger samples and longer counting times. The sodium interference requires a correction, or spectrum stripping.

The analytical use of neutron capture gamma-rays with special emphasis on boron and the rare earth elements, has been discussed by Henckelmann and Born (129,130). Results are given for the La, Nd, Sm, Eu, Gd, Dy and Th content of monazite samples (0.06 to 16 %). Using a counting time of 1000 minutes, the authors could determine boron and all rare earths except Ce, in the Canadian standard syenite rock S1. The results are (in ppm): B(15), La(230), Pr(170), Nd(330), Sm(235), Eu(14), Gd(70), Tb(35), Dy(115), Ho(120), Er(60), Tm(10), Yb(75) and Lu(6). There is a satisfactory agreement with optical spectrographical data. Vobecký *et al.* (131) describe the determination of Gd and Sm in apatite at concentration levels of about 150 ppm.

This "prompt" gamma counting technique can also be utilized with moderated isotopic source neutrons, and some examples are indicated in Table 1: determination of iron in iron ores, concentrates and filings with a  $^{210}\text{Po}/\text{Be}$  source (Ref. 52,53) or a  $^{239}\text{Pu}/\text{Be}$  source (Ref. 38), of Cu(0.5 %) in porphyry copper deposits with an  $^{241}\text{Am}-\text{Be}$  source (Ref. 47), of Ni (1.3 %) in lateritic nickel ore with an  $^{241}\text{Am}-\text{Be}$  source (Ref. 47) and of Ni in low grade nickel ore (> 0.1 %) with a  $^{252}\text{Cf}$  spontaneous fission source (Ref. 19). A  $^{252}\text{Cf}$  source was also used by Duffey *et al.* (132) for copper mining and mill analysis, and by Damkjaer (133) for the analysis of cement raw mix.

Dibbs *et al.* (134) used a 1.1 Ci Ra/Be source for the determination of a number of elements in slurries (Fe, Cu, Zn, S). This technique should be well-suited to the mineral processing industry. Because of the instantaneous emission of gamma radiation following neutron capture, the method is independent of flow rate.

#### Delayed neutron counting.

Delayed neutron counting is a specific method for determining uranium and thorium. If a nuclide having  $Z > 90$  (e.g. isotopes of thorium, uranium, plutonium and other transuranic elements) undergoes fission, some of the fission-product nuclides decay by beta emission, with half-lives in the range 1 s to 60 s to highly excited states of daughter nuclei which, in their turn, decay by emission of a neutron. These neutrons are emitted almost instantaneously after the precursor nuclide has emitted a beta particle, and consequently they exhibit an apparent half-life in their emission which coincides practically with that of the precursor nuclide. These neutrons are known as delayed neutrons, in contrast with those neutrons which are emitted promptly during the process of fission. In order to induce fission, the samples containing uranium and thorium are usually exposed to reactor neutrons.  $^{235}\text{U}$  gives fission with slow neutrons,  $^{232}\text{Th}$  and  $^{238}\text{U}$  with fast neutrons. If two determinations are made for each sample, one in a mixed (fast and slow) neutron flux, one with the slow neutrons screened out by a cadmium shield, both uranium and thorium may be determined.

The delayed neutron emission from the irradiated samples can be measured in a paraffin-moderated  $\text{BF}_3$  counter assembly of roughly 4  $\pi$ -geometry. Assuming an irradiation time of 60 s at a thermal flux of  $5 \times 10^{12} \text{ n.cm}^{-2}.\text{s}^{-1}$ , a delay time of 20 s and a counting time of 60 s, 1  $\mu\text{g}$  of natural uranium gives 200 to 400 counts in such a set-up, for a counter background of 5 to 25 cpm. If the sample weight is ca. 20g, uranium contents of 0.1 ppm can be determined with a standard deviation of  $\pm 5$  %. This shows that the method is both fast and sensitive. For thorium, the technique is less sensitive by more than an order of magnitude. An extensive study of delayed neutron counting was made by Amiel (135), including geological samples, by Dyer *et al.* (136) and by Gale (137).

The applicability of a 14-MeV neutron generator to the non-destructive assay of uranium in ores, concentrates and intermediate processing products by delayed neutron counting was demonstrated by Mayer and Vobecký (138). After activation for 60 seconds at a neutron flux of  $4.10^7 \text{ n.cm}^{-2}.\text{s}^{-1}$ , and a waiting time of 20 seconds, uranium was detected with a sensitivity of more than 2000 counts/g.min, for thorium these values are 1200 counts/g.min (background 1.1 cpm). Under the employed conditions, samples containing 10 to 400 mg of uranium may be analyzed.

A method for the continuous on-stream determination of trace concentrations of uranium and thorium in flowing streams was developed by Al-Shahristani and Jervis (139); a 14 MeV neutron generator was used for irradiation, and the delayed neutron technique utilized to count the induced neutron activity. At optimal conditions, uranium and thorium concentrations could be determined down to 20 and 100 ppm, respectively. Interference of the neutron emitting nuclide  $^{17}\text{mO}$  was reduced by optimizing the decay time.

#### Nuclear track counting.

Some elements, such as uranium, thorium (Ref. 140-144) and boron (Ref. 141) can be determined by nuclear track counting. The sample (a pelletized powder) is pressed against a dielectric detector in the form of a foil and irradiated in a nuclear reactor. The boron analysis is based upon the  $^{10}\text{B}(n,\alpha)^7\text{Li}$  reaction, where the recoiling alpha-particles penetrate into the foil (cellulose acetate butyrate "Triafol EN"); for uranium and thorium, polycarbonate foils ("Lexan", "Makrofol"), polyethylene terephthalate foils ("Lavsan") or mica detectors are commonly used to catch the recoiling fission fragments. The radiation damage produced by fission fragments or alpha particles can afterwards be observed by etching the foil with a suitable reagent. The nuclear tracks have a characteristic form and can be counted under a microscope. Manual optical microscopy is still most widely used as a method for data acquisition, as appears from a 1972 survey on track registration (Ref. 145). The counting can, however, also be performed with automatic scanning devices, for instance, or facilitated by projecting the picture onto a screen, or by counting the tracks on a photomicrograph, etc. It is obvious that standardization can be carried out by simultaneously irradiating a sample with a known U, Th or B content. The state of the art of this technique can be found in a recent monograph (Ref. 146).

A surprisingly simple and inexpensive technique for counting tracks in very thin foils (thickness less than the range of the fission fragments or alpha-particles) has been developed by Cross and Tommasino (147) and is known as "spark counting"; see also Johnson *et al.* (148) and Agard (149) for instance.

The determination of uranium by the fission track method is superior to standard neutron activation analysis in all cases where it is desirable to obtain information on the spatial distribution of the uranium content. In that case, the sample should of course not be powdered. The method allows the determination of uranium contents down to the  $10^{-3}$  ppb range over areas less than  $10^{-6}$  cm<sup>2</sup>, and is therefore suitable for determining very small quantities of uranium, e.g. in mineralogical samples. Flerov and Berzina (150) give a systematic discussion on the determination of the spatial distribution, and local and total concentrations of uranium, thorium, boron and lithium in minerals and rocks, based on the recording of either the spontaneous disintegration products of uranium or the products of (n,f) and (n, $\alpha$ ) reactions of uranium, thorium, boron and lithium. Results are given for uranium in zircon, titanite, apatite, obsidian, cassiterite, basalt, andesitic basalt, pyropic peridotite, pyropic-spinel pyroxenite, enderbite, serpentized harzburgite, apodunitic serpentine, phlogopite and muscovite; for thorium in zircon, pyrochlore, zirconolite and granitoids; for boron in shale, syenite, skarn, epidosite, quartzitic diorite, diorite, porphyry, gneiss, spessartite and amphibolite; and for lithium in mica.

The nuclear track technique is used in such diversified areas as geological studies, cosmic ray studies, dating studies, studies of meteorites and lunar specimens, studies of the solar system origin, solar flare studies, geochemistry of the heavy elements, search for super-heavy elements, to mention just a few in the context of this paper (Ref. 145).

Fission-track dating of impact glasses, obsidian, tektites, apatites, zircons, etc. may well complement other dating methods; it is based on observing the fossil tracks from spontaneous fission of  $^{238}\text{U}$  in the specimen itself, after etching with a suitable reagent (Ref. 151). If a similar sample is irradiated with thermal neutrons, after annealing of the fossil tracks by heating, "fresh" tracks from neutron induced fission of  $^{235}\text{U}$  can be observed after etching. The "fission-track age"  $t$  can be calculated from the equation :

$$t = \frac{P_s}{P_i} n \frac{\sigma_{FI}}{\lambda_{SF}}$$

where  $P_s$  and  $P_i$  : number of spontaneous and induced tracks, respectively, per unit area;  
 $\frac{I_s}{I_i}$  : ratio of the natural isotopic abundances of  $^{235}\text{U}$  to  $^{238}\text{U}$  ( $= 0.0072/0.9927$ );  
 $\sigma_{FI}$  : cross section for the reaction  $^{235}\text{U}(n,f)$  ( $= 577 \times 10^{-24}$  cm<sup>2</sup>);  
 $\lambda_{SF}$  : partial decay constant of  $^{238}\text{U}$  for spontaneous fission ( $= 8.42 \times 10^{-17}$  yr<sup>-1</sup>)  
 $n$  : neutron dose (n.cm<sup>-2</sup>);

This method of age determination assumes that the latent fossil tracks are conserved over the geological times. Evidence for a complex thermal history of the sample can be found by comparing the parameters of spontaneous and induced (fresh!) tracks (track length and/or pit diameter). If the sample has been reheated in geological times, both the mean track diameter and the track density  $P_s$  will be lowered, and  $t$  must be corrected (Ref. 152). The study of

the thermal history of geological samples is quite a unique aspect of the fission track method.

Note : Although for most induced nuclear track work reactor irradiations have been used, there are instances where isotopic neutron sources can be useful, e.g. for determining the  $^{235}\text{U}$  content in enriched uranium samples (Ref. 153).

#### Spectroscopy of gamma-radiation from the inelastic scattering of fast neutrons.

Ahmed et al. (154) describe a technique, where a sample (2 to 20 gram) is irradiated with a reactor fast neutron beam from which gamma rays and thermal neutrons are filtered out by 9 cm of lead, 1 cm of boron carbide and 0.5 cm of cadmium. Spectroscopy (with a GeLi detector) of gamma radiation from the  $(n,n'\gamma)$  reaction is used to determine the concentration of Si, Ca, Mg, Fe, Al, Na, Ti, O, and C in soils, for instance.

Christell and Ljunggren (38) have shown that iron can be determined in iron ores, etc., by observing the 0.84 MeV gamma rays produced by fast neutron inelastic scattering upon  $^{56}\text{Fe}$ . Counting was performed on a 1.78 liter sample during neutron irradiation with a 0.5 Ci  $^{239}\text{Pu}/\text{Be}$  source. A  $^{210}\text{Po}/\text{Be}$  source was unsuitable due to the 0.8 MeV gamma radiation from  $^{210}\text{Po}$ .

Fookes et al. (155) describe the determination of the concentration of iron in high grade iron ores and lead in lead concentrates using Compton scatter of 60 KeV gamma-rays from  $^{241}\text{Am}$  (100 m Ci). Iron in high grade iron ores (ca. 90 % by weight  $\text{Fe}_2\text{O}_3$ ) was determined with an absolute rms error of  $\pm 0.13$  % by weight iron for finely ground and dried samples and  $\pm 0.9$  % by weight iron for coarse drill chippings from blast holes. Lead in lead concentrates (ca. 75 % by weight Pb) was determined to  $\pm 0.56$  % by weight lead.

#### ANALYSIS USING HIGH ENERGY PARTICLE BOMBARDMENT.

Charged particles, such as protons, ranging in energy from 0.8 to 4.0 MeV can be used to induce resonant nuclear reactions, Coulomb excitation (gamma rays) and X-ray emission in both thick (pellets) and thin (solution nebulized onto "Formvar" film) targets. The nuclear reactions are either inelastic proton scattering with subsequent gamma-ray emission ( $(p,p'\gamma)$ ) or proton absorption followed by emission of an alpha-particle and/or decay to the ground state ( $(p,\alpha\gamma)$ ,  $(p,\gamma)$ ); at the resonance energies the reactions are selective in the sense that only one reaction is prevalent. For quantitative analysis, the comparator method must be used.

The excitation of a nucleus by the interaction of its Coulomb field with that of the bombarding nucleus is a purely electromagnetic process. The cross section for Coulomb excitation depends on several parameters including the energy, spin and parity of the excited nuclear state being populated relative to the ground state, the energy of the bombarding particle, and the strength of the Coulomb interaction. However, even under the most favorable circumstances, the cross sections for Coulomb excitation are low, resulting in a lack of sensitivity.

The main advantage of using heavy charged particles (protons) for X-ray excitation is that the background can be quite low while the cross section for X-ray production remains high. For quantitative analysis, the comparator technique can be used, or an internal standard.

For solid materials such as rocks, the best sensitivity is obtained by forming a pellet using 10 % graphite. These samples can withstand larger beam currents than thin films, although the thick target makes it necessary to correct for the loss in energy of the bombarding particle as it passes through the sample; the stopping powers do not vary appreciably between different types of silicate rocks, for instance, indicating that by using a standardized rock powder for comparison, almost any type of rock can be analyzed without additional correction for the small differences in stopping power. In order to show the potential of a combination of the three techniques, several USGS standard rocks were analyzed by Clark et al. (156), using a 5.5-MeV Van de Graaff accelerator, with beam currents up to 2  $\mu\text{A}$ . Granite G-2 was used as the standard and concentrations calculated by comparison. Results were obtained in basalt BCR-1 for Li, F, Na, Mg, Al, Si, P, S and Cl (proton resonance method), K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ag, Sb and Ba (proton induced X-ray excitation); Coulomb excitation yielded results for the elements Ti, V, Mn, Fe and Zn, only.

Charged particles can also be utilized for the production of neutrons, and activation analysis performed in the neutron flux so obtained. As an example we mention the analysis of less than  $10^{-9}\text{g}$  of the isotope  $^{204}\text{Pb}$  in lunar samples by an  $(n,2n)$  activation using high-energy ( $> 8.8$  MeV) neutrons produced by bombardment of a specially designed beryllium sample holder with deuterons in a cyclotron (Ref. 157). Radiochemical separations and X- $\gamma$  coincidence counting techniques were necessary to achieve the required sensitivity. Although the flux of neutrons of sufficient energy from the cyclotron procedure is somewhat lower than can be obtained in the best reactor irradiations, the high radioactivity due to other elements produced by the  $(n,\gamma)$  reactions in the reactor is eliminated. Radiochemical procedures for the analysis of Bi, Tl and Zn in the same samples are also described (Ref. 157).

## PHOTON ACTIVATION ANALYSIS.

The photon induced nuclear reactions are threshold reactions : the threshold energies of the most frequently utilized  $(\gamma, n)$  and  $(\gamma, p)$  reactions are in the 8-20 MeV range, and the cross sections are typically between 0.01 and 1 barn. In order to apply photon induced reactions in activation analysis, one needs photon fluxes of high energy and high intensity. These photon fluxes are obtained as Bremsstrahlung from electron accelerators, with electron energies of 20 to 50 MeV. Linear accelerators (average beam current from 5 to 200  $\mu\text{A}$ ), betatrons ( $< 1\mu\text{A}$ ) and microtrons (5-40  $\mu\text{A}$ ) are being used. Due to its complexity, a "linac" will only be utilized in cases where the accelerator also serves other purposes (nuclear physics research). The beam current of betatrons is often too low for sensitive analyses although good results were obtained for photon activation analysis of copper ores and concentrates (Ref. 158,159). The microtron (Ref. 160,161) might be a good compromise from the point of view of beam current and complexity.

The possibilities, limitations and quantitative aspects of photon activation analysis have been discussed in various review articles (Ref. 162-167). A compilation of photonuclear reaction products and associated gamma energies has been prepared by Toms (168), among others. A preferred application is the determination of the light elements C, N and O in the most diversified materials, also in rocks and ores with detection limits between 100 and 10  $\mu\text{g}$  (Ref. 7 and 169).

The applicability of instrumental photon analysis to silicate rocks has been demonstrated by Kato *et al.* (170-172). Rock samples and multielement standards were irradiated simultaneously in Bremsstrahlung of 30 MeV, and the induced radioactivities from  $(\gamma, n)$  and  $(\gamma, p)$  reactions were measured with a GeLi detector. Results were obtained for major, minor and trace elements : Na, Mg, Ca, Ti, Fe, Mn, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba and Ce in basic, intermediate and acid rocks; in the case of peridotite and dunite rocks, Mg, Ca, Ti, Fe, Cr, Mn, Co and Ni could be determined, with an average beam current of 70  $\mu\text{A}$  in a linear accelerator. Das *et al.* (173) determined Mg, Ca, Ti, Mn, Sr, Zr and Nb in acidic rocks, and Mg, Cr, Ni and Mn in ultramafic rocks. The incorporation of photon activation analysis of rocks in combined irradiation schemes will be discussed later.

The main trends in using Bremsstrahlung sources for the study of rocks and ores have been discussed by Savosin *et al.* (15). Sulin (174) utilizes a system allowing the activation of a sample with photons from a betatron or a microtron and photoneutrons obtained with a suitable convector, either separately or simultaneously. In this way he could determine a number of elements in porphyrite, using a NaI(Tl) detector for measuring the activation products of  $(\gamma, n)$ ,  $(\gamma, \gamma')$  and  $(n, \gamma)$  reactions : Cu, Zn, Ba, Mn, Al, and F (contents 0.01; 0.01; 0.1; 0.2; ca. 5 and 0.1 wt % respectively). A polymetallic mineral (sulfide bearing dolomitic limestone) was analyzed for Cu, Zn, Pb, Ba, F, Mn, Sr and Al (contents 0.012; 0.84; 2.2; 1.6; 0.09; 1.5; 0.5 and 0.82 wt % respectively). This procedure was also used for the determination of Na, Mg, Ca, Ti, Mn, Fe, Zr and Nb in alkaline minerals, by measuring the radioactivities induced by  $(\gamma, n)$ ,  $(\gamma, p)$  and  $(n, \gamma)$  reactions. W-Mo bearing minerals (garnet pyroxene) were analyzed for Mo, W, Cu and Mn (contents 0.065, 0.58, 0.01 and 3 wt % respectively) via the reactions  $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$ ,  $^{186}\text{W}(n, \gamma)^{187}\text{W}$ ,  $^{65}\text{Cu}(\gamma, n)^{64}\text{Cu}$  and  $^{55}\text{Mn}(\gamma, n)^{54}\text{Mn}$ . A polymetallic oxide was analyzed for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Pb}$ ,  $\text{Zn}$ ,  $\text{Cu}$ ,  $\text{Ba}$ ,  $\text{As}$ ,  $\text{Sb}$ ,  $\text{Cd}$  and  $\text{Au}$  using a Ge Li detector for measuring the induced radioactivities, at concentrations of 86.4; 4.3; 0.6; 0.28; 0.1; 0.17; 0.51; 0.02; 1.5; 0.08; 0.03; 0.05 and 0.00016 wt % respectively. In most cases large sample sizes were taken, about 100 grams. The sensitivity of the method was reported to be sufficient in order to resolve problems connected with the prospection and the geochemical study of the ores.

The rapid determination of gold in mineral raw materials at concentration levels of 1 p.p.m. can be carried out via the reaction  $^{197}\text{Au}(\gamma, \gamma')^{197\text{m}}\text{Au}$ , (Ref. 175) using 100-g samples (beam current 700  $\mu\text{A}$ , upper limit of Bremsstrahlung photon energy 8 MeV). For lower concentrations, activation with thermal neutrons from a nuclear reactor was proposed by these authors.

In some cases, isotopic gamma sources can be used to photoexcite a nucleus by  $(\gamma, \gamma')$  reaction. As an example we cite the determination of erbium via the  $^{167}\text{Er}(\gamma, \gamma')^{167\text{m}}\text{Er}$  reaction, using a 200 Ci source of  $^{24}\text{Na}$  (Ref. 176). This source was prepared by irradiating high-purity NaOH for 75 hrs in a nuclear reactor at more than  $4 \times 10^{13}$  thermal  $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ . The limit of detection for erbium was 1  $\mu\text{g}$  Er; using samples of 10 gram, the sensitivity proved to be satisfactory for the routine analysis of this element in rock samples; the half-life of  $^{167\text{m}}\text{Er}$  is 2.5 seconds.

## COMBINATION OF VARIOUS TECHNIQUES.

In connection with meteoritic and especially lunar specimen studies, a tendency has developed for combining various instrumental techniques (14 MeV neutron activation, photon activation, short and long thermal and/or epithermal neutron activation, followed by direct Ge(Li) counting or other instrumental measurements, such as delayed neutron counting), and/or radiochemical techniques.

The analytical scheme proposed by Brunfelt and Steinnes (177, 178) is based on seven different irradiations, involving five independent portions of the sample. Four of these runs are based on purely instrumental work, the remaining three irradiations are followed by radiochemical separations. Most radioactivity measurements are carried out by Ge(Li) gamma-ray spectrometry.

Schmitt *et al.* (179) used the following irradiation scheme: 14 MeV neutron activation (O, Si), thermal neutron activation, followed by Ge(Li) spectrometry (Al, Na, Mn, K, Cr, Fe, Co, Ba, Sc, Cu) and 23 MeV photon activation (Ca, Ti, Ni). The method has subsequently been extended (RNAA) and applied to lunar samples.

Goles *et al.* (180) made use of essentially the same scheme for lunar rocks but determined, in addition, La, Ce, Sm, Eu, Tb, Ho, Yb, Lu, Zr, Hf and Ta by INAA. Uranium was determined by delayed neutron counting. The latter technique was also employed by Randa *et al.* (181); these authors determined Ti, Fe, Sr, Y and Zr in lunar rocks by non-dispersive X-ray fluorescence.

Kharkar and Turekian (182) combined INAA (Na, Mn, Dy, Sm, Lu, La, Yb, Ce, Eu, Tb, Sc, Hf, Cr, Co, Fe, Ti, Ta) with fission track counting and RNAA, again for lunar rocks. Smales *et al.* (183) determined Na, Sc, Cr, Mn, Sm, Eu, Dy, Yb, Al, La, Tb, Ho, Lu and Hf by INAA, Co, Cu, Zn, Rb, Ag, Cs and Ba by RNAA and F, Sr, Fe, Ca and Ti by photon activation. Isotope dilution (K, Rb, Sr, Cs, Ba, Nd, Sm, Eu), emission spectrography (Ni, V, Cu, Zr, Y) and X-ray fluorescence (Si, Al, Fe, Mg, Ca, Ti) completed the analysis.

Information on cosmic-ray produced  $^{21}\text{Na}$ ,  $^{22}\text{Na}$ ,  $^{26}\text{Al}$ ,  $^{53}\text{Mn}$ ,  $^{59}\text{Ni}$ ,  $^{60}\text{Co}$ , (from Na, Mg, Al, Si, Cr, Fe, Co, Ni and Mn "targets") was obtained by 14 MeV, thermal and fast reactor neutron irradiation (184).

Wänke *et al.* (185) made use of the following scheme:

14 MeV neutron activation (O, Si); 14 MeV neutron activation analysis of Fe, Al and Mg with a large volume Ge(Li) detector; reactor neutron activation (6 hrs at  $7 \times 10^{11} \text{ n.cm}^{-2}.\text{s}^{-1}$ ) for the determination of Na, K, Sc, Ti, Cr, Mn, Fe, Co, La, Ce, Nd, Sm, Tb, Yb, Lu, Hf and Ta by Ge(Li) spectrometry, and a similar irradiation followed by radiochemical separations for determining Ni ( $^{58}\text{Co}$ ), Cu, Ga, Ge, Rb, Sr, Pd, In, Cs, Ba, Pr, Gd, Dy, Ho, Er, Ir, Au, W, Th ( $^{233}\text{Pa}$ ) and U ( $^{135}\text{Xe}$ ).

Filby *et al.* (186-187) determined Al, Mn, Na, V, Ti, and Ca by INAA via short-lived radioisotopes, and Sb, Co, Zn, Sc, Cr, Eu, Th, U, Ba, Ta and Fe via long-lived species. The high  $^{24}\text{Na}$  activity, which in most irradiated silicate rocks and meteorites masks several (n, $\gamma$ ) activation products of interest, was eliminated by adsorption on hydrated antimony pentoxide; this allowed  $^{42}\text{K}$ ,  $^{72}\text{Ca}$ ,  $^{69}\text{mZn}$ ,  $^{140}\text{La}$ ,  $^{64}\text{Cu}$ ,  $^{87}\text{mSr}$ ,  $^{139}\text{Ba}$  and  $^{152}\text{mEu}$  to be measured shortly after a 2-hr activation at a thermal flux of  $8 \times 10^{12} \text{ n.cm}^{-2}.\text{s}^{-1}$ .

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