Photon Activation Analysis—A Review

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Prior to the availability of high-energy electron accelerators, photon activation analysis was limited to the determination of deuterium and beryllium with isotopic gamma-ray sources. During the past 15 years, however, the development of high-current cyclic and linear electron accelerators has made possible many analyses not readily acomplished by other methods. These include the determination of carbon, nitrogen, and oxygen at levels well below 1 μg. This review discusses the determination of beryllium and deuterium with isotope sources; accelerator-produced photons and nuclear considerations in photon activation analysis; the determination of carbon, nitrogen, and oxygen; the determination of heavier elements, with emphasis on biological, geochemical, oceanographic, and forensic matrices; and errors and corrections in photon activation analysis.

ACTIVATION ANALYSIS is now being widely used in a variety of analytical problems, particularly where high sensitivity is required. Because of the general availability of nuclear reactors, and the large cross sections of many nuclides for thermal-neutron capture, the greater part of this work is being performed with thermal neutrons. Sensitivities of 10^{-9} gram are not unusual.

There are, however, a number of elements, such as beryllium, carbon, nitrogen, oxygen, iron, and lead, which are not highly activated with thermal neutrons. In addition, severe difficulties due to sample self-shielding are encountered when a mixture to be analyzed contains substantial amounts of elements with large thermal-neutron capture cross sections. Photon activation analysis is useful in many of these situations.

Apparently, the earliest work in photonuclear activation analysis was done by Gorshov and coworkers (*1*), who determined beryllium by prompt neutron emission with a radium source. This work was accomplished in the late 1930's, which makes it contemporary with the experiments of Hevesy and Levi (*2*) and of Seaborg and Livingood (*3*), which are considered the genesis of activation analysis.

The initial efforts utilizing bremsstrahlung from an electron accelerator were made by Basile, Hure, Leveque, and Schuhl (*4*), in 1954. They determined oxygen in various organic materials with a betatron.

Much of the early systematic work in photonuclear activation analysis can be attributed to Engelmann (*5*) and Albert (*6*). They have discussed the practical aspects of bremsstrahlung production with an electron accelerator, the principles of photon activation analysis, and a number of useful determinations. Subsequently, journal articles and conference proceedings numbering almost 200 have described the determination of about 40 of the elements with photons varying in energy from 1.33 to 70 MeV.

This review will consider, in order, the determination of beryllium and deuterium with isotope sources; accelerator-produced photons and nuclear considerations in photon activation analysis; applications in the determination of carbon, nitrogen, and oxygen; applications in the determination of the heavier elements; production and analytical uses of metastable isomers; and errors and corrections in photon activation analysis.

DETERMINATION OF BERYLLIUM AND DEUTERIUM

The only stable nuclides with neutron binding energies less than the energies of gamma rays emitted in radioactive decay are ^{9}Be and deuterium. Their thresholds for (γ,n) reactions are 1.67 and 2.23 MeV, respectively. At photon energies less than about 4 MeV, the photodisintegration of these two nuclides and some isomeric excitations are the only nuclear reactions of consequence to activation analysis.

As noted in the introduction, the determination of beryllium was first accomplished by Gorshov and coworkers in the later 1930's. Contemporary methods were developed by Gaudin *et al.* (*7*, *8*) in the early 1950's. The isotope source used is almost invariably ^{124}Sb, of activity levels ranging from 0.2–2 curies. For most efficient utilization of the source activity, the sample is usually arranged in an annular configuration surrounding the source. The photoneutrons are moderated and detected with BF_3 tubes or scintillation counters, or are captured in a suitable target such as indium or silver and the induced radioactivity in the target is then measured. The whole assembly is shielded so that there is no gamma-ray or neutron hazard to personnel working with the equipment. With efficient neutron detectors and a source strength of about a curie, sensitivities of a few micrograms are possible. A serious potential source of error is absorption of neutrons by elements in the sample.

Useful descriptions of equipment and technique include those by Goldstein (*9*), Bisby (*10*), Knight *et al.* (*11*), Plaksin *et al.* (*12*), and Mountjoy and Lipp (*13*). Brownell (*14*) has described a portable instrument for field work. Mezhiborskaya (*1*) has written a treatise on the determination which contains much worthwhile material on safety considerations as well as on laboratory equipment.

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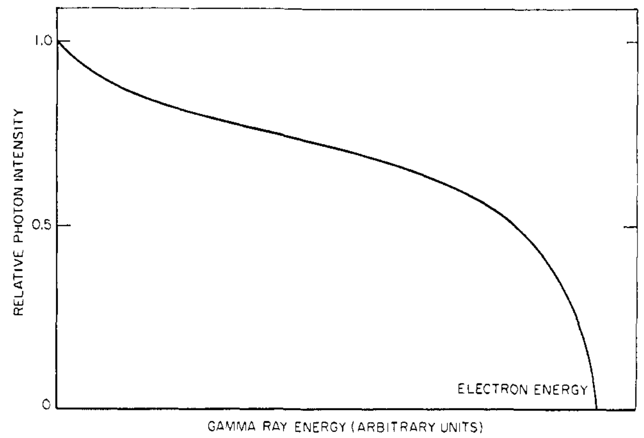

Figure 1. Typical photon intensity *vs.* energy relationship for bremsstrahlung from high-energy electrons

Rook (*15*) and Postma and McMurray (*16*) have developed the techniques for determining beryllium in beryllium metal, thus assessing its purity. Precisions and accuracies of about 2 parts in 1000 are apparently practical, making this the most precise and accurate activation analysis yet accomplished.

Levine and Surls (*17*) have described the determination of trace amounts of beryllium using a Van de Graaff accelerator. The activating photons were produced by converting 2.1 MeV electrons with a tungsten target. Photoneutrons were captured in a silver disk and the radioactive silver was counted with a G-M detector. The photon flux from this machine was about 1000 times that of a typical ^{124}Sb source. The accelerator has the additional advantages of relative freedom from radiation hazards and from frequent source replacements. However, reproducibility of photon flux position, intensity, and energy is not so good as with an isotope source.

The only radionuclides of sufficiently long half-life, whose gamma-ray energies exceed the 2.23 MeV required for deuteron photodisintegration, are ^{24}Na, with a half-life of 15 hours, and ThC″ (^{208}Tl) in equilibrium with ^{228}Th, with a half-life of 1.91 years. The radiothorium mixture is expensive, and most work has been done with ^{24}Na, a technique which was developed by Haigh (*18*, *19*). Source strengths of about a curie are frequently used. The sample-source-detector-shielding configuration is similar to that used in beryllium determinations. Samples are usually water. Detection limits of less than naturally-occurring deuterium in a few milliliters of water are practical. Khristianov and coworkers (*20, 21*) have used the method for investigating isotopic fractionation of hydrogen in natural waters. Overman *et al.* (*22*) have used the reaction to monitor heavy-water production and have used deuterium oxide in tracing soil moisture.

Guinn and Lukens (*23*) have demonstrated that bremsstrahlung from a 1-mA beam of 3 MeV electrons improves the sensitivity for deuterium determination to 1/500 of its concentration in natural water. Their neutron detector was the ^{55}Mn (n,γ)^{56}Mn reaction.

Mazyukevich and Shkoda-Ul'yanov (*24*) have discussed the possibility of determining hydrogen in metals, utilizing the deuteron photodisintegration. They estimate that with a 50-μA electron beam of 4.5 MeV in energy, metals containing as little as $10^{-4}\%$ hydrogen can be analyzed. It is necessary that the beryllium level in a sample be two or three orders of magnitude lower than that of hydrogen.

NUCLEAR CONSIDERATIONS

The induction of a photonuclear reaction, involving the removal of a nucleon, on stable nuclides other than ^{9}Be and ^{2}H, requires gamma radiation of energies in excess of those available by radioactive decay. These photons must be produced by stopping charged particles, accelerated to high energies, in matter. In photon activation analysis, this is accomplished with electrons, which after acceleration in a linear or cyclic accelerator, are allowed to strike a target, preferably of high atomic-number material. The continuous gamma-ray spectrum produced when the electrons are decelerated in the Coulomb field of nuclei of the target is called bremsstrahlung.

The cross-section equations for production of bremsstrahlung from relativistic electrons were derived by Bethe and Heitler (*25*, *26*), and have been discussed by Koch and Motz (*27*). Some of the considerations of bremsstrahlung production of interest to activation analysis will be summarized.

Figure 1 shows, qualitatively, the energy distribution of bremsstrahlung from a monoenergetic source of electrons. The distribution is continuous and extends up to the electron energy.

Electrons passing through matter lose energy by excitation and ionization, as well as radiative (bremsstrahlung), processes. In the case of a thick target, *i.e.*, a target in which scattering and energy-loss processes occur as the electron traverses the target, a situation which invariably prevails in a photon activation analysis, the efficiency, which is the fraction of the electron energy converted to bremsstrahlung, can be calculated from an expression given by Koch and Motz:

$$\epsilon = \frac{1 - \ln(1 + 1.2 \times 10^{-3}EZ)}{1.2 \times 10^{-3}EZ}$$

where ϵ is the fractional efficiency, Z is the atomic number, and E is the electron energy, in MeV. Results for various atomic numbers at different electron energies are given in Table I.

The angular distribution of bremsstrahlung can be estimated from an equation due to Schiff (*28*), from which the ratio of the radiation intensity per unit solid angle at an angle θ to the intensity at $\theta = 0$, the direction of travel of the electrons, is calculated. Figure 2 shows this distribution

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Table I. Approximate Thick-Target X-ray Efficiencies, in Per Cent

Atomic number of target	Electron energy (MeV) 10	20	30	40	50
10	5.5	10.4	14.6	18.3	21.7
20	10.4	18.3	24.7	29.9	34.3
30	14.6	24.7	32.2	38.1	42.8
40	18.3	29.9	38.1	44.2	49.0
50	21.7	34.3	42.8	49.0	53.8
60	24.7	38.1	46.7	52.9	57.6
70	27.4	41.3	50.0	56.2	60.7
80	29.9	44.2	52.9	58.9	63.4

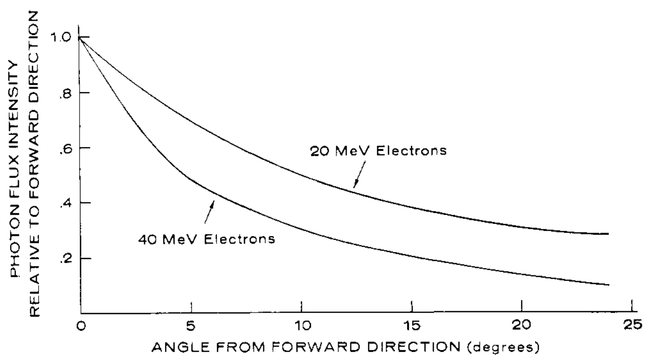

Figure 2. Relative angular distribution of bremsstrahlung from electrons of 20 and 40 MeV striking a tungsten target of 6-mm thickness

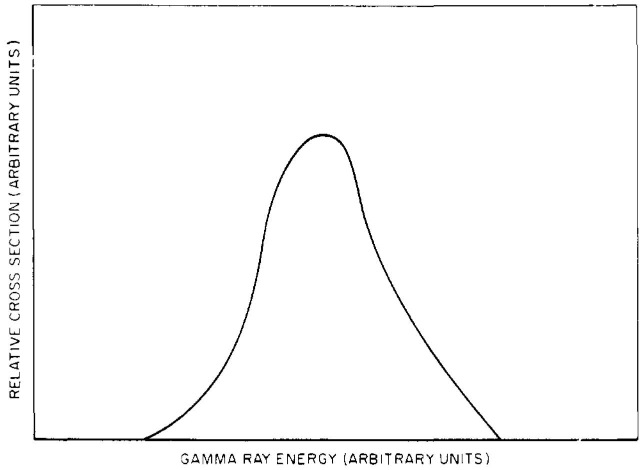

Figure 3. Typical cross-section *vs.* energy relationship for (γ,n) reactions

for electrons of 20 and 40 MeV striking a tungsten target of 6-mm thickness.

In most photon activation work, the target is constructed of a high atomic-number material which has satisfactory mechanical and heat-transfer characteristics. Gold, platinum, tungsten, and tantalum have been used successfully. Since a substantial fraction of the electron-beam energy is deposited in the target *via* excitation and ionization processes, it is usually necessary to water-cool the target. Although the thickness of target for the production of the optimum amount of bremsstrahlung may be less at some energies than the range of electrons in the target, it is generally desirable that the target or an electron absorber stop the electrons completely, so that they do not strike the sample. Several target facilities have been described (*29–31*).

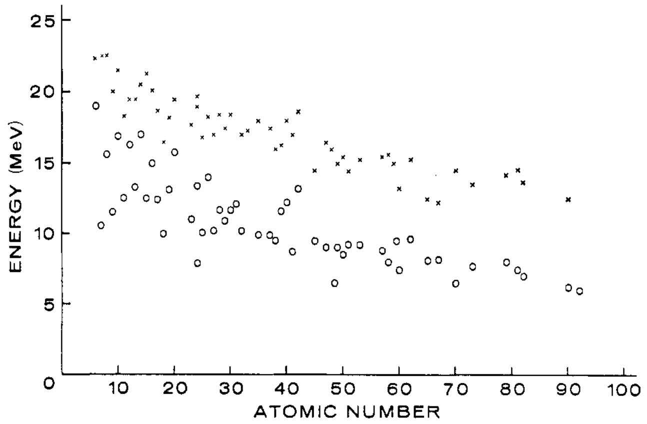

Figure 4. Threshold energy and energy of maximum cross section for (γ,n) reactions

○ **Threshold energy**
× **Maximum cross section energy**

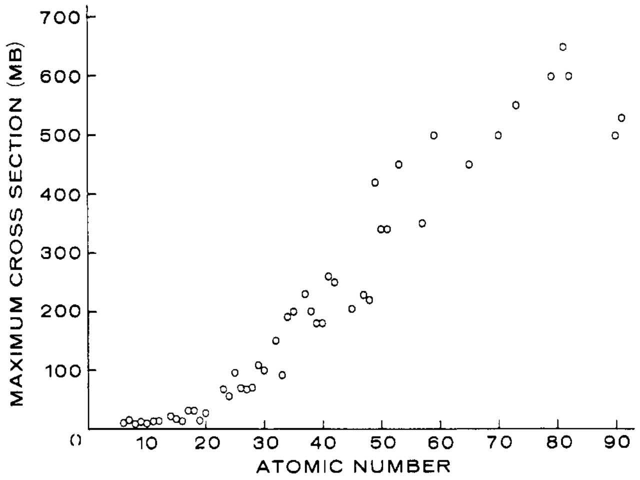

Figure 5. Peak cross section for (γ,n) reactions

The cross section-energy relationship for a (γ,n) reaction, the reaction most commonly used in photon activation analysis, is qualitatively shown in Figure 3. The shape is that of a Lorenzian function. The curve is characterized by a threshold energy, an energy of maximum cross section, the cross section at that energy, and a width at half-height. Figure 4 shows the threshold energy of maximum cross section for (γ,n) reactions as a function of atomic number. Figure 5 shows the peak cross section for (γ,n) reactions as a function of atomic number. Widths at half-height are usually in the range of 4–8 MeV.

The production rate for any particular photonuclear reaction is determined by the summation of the product of cross section and flux from the threshold of the reaction up to the

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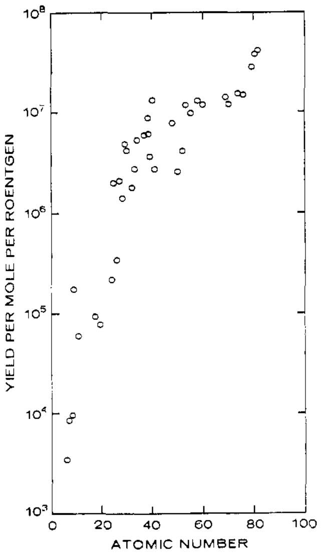

Figure 6. Yields for (γ,n) reactions from 20-MeV bremsstrahlung

electron energy. As would be expected from the trend of cross section with atomic number, and of photon flux with photon energy at a given electron energy, the production rate increases with atomic number. This intrinsic sensitivity has been measured for 20-MeV bremsstrahlung by Oka *et al.* (*32*). Their normalized yield-per-mole data for (γ,n) reactions for many of the elements are shown in Figure 6.

Lutz (*33*) has estimated the specific activities to be expected for most of the elements from bremsstrahlung produced from an electron beam current of 100 μA striking a tungsten target 0.6 cm in thickness, for electron energies of 25, 30, and 35 MeV. The photon-energy distribution was estimated by the method of Hansen and Fultz (*34*). A correction was made for the attenuation of the photons in the target. The angular distribution of the flux was calculated from the Schiff equation. It was assumed that a sample could be positioned to intercept the beam included in the cone described by a five degree angle from the forward direction. Results for irradiations of 10 minutes and 4 hours at the three energies are shown in Table II.

In the range of electron energies from 20–40 MeV, the yield at constant beam current of most (γ,n) reactions will approximately double with a 3–4 MeV increase in electron energy. This is due not only to an increase in the total number of photons of sufficiently high energy, but also to a more favorable (more forward-peaked) angular distribution. The choice of electron energy is usually a compromise between the required sensitivity and the occurrence of interfering reactions. In addition, the operating characteristics of the electron accelerator may be an important consideration.

DETERMINATION OF OXYGEN, NITROGEN, AND CARBON

Photon activation analysts have concentrated a substantial, although perhaps not adequate, portion of their efforts on the determination of three nonmetals: oxygen, nitrogen, and carbon. Although among the least sensitive of the elements for determination by gamma activation, because of their relatively high thresholds and small cross sections, they have nevertheless been determined by photonuclear methods at levels down to less than a microgram. These elements are frequently difficult to determine at very low levels by traditional methods, because of reagent and equipment blanks and the possibility of surface contamination, which would yield a higher result than is representative of the bulk of the sample. In these cases, photon activation is an attractive alternative.

The (γ,n) activation products of carbon, nitrogen, and oxygen all decay exclusively by positron emission, and are detected by the associated annihilation radiation. At low levels, unless the sample is quite simple and its gamma activation products do not yield positron emitters, it is frequently necessary to effect a chemical separation.

Table II. Calculated Sensitivities for Photon Activation Analysis

Element	Reaction	Product half-life	Disintegrations per second (per microgram of element)					
			10-minute irradiation, MeV			4-hour irradiation, MeV		
			25 M	30	35	25	30	35
Carbon	$^{12}\mathrm{C}(\gamma,\mathrm{n})^{11}\mathrm{C}$	20.5m	2×10^{1}	7×10^{1}	1×10^{2}	6×10^{1}	2×10^{2}	5×10^{2}
Nitrogen	$^{14}\mathrm{N}(\gamma,\mathrm{n})^{13}\mathrm{N}$	10.0m	7×10^{1}	2×10^{2}	4×10^{2}	1×10^{2}	4×10^{2}	8×10^{2}
Oxygen	$^{16}\mathrm{O}(\gamma,\mathrm{n})^{15}\mathrm{O}$	2.1m	1×10^{2}	3×10^{2}	6×10^{2}	1×10^{2}	3×10^{2}	6×10^{2}
Fluorine	$^{19}\mathrm{F}(\gamma,\mathrm{n})^{18}\mathrm{F}$	1.83h	3	8	1×10^{1}	4×10^{1}	1×10^{2}	2×10^{2}
Sodium	$^{23}\mathrm{Na}(\gamma,\mathrm{n})^{22}\mathrm{Na}$	2.6y	9×10^{-4}	2×10^{-3}	4×10^{-3}	2×10^{-2}	5×10^{-2}	9×10^{-2}
Magnesium	$^{25}\mathrm{Mg}(\gamma,\mathrm{p})^{24}\mathrm{Na}$	15.0h	1×10^{-1}	4×10^{-1}	7×10^{-1}	3	9	2×10^{1}
Magnesium	$^{26}\mathrm{Mg}(\gamma,\mathrm{p})^{25}\mathrm{Na}$	60s	1×10^{1}	3×10^{1}	7×10^{1}	1×10^{1}	3×10^{1}	7×10^{1}
Silicon	$^{29}\mathrm{Si}(\gamma,\mathrm{p})^{28}\mathrm{Al}$	2.31m	1×10^{1}	3×10^{1}	5×10^{1}	1×10^{1}	3×10^{1}	5×10^{1}
Silicon	$^{30}\mathrm{Si}(\gamma,\mathrm{p})^{29}\mathrm{Al}$	6.6m	3	9	2×10^{1}	4	1×10^{1}	3×10^{1}
Phosphorus	$^{31}\mathrm{P}(\gamma,\mathrm{n})^{30}\mathrm{P}$	2.50m	1×10^{2}	3×10^{2}	6×10^{2}	1×10^{2}	4×10^{2}	6×10^{2}
Sulfur	$^{32}\mathrm{S}(\gamma,\mathrm{n})^{31}\mathrm{S}$	2.7s	7×10^{1}	2×10^{2}	4×10^{2}	7×10^{1}	2×10^{2}	4×10^{2}
Chlorine	$^{35}\mathrm{Cl}(\gamma,\mathrm{n})^{34}\mathrm{Cl}$	32.0m	2×10^{1}	5×10^{1}	8×10^{1}	1×10^{2}	2×10^{2}	4×10^{2}
Argon	$^{40}\mathrm{A}(\gamma,\mathrm{p})^{39}\mathrm{Cl}$	55.5m	1×10^{1}	5×10^{1}	1×10^{2}	1×10^{2}	4×10^{2}	9×10^{2}
Potassium	$^{39}\mathrm{K}(\gamma,\mathrm{n})^{38}\mathrm{K}$	7.71m	5×10^{1}	1×10^{2}	2×10^{2}	9×10^{1}	2×10^{2}	4×10^{2}
Titanium	$^{46}\mathrm{Ti}(\gamma,\mathrm{n})^{45}\mathrm{Ti}$	3.09h	5×10^{-1}	1	2	8	2×10^{1}	4×10^{1}
Titanium	$^{48}\mathrm{Ti}(\gamma,\mathrm{p})^{47}\mathrm{Sc}$	3.4d	8×10^{-2}	2×10^{-1}	5×10^{-1}	2	6	1×10^{1}
Chromium	$^{50}\mathrm{Cr}(\gamma,\mathrm{n})^{49}\mathrm{Cr}$	42m	2	4	8	1×10^{1}	3×10^{1}	5×10^{1}
Chromium	$^{53}\mathrm{Cr}(\gamma,\mathrm{p})^{52}\mathrm{V}$	3.76m	8	2×10^{1}	4×10^{1}	9	2×10^{1}	4×10^{1}
Manganese	$^{55}\mathrm{Mn}(\gamma,\mathrm{n})^{54}\mathrm{Mn}$	303d	1×10^{-2}	2×10^{-2}	4×10^{-2}	2×10^{-1}	6×10^{-1}	1
Iron	$^{54}\mathrm{Fe}(\gamma,\mathrm{n})^{53}\mathrm{Fe}$	8.5m	1×10^{1}	3×10^{1}	5×10^{1}	2×10^{1}	5×10^{1}	9×10^{1}

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Table II. (Continued)

Element	Reaction	Product half-life	Disintegrations per second (per microgram of element)					
			10-minute irradiation, MeV			4-hour irradiation, MeV		
			25 M	30	35	25	30	35
Cobalt	$^{59}\mathrm{Co}(\gamma,n)^{58}\mathrm{Co}$	71.3d	3×10^{-2}	7×10^{-2}	1×10^{-1}	8×10^{-1}	2	3
Nickel	$^{58}\mathrm{Ni}(\gamma,n)^{57}\mathrm{Ni}$	36h	3×10^{-1}	7×10^{-1}	1	7	2×10^{1}	3×10^{1}
Copper	$^{63}\mathrm{Cu}(\gamma,n)^{62}\mathrm{Cu}$	9.9m	2×10^{2}	5×10^{2}	9×10^{2}	5×10^{2}	1×10^{3}	2×10^{3}
Copper	$^{65}\mathrm{Cu}(\gamma,n)^{64}\mathrm{Cu}$	12.8h	2	5	9	5×10^{1}	1×10^{2}	2×10^{2}
Zinc	$^{64}\mathrm{Zn}(\gamma,n)^{63}\mathrm{Zn}$	38.4m	5×10^{1}	1×10^{2}	2×10^{2}	3×10^{2}	7×10^{2}	1×10^{3}
Germanium	$^{76}\mathrm{Ge}(\gamma,n)^{75}\mathrm{Ge}$	82m	7	2×10^{1}	3×10^{1}	7×10^{1}	2×10^{2}	3×10^{2}
Germanium	$^{70}\mathrm{Ge}(\gamma,n)^{69}\mathrm{Ge}$	38h	6×10^{-1}	1	2	1×10^{1}	3×10^{1}	5×10^{1}
Arsenic	$^{75}\mathrm{As}(\gamma,n)^{74}\mathrm{As}$	17.9d	2×10^{-1}	4×10^{-1}	6×10^{-1}	4	8	1×10^{1}
Bromine	$^{79}\mathrm{Br}(\gamma,n)^{78}\mathrm{Br}$	6.5m	5×10^{2}	1×10^{3}	2×10^{3}	8×10^{2}	2×10^{3}	3×10^{3}
Bromine	$^{81}\mathrm{Br}(\gamma,n)^{80m}\mathrm{Br}$	4.4h	3	6	1×10^{1}	5×10^{1}	1×10^{2}	2×10^{2}
Rubidium	$^{87}\mathrm{Rb}(\gamma,n)^{86}\mathrm{Rb}$	18.7d	8×10^{-2}	2×10^{-1}	3×10^{-1}	2	4	7
Strontium	$^{86}\mathrm{Sr}(\gamma,n)^{85}\mathrm{Sr}$	64d	7×10^{-3}	1×10^{-2}	2×10^{-2}	2×10^{-1}	3×10^{-1}	6×10^{-1}
Yttrium	$^{89}\mathrm{Y}(\gamma,n)^{88}\mathrm{Y}$	108d	4×10^{-2}	9×10^{-2}	1×10^{-1}	1	2	4
Zirconium	$^{90}\mathrm{Zr}(\gamma,n)^{89}\mathrm{Zr}$	78.4h	7×10^{-1}	2	3	2×10^{1}	4×10^{1}	7×10^{1}
Niobium	$^{93}\mathrm{Nb}(\gamma,n)^{92}\mathrm{Nb}$	10.2d	6×10^{-1}	1	2	1×10^{1}	3×10^{1}	5×10^{1}
Molybdenum	$^{92}\mathrm{Mo}(\gamma,n)^{91}\mathrm{Mo}$	15.5m	2×10^{1}	6×10^{1}	1×10^{2}	6×10^{1}	2×10^{2}	3×10^{2}
Molybdenum	$^{100}\mathrm{Mo}(\gamma,n)^{99}\mathrm{Mo}$	66h	2×10^{-1}	5×10^{-1}	7×10^{-1}	5	1×10^{1}	2×10^{1}
Ruthenium	$^{96}\mathrm{Ru}(\gamma,n)^{95}\mathrm{Ru}$	99m	4	9	2×10^{1}	5×10^{1}	1×10^{2}	2×10^{2}
Ruthenium	$^{104}\mathrm{Ru}(\gamma,n)^{103}\mathrm{Ru}$	40d	3×10^{-2}	6×10^{-2}	1×10^{-1}	7×10^{-1}	2	3
Rhodium	$^{103}\mathrm{Rh}(\gamma,n)^{102}\mathrm{Rh}$	206d	3×10^{-2}	5×10^{-2}	9×10^{-2}	6×10^{-1}	1	2
Palladium	$^{104}\mathrm{Pd}(\gamma,n)^{103}\mathrm{Pd}$	17d	4×10^{-2}	9×10^{-2}	1×10^{-1}	1	2	3
Silver	$^{107}\mathrm{Ag}(\gamma,n)^{106}\mathrm{Ag}$	24m	2×10^{2}	4×10^{2}	6×10^{2}	7×10^{2}	1×10^{3}	2×10^{3}
Cadmium	$^{113}\mathrm{Cd}(\gamma,p)^{112}\mathrm{Ag}$	3.2h	8×10^{-2}	2×10^{-1}	4×10^{-1}	1	4	6
Cadmium	$^{114}\mathrm{Cd}(\gamma,p)^{113}\mathrm{Ag}$	5.3h	1×10^{-1}	3×10^{-1}	5×10^{-1}	2	5	9
Indium	$^{115}\mathrm{In}(\gamma,n)^{114}\mathrm{In}$	50d	2×10^{-1}	4×10^{-1}	6×10^{-1}	5	9	1×10^{1}
Indium	$^{115}\mathrm{In}(\gamma,\gamma')^{115m}\mathrm{In}$	4.5h	2	4	5	4×10^{1}	7×10^{1}	9×10^{1}
Tin	$^{112}\mathrm{Sn}(\gamma,n)^{111}\mathrm{Sn}$	35m	3	6	9	2×10^{1}	3×10^{1}	5×10^{1}
Tin	$^{124}\mathrm{Sn}(\gamma,n)^{123}\mathrm{Sn}$	125d	3×10^{-3}	7×10^{-3}	1×10^{-2}	8×10^{-2}	2×10^{-1}	3×10^{-1}
Antimony	$^{121}\mathrm{Sb}(\gamma,n)^{120m}\mathrm{Sb}$	5.8d	6×10^{-1}	1	2	1×10^{1}	3×10^{1}	4×10^{1}
Antimony	$^{123}\mathrm{Sb}(\gamma,n)^{122}\mathrm{Sb}$	2.8d	2	3	5	4×10^{1}	8×10^{1}	1×10^{2}
Iodine	$^{127}\mathrm{I}(\gamma,n)^{126}\mathrm{I}$	13.2d	8×10^{-1}	2	3	2×10^{1}	4×10^{1}	6×10^{1}
Cesium	$^{133}\mathrm{Cs}(\gamma,n)^{132}\mathrm{Cs}$	6.58d	1	3	4	3×10^{1}	6×10^{1}	1×10^{2}
Cerium	$^{140}\mathrm{Ce}(\gamma,n)^{139}\mathrm{Ce}$	140d	6×10^{-2}	1×10^{-1}	2×10^{-1}	1	3	4
Praseodymium	$^{141}\mathrm{Pr}(\gamma,n)^{140}\mathrm{Pr}$	3.4m	1×10^{3}	3×10^{3}	4×10^{3}	2×10^{3}	3×10^{3}	5×10^{3}
Neodymium	$^{142}\mathrm{Nd}(\gamma,n)^{141}\mathrm{Nd}$	2.5h	2×10^{1}	4×10^{1}	6×10^{1}	3×10^{2}	5×10^{2}	8×10^{2}
Neodymium	$^{150}\mathrm{Nd}(\gamma,n)^{149}\mathrm{Nd}$	1.8h	8	1×10^{1}	2×10^{1}	1×10^{2}	2×10^{2}	3×10^{2}
Samarium	$^{144}\mathrm{Sm}(\gamma,n)^{143}\mathrm{Sm}$	8.9m	2×10^{1}	5×10^{1}	8×10^{1}	5×10^{1}	9×10^{1}	1×10^{2}
Samarium	$^{154}\mathrm{Sm}(\gamma,n)^{153}\mathrm{Sm}$	47h	1	2	3	2×10^{1}	5×10^{1}	7×10^{1}
Gadolinium	$^{160}\mathrm{Gd}(\gamma,n)^{159}\mathrm{Gd}$	18h	3	5	7	6×10^{1}	1×10^{2}	2×10^{2}
Terbium	$^{159}\mathrm{Tb}(\gamma,n)^{158}\mathrm{Tb}$	150y	2×10^{-4}	3×10^{-4}	5×10^{-4}	4×10^{-3}	8×10^{-3}	1×10^{-2}
Dysprosium	$^{158}\mathrm{Dy}(\gamma,n)^{157}\mathrm{Dy}$	8.1h	2×10^{-2}	4×10^{-2}	7×10^{-2}	5×10^{-1}	9×10^{-1}	1
Holmium	$^{165}\mathrm{Ho}(\gamma,n)^{164}\mathrm{Ho}$	37m	3×10^{2}	6×10^{2}	1×10^{3}	2×10^{3}	4×10^{3}	6×10^{3}
Erbium	$^{166}\mathrm{Er}(\gamma,n)^{165}\mathrm{Er}$	10.3h	7	1×10^{1}	2×10^{1}	1×10^{2}	3×10^{2}	4×10^{2}
Thulium	$^{169}\mathrm{Tm}(\gamma,n)^{168}\mathrm{Tm}$	85d	1×10^{-1}	2×10^{-1}	3×10^{-1}	3	5	8
Ytterbium	$^{168}\mathrm{Yb}(\gamma,n)^{167}\mathrm{Yb}$	18m	1	2	3	3	5	8
Ytterbium	$^{176}\mathrm{Yb}(\gamma,n)^{175}\mathrm{Yb}$	4.2d	3×10^{-1}	6×10^{-1}	9×10^{-1}	8	1×10^{1}	2×10^{1}
Lutetium	$^{175}\mathrm{Lu}(\gamma,n)^{174}\mathrm{Lu}$	300d	1×10^{-2}	3×10^{-2}	4×10^{-2}	3×10^{-1}	6×10^{-1}	1
Tantalum	$^{181}\mathrm{Ta}(\gamma,n)^{180m}\mathrm{Ta}$	8.1h	4×10^{1}	7×10^{1}	1×10^{2}	8×10^{2}	1×10^{3}	2×10^{3}
Tungsten	$^{186}\mathrm{W}(\gamma,n)^{185}\mathrm{W}$	75d	5×10^{-2}	9×10^{-2}	1×10^{-1}	1	2	3
Rhenium	$^{187}\mathrm{Re}(\gamma,n)^{186}\mathrm{Re}$	90h	2	4	6	5×10^{1}	9×10^{1}	1×10^{2}
Osmium	$^{192}\mathrm{Os}(\gamma,n)^{191}\mathrm{Os}$	15d	3×10^{-1}	6×10^{-1}	1	8	1×10^{1}	2×10^{1}
Iridium	$^{191}\mathrm{Ir}(\gamma,n)^{190}\mathrm{Ir}$	11d	4×10^{-1}	7×10^{-1}	1	9	2×10^{1}	3×10^{1}
Gold	$^{197}\mathrm{Au}(\gamma,n)^{196}\mathrm{Au}$	6.2d	2	4	6	5×10^{1}	9×10^{1}	1×10^{3}
Mercury	$^{198}\mathrm{Hg}(\gamma,n)^{197}\mathrm{Hg}$	65h	5×10^{-1}	9×10^{-1}	1	1×10^{1}	2×10^{1}	3×10^{1}
Thallium	$^{203}\mathrm{Tl}(\gamma,n)^{202}\mathrm{Tl}$	12d	3×10^{-1}	6×10^{-1}	9×10^{-1}	8	1×10^{1}	2×10^{1}
Lead	$^{204}\mathrm{Pb}(\gamma,n)^{203}\mathrm{Pb}$	52h	1×10^{-1}	2×10^{-1}	3×10^{-1}	2	4	6

Oxygen. The nuclear reaction involved is

$$^{16}\mathrm{O}(\gamma,n)^{15}\mathrm{O}$$

The product nuclide has a half-life of 2.05 minutes.

As noted in the introduction, this reaction was used by Basile, Hure, Leveque, and Schuhl in 1953 for the determination of oxygen in organic materials. Much early work in photon activation analysis was concentrated on the determination of oxygen, along with carbon and nitrogen, in beryllium—programs for development of a ductile metal having shown the need for precise analytical methods for these impurities.

The development of this analytical method was furthered by Beard, Johnson, and Bradshaw (*35*), Gilman and Isserow (*36*), and Engelmann and his colleagues (*37*). The method consists of irradiating the sample with bremsstrahlung from 28–40 MeV electrons and counting the resulting annihilation radiation by means of coincidence gamma-ray spectrometry.

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(35) D. B. Beard, R. G. Johnson, and W. G. Bradshaw, *Nucleonics*, **17**, 90 (1959).

(36) A. R. Gilman and S. Isserow, *AEC Rep.* **NMI-1234**, Concord, Mass., May 3, 1960.

(37) C. Engelmann, J. Gosset, and M. Loeuillet, *Bull. Soc. Chim. Fr.*, **1967**, 544.

The decay curve obtained is resolved graphically or by more sophisticated computer methods. Sensitivities of the order of 1 ppm are claimed, but this is very dependent on the levels of other impurities.

As they have favorable thermodynamic and nuclear properties, the alkali metals have potential use as heat-transfer media for nuclear power reactors. However, they may cause corrosion or embrittlement of structural components with which they come in contact. This is associated with traces of oxygen and other nonmetals in the sodium. Engelmann and Loeuillet (*38*) have pointed out that, for a nondestructive determination of oxygen in sodium, it is necessary to irradiate at energies below the threshold for production of the positron-emitting ^{18}F produced by the reaction $^{23}\text{Na}(\gamma, \alpha n)^{18}\text{F}$. In addition, the 7.71-minute activity from ^{38}K interferes with counting.

Lutz (*39*) has determined oxygen in sodium at levels of a few ppm with a chemical separation. The sodium sample, after irradiation and etching, is dissolved in water. The radioactive oxygen exchanges with water, a portion of which is rapidly distilled from the sample, and the ^{15}O counted. A small amount of entrainment occurs, and it is necessary to evaluate a long-lived component for subtraction from the oxygen activity.

Holm and Sanders (*40*) determined oxygen at the 30-ppm level by coincidence and gated well techniques. The electron energy was 19 MeV, and the decay curve was analyzed by computer methods. Persiani, Spira, and Bastian (*41*) have described a nondestructive determination of oxygen in cesium, using a 30-MeV betatron. Under optimum conditions, less than 100 ppm of the element could be determined.

Engelmann (*42*) has pointed out that oxygen can be determined in calcium and boron nondestructively. The photonuclear products of these elements do not interfere with the counting of the oxygen activity, and, if other impurities are present only at very low levels, sensitivities of 1 to 0.01 ppm are obtained. Mackintosh and Jervis (*43*) have reported the nondestructive determination of oxygen in a lead-bismuth alloy. Kobayashi *et al.* (*44*) studied the instrumental photon activation analysis determination of oxygen in pure aluminum ingots and oxide films. Utilizing bombarding energies of 31 MeV and a dose of 10^6r/min, it was possible to determine 20 ppm of oxygen.

The betatron at the Karpov Institute has been used for the determination of several per cent of oxygen in natural and butadiene rubbers (*45*, *46*). The method is useful for rapid analysis in the course of processing the rubber.

The fraction of samples that the photon activation analyst encounters in which he can measure trace levels of oxygen nondestructively is certainly very small. Engelmann and his colleagues (*47–49*), and Baker and Williams (*50*), have investigated the application of inert gas-fusion to the separation of ^{15}O from irradiated samples. The usual advantages of activation analysis are present; a massive sample may be etched after irradiation, but before separation and counting, and equipment and reagent contamination do not affect the determination. Engelmann deliberately added iron chips with a high oxygen content to the sample. The added oxygen in the bath acted as a carrier and expedited the ^{15}O extraction. Baker and Williams have pointed out that there is no reason why one may not increase the speed and completeness of the separation by operating the furnace at extremely high temperatures with outgassing, which is unacceptable in traditional inert-gas fusion. They noted that the extracted oxygen is rarely radiochemically pure, and a longer-lived component (usually ^{11}C) appears after several half-lives decay. They analyzed their counting data by a least-squares method for the two components. A sensitivity of about 10^{-7} gram seems to be feasible, but data on precision and accuracy are lacking.

Dorosh *et al.* (*51*) have discussed the possibility of using the reaction, $^{16}\text{O}(\gamma,p)^{17}\text{N}$, for the determination of oxygen in metals. This is a very attractive nuclear reaction as ^{17}N decays by delayed-neutron emission with a half-life of 4.16 seconds, making its detection in many samples quite simple. The abundance, however, of ^{18}O is only 0.204%, reducing the sensitivity for oxygen to about that available with 14-MeV neutron generators. Nevertheless, it should find utility in determinations where there is an interference with 14-MeV neutrons, such as substantial amounts of boron or fluorine in the sample.

Nitrogen. The nuclear reaction used is

$$^{14}\text{N}(\gamma,n)^{13}\text{N}.$$

The product nuclide has a half-life of 9.96 minutes.

The nondestructive determination of nitrogen is complicated by the fact that copper and iron both yield photon activation products that also decay by positron emission and have half-lives similar to that of nitrogen-13. Engelmann (*42*) has observed that the yield of nitrogen relative to either copper or iron does not change much with bombarding energy, and it appears that one cannot make corrections for copper or iron this way.

Most nondestructive determinations, therefore, involve the independent determination of copper and iron, and, if necessary, the application of corrections for the two elements. Rocco, Garzon, and Cali (*52*) have determined nitrogen in 40-mg diamond samples. Electron energies of 17.6 MeV, below the threshold for carbon activation, were used. Various nitrogen-containing substances were irradiated and counted to demonstrate a linear relationship between activity and nitrogen content. They were able to conclude from the gamma-ray spectrum that the only possible inter-

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(38) C. Engelmann and M. Loeuillet, *Bull. Soc. Chim. Fr.*, **1969,** 680.

(39) G. J. Lutz, Anal. Chem., **42,** 531 (1970).

(40) D. M. Holm and W. M. Sanders, *AEC Rep.* **LA-DC-7931,** Los Alamos, N. M. (1964).

(41) C. Persiani, J. Spira, and R. Bastian, *Talanta*, **14,** 565 (1967).

(42) C. Engelmann, Radiochemical Methods of Analysis, IAEA, Vienna, Vol. I, pp 341–59 (1965).

(43) W. D. Mackintosh and R. E. Jervis, *NBS Spec. Publ.* **312,** Vol. II, Modern Trends in Activation Analysis, pp 835–7 (1969).

(44) M. Kobayashi, T. Sawai, S. Nagatsuka, and S. Maeda, *Proc. Jap. Conf. Radioisotope*, No. 3, pp 179–181 (1963).

(45) L. V. Chepel, B. A. Chapyzhnikov, G. N. Mikhailova, E. V. Zhuravskaya, and A. S. Kuzminskii, *Kauch. Rezina*, **25,** 49 (1966).

(46) L. V. Chepel, B. A. Chapyzhnikov, and B. I. Viting, *J. Anal. Chem. USSR*, **18,** 749 (1963).

(47) C. Engelmann, *Int. J. Appl. Radiat. Isotopes*, **18,** 569 (1967).

(48) C. Engelmann, B. Fritz, J. Gosset, P. Graeff, and M. Loeuillet, "Proceedings of the 2nd Conference on Practical Aspects of Activation Analysis with Charged Particles, Liege, Sept. 1967," H. G. Ebert, Ed., Brussels, European Atomic Energy Community, pp 319–50 (1968).

(49) C. Engelmann, J. Gosset, M. Loeuillet, A. Marschal, P. Ossart, and M. Boissier, *NBS Spec. Publ.* **312,** Vol. II, Modern Trends in Activation Analysis, pp 819–28 (1969).

(50) C. A. Baker and D. R. Williams, *Talanta*, **15,** 1143 (1968).

(51) M. M. Dorosh, N. P. Mazyukevich, and V. A. Shkoda-Ulyanov, *Sov. At. Energy*, 807 (1966).

(52) G. G. Rocco, O. L. Garzon, and J. P. Cali, *Int. J. Appl. Radiat. Isotop.*, **17,** 433 (1966).

ference could be from copper. The diamonds were subsequently analyzed for copper by thermal neutron activation, and it was demonstrated that the copper content was negligible, compared to that of nitrogen.

Post-irradiation separations of nitrogen have followed two courses. Albert (*6*) described the use of the Kjeldahl separation for the determination of nitrogen in aluminum, beryllium, and zirconium. The samples, after irradiation, are dissolved in a suitable acid to which a few milliliters of $HgCl_2$ solution have been added. Ammonium chloride carrier is added, and the solution is neutralized with a large excess of base. The ammonia is distilled out and collected in an acid solution, and the activity of the distillate solution is measured. Samples of highly-purified aluminum were found to have a nitrogen content of 0.1–0.2 ppm.

Engelmann *et al.* (*47, 48*) have separated nitrogen with oxidizing fusion. After irradiation, the sample is placed in a crucible containing 20–30 grams of an oxidizing flux (87.5% Pb_3O_4–12.5% B_2O_3). During induction heating, the sample is oxidized, nitrogen being converted to molecular nitrogen and nitrogen oxides. These gases are swept in a stream of helium through a glass filter and a halogen trap over copper at 500°C, which reduces nitrogen oxides to nitrogen. The nitrogen is subsequently trapped on liquid nitrogen-cooled molecular sieve. Sensitivities of less than 0.1 ppm are possible.

Carbon. The reaction used is $^{12}C(\gamma,n)^{11}C$, and the half-life of the product nuclide is 20.34 minutes.

Considerations of the nondestructive determination of trace levels of carbon are about the same as for oxygen. Relative to the activity of carbon produced, there must not be much other positron-emitting activity that can interfere. Many of the nondestructive oxygen determinations cited in the section on that element also involved the determination of carbon.

Voigt and Abu-Samra (*53*) have determined carbon nondestructively in a sample taken from a Damascus steel sword of the sixteenth century. A synchrotron was used, and the irradiation energy was 70 MeV. This also induced the 21.1 min ^{52m}Mn activity *via* the reaction $^{54}Fe(\gamma,np)^{52m}Mn$ which interfered with the carbon counting. Fortunately, the interfering radionuclide has a gamma ray of 1.434-MeV energy and, by measurement of the gamma spectrum, it was possible to correct for this interference.

Albert (*6*), Engelmann *et al.* (*47–49*), Revel *et al.* (*54*), Baker and Williams (*50*), and Lutz and Masters (*55*) have all described methods for the separation of ^{11}C activity from a variety of metals. The separations follow, in general, conventional techniques. The sample is burned in a stream of oxygen gas, or oxidized in a Pb_3O_4–B_2O_3 melt, with subsequent trapping of the carbon dioxide in an alkaline solution or a liquid-air trap. In an activation analysis, it is, of course, not necessary to purify the oxygen or other reagents used. One may use fluxes to improve the fluidity of the melt or to initiate and accelerate combustion, without regard for their carbon content.

A large variety of metals have been analyzed for trace levels of carbon by this method. Most of the papers cited give details on specific topics such as monitoring, standards, sample positioning, and counting. Several compare results at higher levels of carbon in samples which have been carefully analyzed by other methods. Sensitivities of 10^{-8} gram are possible.

The separation of ^{11}C activity from irradiated sodium requires a different separation method. It is difficult to extract carbon from sodium oxide at high temperatures, because of the stability of sodium carbonate. In a method described by Lutz and DeSoete (*56*), the irradiated sodium sample is burned in a stream of oxygen to sodium monoxide, the carbon being converted to sodium carbonate. This is then decomposed with acid, the liberated CO_2 being trapped in a dilute alkaline solution. A sulfuric acid–boric acid solution prior to the alkali trap, removes—as a fluoboric acid complex—the ^{18}F that has been produced from the reaction, $^{23}Na(\gamma,\alpha n)^{18}F$.

DETERMINATION OF HEAVIER ELEMENTS

There are a number of elements heavier than oxygen that may be determined more easily, or more advantageously, by photon activation than by activation with reactor neutrons. The following conditions apply:

There may be greater intrinsic sensitivity for photon activation. Examples are fluorine, iron, and lead.

The photon-activation product has a more convenient half-life or decay mode than the thermal-neutron activation product.

Major constituents of the sample have large thermal-neutron cross sections, requiring the evaluation of self-shielding corrections or the handling of large amounts of unwanted radioactivity.

Interfering nuclear reactions may interfere with the neutron determination. The thermal-neutron activation determination of nickel by the reaction, $^{64}Ni(n,\gamma)^{65}Ni$, is subject to interference when copper is present, because of the reaction, $^{65}Cu(n,p)^{65}Ni$. The photon-activation product, ^{57}Ni, produced by the (γ,n) reaction on ^{58}Ni, cannot be produced from any other element at bombarding energies less than about 45 MeV.

Schweikert and Albert (*57*) have irradiated 25 elements with bremsstrahlung from electrons varying between 20 and 27 MeV, and have published specific activities obtained for these elements for five-minute and eight-day irradiations and have described a number of useful analyses. These include the nondestructive determination of zirconium in hafnium, utilizing the 4.18-minute ^{89m}Zr product. They determined titanium in iron and copper; counting the 3.09-hour positron-emitting ^{45}Ti after an oxime extraction. Nickel was determined in copper with chemical separation.

Oka *et al.* (*32*) have used a linear accelerator to irradiate all of the elements from lithium to bismuth, except technetium, promethium, and the inert gases, for 1 hour with bremsstrahlung from 20-MeV electrons. The dose rate was estimated to be 9.4×10^6r/min. After irradiation, the gamma-ray spectra of the elements were measured with a sodium-iodide detector, and prominent gamma rays and specific activities were noted.

Biological Samples. Andersen *et al.* (*29*) surveyed the application of photon activation analysis to biological samples. They have pointed out that most of the major and minor constituents yield either quite short or very long-lived activities

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(53) A. F. Voigt and A. Abu-Samra, Proceedings of the 1965 International Conference on Modern Trends in Activation Analysis, College Station, pp 22–25 (1965).

(54) G. Revel, I. Chaudron, J. L. DeBrun, and P. Albert, *NBS Spec. Publ.* **312**, Vol. II, Modern Trends in Activation Analysis, pp 838–41 (1969).

(55) G. J. Lutz and L. W. Masters, ANAL. CHEM., **42**, 948 (1970).

(56) G. J. Lutz and D. A. DeSoete, *ibid.*, **40**, 820 (1968).

(57) E. A. Schweikert and P. Albert, "Radiochemical Methods of Analysis," IAEA, Vienna, Vol. I, pp 323–39 (1965).

after photon bombardment so that radioactivity associated with many trace elements may be readily observed. A number of elements difficult to determine with thermal-neutron activation, such as magnesium, calcium, strontium, and tin were detected in a wide variety of biological materials. Fluorine and strontium were determined instrumentally down to levels of a few tens of ppm in teeth and other samples with 12 MeV photons. This energy is sufficiently low that chlorine, sodium, and carbon do not interfere.

Mulvey, Cardarelli, Burrows *et al.* (*58–61*) have determined iodine and mercury in several biological materials after a pre-irradiation separation of the elements of interest. Dowex 1-X8 resin, in the acetate form, was placed in a polyethylene syringe, and the dissolved sample passed through it. Experiments with known amounts of material demonstrated that the separation was quantitative. The samples were then irradiated for over an hour with bremsstrahlung from 22-MeV electrons. The beam current was 250 μA. The resultant activity was assayed with a sodium–iodide detector. Radioactivities from impurities in the syringe and resin were usually of lower energy and shorter half-life than of the elements of interest, and did not interfere with the counting. These authors have also suggested the use of the reaction, $^{12}\mathrm{C}(\gamma,\alpha n)^{7}\mathrm{Be}$ as an internal flux monitor at higher energies for biological samples.

Cooper, Linekin, and Brownell (*58*, *62*) have examined photon irradiated blood and tissue with a Ge(Li) detector. Magnesium, cadmium, lead, iodine, and tin were observed, along with unidentified positron emitters. Asai *et al.* (*63*) examined activated blood with a NaI detector and tentatively identified fourteen elements.

Meyers (*64*) has described a novel application. The composition of fossil bones and teeth buried in the ground is influenced by the ground-water. Nitrogen in bone protein will slowly leave the bones, while fluorine ions in the water will slowly be picked up. A relative age determination of a series of bones from the same ground matrix is possible by determining the content of nitrogen and fluorine. This can be done nondestructively by photon activation analysis, thus preserving the precious samples for other purposes.

Geochemistry and Oceanography. Sulin, Vitozhents, and their colleagues of the All-Union Scientific Research Institute (*65–68*) have used a betatron for the determination of many elements of industrial interest in minerals and ores. Many useful determinations could be done nondestructively by selective activation at different irradiation energies and judicious choice of irradiation and cooling times. Copper, zinc, zirconium, and silver were among the elements determined in this way in complex ores. Servomechanism devices were developed for automatic irradiation and counting. Gerrard (*69*) has reviewed some of this work in English.

Wilkniss and Linnenbom (*70*) developed a method for the photon activation determination of fluorine in seawater. Three-milliliter samples were freeze-dried, encapsulated in aluminum foil, and irradiated for 20 minutes in the bremsstrahlung beam obtained from a 22-MeV, 30-μA electron beam. The reaction induced was the $^{19}\mathrm{F}(\gamma,n)^{18}\mathrm{F}$ reaction. The low energy was required to prevent interference from the reaction, $^{23}\mathrm{Na}(\gamma,\alpha n)^{18}\mathrm{F}$, which has a threshold of 23 MeV. The separation consisted of a distillation, followed by a lead chlorofluoride precipitation. The positron activity of ^{18}F was coincidence-counted. The limit of detection was determined to be a few ppb. Wilkniss (*71*) has subsequently developed the methods for the determination of all of the halogens in a single sample.

Meijers and Aten (*72*) instrumentally determined the major constituents, iron, nickel, and cobalt in meteorites. Activities due to the different components were determined by decay curve resolution.

Forensic. Guinn and coworkers (*73*, *74*) have studied a variety of forensic samples by photon activation. Several samples of moonshine whiskey were analyzed for lead using the reaction, $^{204}\mathrm{Pb}(\gamma,n)^{203}\mathrm{Pb}$. The lead content varied from about four to eighty milligrams per liter of sample. Agreement with colorimetric analysis was good. They have pointed out that an advantage of photonuclear activation of forensic samples over thermal-neutron activation is the avoidance of ^{24}Na production in materials containing large amounts of sodium. They have made exploratory studies on biological samples, drugs, glass, soil, and paper, and have detailed the advantages and problems associated with photonuclear forensic work (*74*).

There has been a great deal of useful work on the determination of the heavier elements in a variety of samples by photon activation. Because of space limitations, the applications of photon activation analysis to the determination of elements heavier than oxygen have not been discussed exhaustively here. Most of the reported applications of photon activation analysis to these elements not referred to in the text are, however, summarized in Table III.

METASTABLE ISOMERS

There are about 40 stable nuclides which have metastable isomers with half-lives greater than 0.5 second. Many of

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(58) B. A. Burrows, P. F. Mulvey, Jr., R. D. Cooper, and J. A. Cardarelli, *Strahlentherapie, Sonderb.*, **65**, 365 (1967).

(59) J. A. Cardarelli, E. S. Dell, and B. A. Burrows, *NBS Spec. Publ.* **312,** Vol. II, Modern Trends in Activation Analysis, pp 847–52 (1969).

(60) P. F. Mulvey, Jr., J. A. Cardarelli, R. A. Meyer, R. D. Cooper, and B. A. Burrows, "Radioisotope Sample Measurement Techniques in Medicine and Biology," IAEA, Vienna, pp 249–258 (1965).

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(64) P. Meyers, "Proceedings of the 2nd Conference on Practical Aspects of Activation Analysis with Charged Particles, Liege, Sept. 1967," H. G. Ebert, Ed., Brussels, European Atomic Energy Community, pp 195–224 (1968).

(65) A. K. Berzin, V. V. Sulin, V. I. Belov, G. C. Vitozhents, Y. T. Martynov, V. G. Suslow, and S. I. Shornikov, Radioisotope Instruments in Industry and Geophysics, IAEA, Vienna, **STI/PUB/112,** pp 323–347 (1966).

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Table III. Determination of Heavier Elements by Photon Activation Analysis

Element determined		Matrix analyzed	
Arsenic	*(75)*	Alkali halides	*(78)*
Barium	*(76, 77)*	Barium	*(95)*
Cadmium	*(76, 77)*	Calcium	*(95)*
Chlorine	*(78, 79)*	Chromium	*(89)*
Cobalt	*(80)*	Cobalt	*(89)*
Copper	*(81)*	Copper	*(89)*
Europium	*(82)*	Hafnium	*(100, 101)*
Fluorine	*(79, 83, 84)*	Indium	*(85)*
Gadolinium	*(82)*	Iron	*(80, 88, 97)*
Gallium	*(85, 86)*	Niobium	*(96)*
Germanium	*(87, 88)*	Osmium	*(94)*
Indium	*(86)*	Plastics	*(76, 77, 79)*
Iodine	*(78, 83)*	Platinum	*(93)*
Lead	*(76, 77, 83, 89)*	Rare earths	*(99)*
Mercury	*(83)*	Rhodium	*(94)*
Nickel	*(80, 89)*	Selenium	*(75)*
Potassium	*(90)*	Thallium	*(86)*
Rare earths	*(91, 92)*	Titanium	*(87)*
Rhenium	*(93)*	Tungsten	*(84)*
Rhodium	*(93)*	Tungsten bronzes	*(82, 90)*
Ruthenium	*(94)*	Vanadium	*(98)*
Strontium	*(95)*	Zinc	*(81)*
Tantalum	*(96)*		
Thallium	*(85, 89)*		
Titanium	*(97, 98)*		
Yttrium	*(99)*		
Zirconium	*(100, 101)*		

Table IV. Specific Activities of Metastable Isomers (Ref *106*)

Element	Isotope produced	Half-life	Beam energy, MeV	cpm per gram of element at end of irradiation
Se	^{77m}Se	17.5 sec	5	1.3×10^7
Br	^{79m}Br	4.8 sec	4	1.6×10^7
Sr	^{87m}Sr	2.83 hr	6	3×10^3
Y	^{89m}Y	16 sec	5	9×10^5
Rh	^{103m}Rh	57 min	5	2×10^3
Ag	^{107m}Ag + ^{109m}Ag	44.3 sec 40 sec	5	1.8×10^6
Cd	^{111m}Cd	48.6 min	6	5×10^3
In	^{115m}In	4.5 hr	6	8×10^4
Sn	^{117m}Sn	14 d	6	5
Ba	^{137m}Ba	2.55 min	5	6×10^3
Er	^{167m}Er	2.3 sec	4	4.9×10^7
Hf	^{179m}Hf	18.6 sec	5	1.6×10^7
W	^{183m}W	5.3 sec	5	1.2×10^6
Ir	^{191m}Ir	4.9 sec	5	2.1×10^7
Pt	^{195m}Pt	4.1 d	5	3×10^3
Au	^{197m}Au	7.2 sec	4	4.3×10^7
Hg	^{19m9}Hg	43 min	6	9×10^2

these isomers can be produced from the corresponding stable state by excitation with photons of sufficiently low energy that there will be no photonuclear disintegration reactions produced in any stable nuclides except beryllium and deuterium.

The mechanism of isomer production involves the absorption of a photon by the nucleus. The nucleus is excited to an activation level from whence it decays very rapidly ($<10^{-10}$ sec) to the metastable level. The transition from the metastable state to the ground state then occurs with a characteristic half-life, and with the emission of a photon of energy that is the difference in energy levels of the two states.

The cross section-energy relationship for these reactions, frequently referred to as (γ,γ') reactions, is similar in shape to those of other photonuclear reactions. The peak cross section usually occurs at an energy of about 10 MeV and is usually less than one millibarn. Although the sensitivity is not particularly favorable, the specificity is very good. If irradiations are conducted at a suitably low energy (<7 MeV), the only activities produced will be due to the metastable isomers.

Lukens and coworkers (*102–105*), using a 3-MeV Van de Graaff accelerator and a 15-MeV linear accelerator, and Kaminishi and Kojima (*106*), using a 6-MeV linear accelerator, have examined most of the elements for isomerism, and have published tables of isomers observed, their half-lives, transition energies, and yields. The yield data of Kaminishi and Kojima are shown in Table IV. The irradiation conditions were a 1-minute bombardment with an electron beam current of 1 mA, and the electron energy shown in the table. The samples were counted in the well of a 1.75-inch × 2-inch NaI(Tl) detector. The data imply sensitivities of about 10–100 micrograms for many of the elements.

The amount of activation is very dependent on electron energy. Data by Kaminshi and Kojima show, in the range of 3 to 7 MeV, that the yield from silver is approximately propor-

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tional to the eighth power of the electron energy. This is due not only to the production of more photons of sufficiently high energy to cause activation, but also to the more favorable distribution of bremsstrahlung at high energies. Boivin *et al.* (*107*), and Engelmann and Jerome (*108*), have also made systematic studies of the analytical aspects of isomer production with photons.

Bilefield (*109*) has applied this method to the determination of silver in alloys and solders. Abrams and Pelekis (*110*) have described the determination of bromine, silver, and indium in a variety of materials.

Veres (*111, 112*) has described the production of isomers of cadmium, indium, selenium, strontium, and silver with ^{60}Co sources with strengths in excess of 100 curies. Sensitivities of several tens of milligrams of the elements were possible. Veal and Armstrong (*113*) have produced ^{87m}Sr with a 9740-curie ^{60}Co source. A 16-hour irradiation allowed the determination of 0.1% of strontium in a sample of oilfield brine. Yoshihara (*114*) determined indium in alloys by this method. Law and Iddings (*115*) have also studied radionuclide-source photoactivation with sources of 5000 and 30,000 curies.

ERRORS AND CORRECTIONS

Activation analysis is subject to a variety of errors. These include potential errors due to flux gradients, self-shielding, and interfering nuclear reactions.

The angular distribution of bremsstrahlung from a thick target is governed primarily by the multiple scattering of electrons in the target before radiation, and is described by the Schiff equation. This distribution may cause sharp flux gradients in a small space. Unless an internal standard is used, it is necessary that standard and sample occupy well characterized spaces during their irradiation. In the case of an irregularly-shaped sample, an internal standard, utilizing an element whose amount in the sample is known, is useful. This has been used in the determination of carbon and oxygen in sodium (*39, 56*), and in the determination of potassium, gadolinium, and europium in their tungsten bronzes (*82, 90*).

Self-shielding, which can frequently be of great importance in thermal-neutron activation analysis, is usually not critical in photon activation unless the samples are large or very accurate results are required. Niewodniczanski *et al.* (*67*), in their work on the determination of zinc in ores, utilized large samples with copper foils in front of and behind the samples. The average of these foils was taken as a measure of the flux associated with a specific sample. Lutz (*116*) estimated the attenuation to be expected in cylindrical samples of 1-cm diameter irradiated with the beam perpendicular to the axis of the cylinder. A simple expression was developed, giving the ratio of the flux seen by a given sample relative to a hypothetical zero-attenuation sample. This ratio is equal to:

$$e^{-t\Sigma\mu\rho}$$

where t = half of the average thickness of the sample as seen by the flux (= 0.383 × radius for a circular cross section)
Σ = sum over all elements in the sample
μ = gamma-ray absorption coefficient for each element, taken at energy of peak cross section
ρ = density of each element in the sample

Experimental results verified this simple model.

Table V. Nuclear Reactions Used for the Determination of Nitrogen and Carbon, and Interfering Reactions (Ref *49*)

Nuclear reaction used for determination	Threshold in MeV	Principal interfering reactions	Threshold in MeV
^{12}C(γ,n)^{11}C	18.7	^{14}N(γ,t)^{11}C	22.7
		^{16}O(γ,αn)^{11}C	26
^{14}N(γ,n)^{13}N	10.6	^{16}O(γ,t)^{13}N	25

Table VI. Amounts of Nitrogen and Oxygen Giving the Same ^{11}C Activity as Given by One Microgram of Carbon by Gamma Activation (Ref *49*)

Electron beam energy, MeV	Oxygen, μg	Nitrogen, μg
30	>6000	>2000
35	680	150
40	180	60
45	90	

Table VII. Amount of Oxygen Giving the Same ^{13}N Activity as Given by One Microgram of Nitrogen by Gamma Activation (Ref *49*)

Electron beam energy, MeV	Oxygen, μg
25	>2500
30	780
35	270
40	140
45	110

The problem of interfering nuclear reactions is more complicated in photon activation analysis than in thermal neutron activation analysis. This is not only because several photonuclear reactions, producing the same radionuclide from more than one stable nuclide, are frequently energetically possible, but also because neutrons are produced in the bremsstrahlung target, the sample, and structural components of the irradiation facility, and may also produce interfering nuclear reactions.

It is not possible to generalize on the extent of interference by neutrons, as this depends substantially on equipment configuration, as well as on electron energy. At the author's laboratory, ^{23}Na(n,γ)^{24}Na and ^{27}Al(n,α)^{24}Na yields are sufficiently large in the energy range of 25–45 MeV so as to make the reaction, ^{25}Mg(γ,p)^{24}Na, for the determination of magnesium worthless in most cases.

Engelmann *et al.* (*49*) have systematically studied the photonuclear interference reactions of oxygen and nitrogen in the determination of carbon, and of oxygen in the determination of nitrogen. The reactions of analytical interest, and the interfering reactions and their Q values are shown in Table V. Ratios of yields are shown in Tables VI and VII. It is neces-

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sary, of course, when large amounts of the interfering elements are known or suspected to be present, that the irradiation be carried out at electron energies below the thresholds of the interfering nuclear reactions.

For heavier elements, interfering reactions involving emission of a charged particle become less significant, because of the increasing potential barrier. A cursory study was conducted in the author's laboratory to investigate the interferences from the reactions $^{93}Nb(\gamma,\alpha n)^{88}Y$, $^{90}Zr(\gamma,n^dp)^{88}Y$ and $^{90}Zr(\gamma,2n)^{88}Zr$; ($^{88}Zr \xrightarrow{\epsilon} Y^{88}$), in the determination of yttrium, using the reaction, $^{89}Y(\gamma,n)^{88}Y$, with 35 MeV bremsstrahlung. The half-lives of ^{88}Y and ^{88}Zr are 105 days and 85 days, respectively. In the case of niobium, no ^{88}Y was observed, and an upper-limit ratio for production from niobium, relative to production from yttrium, on an atom basis, could be set at 5×10^{-5}. The zirconium sample was counted initially about three hours after irradiation, and an apparent ratio for production, assuming all of the ^{88}Y in the zirconium was produced *via* $^{90}Zr(\gamma,n^dp)$, of ^{90}Zr to ^{89}Y was about 1×10^{-4}. After several weeks, sufficient ^{88}Y had grown into the zirconium sample, that its count rate per atom of target material, corrected for length of irradiation, was of the order of 1% of that due to the yttrium. Since the ratio of the cross sections (not yields) of (γ,2n) to (γ,n) reactions of adjacent elements may be as high as 0.20, this type of error may be important in some analyses. Irradiation below the threshold of the (γ,2n) reaction eliminates this problem, but sensitivity is substantially reduced. Thresholds for (γ,2n) reactions are approximately double those of (γ,n) reactions for the same or adjacent elements.

CONCLUSIONS

Although the emphasis in photon activation analysis is on the determination of trace amounts of the light elements, it should be appreciated that the method determines many elements at trace levels. The author estimates that, at levels of 10^{-7} gram, one may determine approximately as many of the elements with an electron accelerator generating 100 μA of beam current as with a reactor source of 10^{13} n/cm²-sec. The list for photon activation includes, of course, carbon, nitrogen, and oxygen, for which it may be assumed that reactor activation analysts would be pleased to trade gold, dysprosium, and europium.

Improvements in sensitivity, accuracy, and speed in the determination of the heavier elements by photon activation will come from innovations in separation methods, radiation detector systems, and computer schemes, as well as in improved accelerator irradiation facilities. In the case of the determination of carbon, nitrogen, and oxygen, however, improvements will come almost exclusively from chemistry—rapid and specific separations.

RECEIVED for review June 29, 1970. Accepted September 23, 1970.

Use of Static Argon Atmosphere in Emission Spectrochemical Determination of Chromium in Biological Materials

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Major improvements in stability of the direct current arc and in sensitivity and precision of spectrochemical analyses have been achieved by arcing in a static argon atmosphere, with refinements of the excitation chamber described by Gordon. These techniques have been adapted to the trace analysis of ashed biological materials, especially the measurement of nanogram quantities of chromium in blood, hair, and urine. The mean relative standard deviation for quantities of chromium ranging from 1–7 nanograms in 0.2-ml aliquots of serum was 6% (triplicate analyses).

RECOGNITION OF CHROMIUM as an essential micronutrient (*1*) has increased the need for accurate determination at the nanogram level in biological materials. Human deficiency of this trace element, which may be relatively common (*2*), has been implicated in a number of disease processes (*3–5*).

Emission spectrochemical techniques have been used extensively for the determination of trace elements in biological samples, especially in large-scale survey work (*6*) for which the potential for simultaneous multielement analysis is an important advantage. These techniques, particularly with refinements of excitation conditions, are potentially very sensitive, and absolute sensitivities of the order of one nanogram or less have been achieved for many elements (*7*). Routine use of these achievements in the analysis of biological samples has been restricted by such factors as complex sample preparation or impracticable limitations of sample size.

Instability of the primitive direct current (dc) arc, and associated indifferent reproducibility, have limited the value of its inherent sensitivity (*8*). However, the static inert gas atmosphere developed and refined by Gordon (*8–10*) has

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