

# Principles, methodologies, and applications of photon activation analysis: a review

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**Abstract** This review describes the basic principles of photon activation analysis (PAA) and gives an extensive overview of its numerous applications. Uses of PAA for environmental, biological, geological, archeological, and forensic samples are reviewed. Both scientific and industrial applications of PAA are covered. Potential future uses of PAA are addressed.

**Keywords** Photon activation analysis · Applications · Review

## Introduction

There are many techniques which assure an automated, all-elemental instrumental analysis. Unfortunately, many of them require a series of subsequent dissolution and chemical separation and thus have the inherent possibility of losing analytes or altering the contamination level. In the case of activation analysis, sample preparation is simple and for a majority of samples chemical separation is not necessary. As a result, activation analysis is now being widely used in a variety of analytical problems, particularly where high sensitivity is required. Activation analysis starts with sample bombardment using neutrons in the case of neutron activation analysis (NAA), charged particles in the case of charged particle activation analysis (CPAA), or

photons in the case of photon activation analysis (PAA). During this stage a small number of atoms in the sample are transmuted into radioisotopes. The transmutation is often followed by secondary emissions from the decay of the produced radioisotopes, which may be detected and allows identifying the original elements in the sample. With careful calibration of these two steps, not only can the elements be identified, but their concentrations can also be obtained.

Because of the high neutron capture cross sections of many nuclides, NAA can be the most sensitive method of the three described above for the detection of many elements. However, the high thermal neutron flux, necessary for NAA, requires a nuclear reactor, which is not practical at most scientific institutions. Additionally, the sample size is limited—often not larger than few grams—to minimize both neutron flux disturbance and neutron and gamma-ray self-shielding. Thus, one must often destructively take small subsamples from a larger sample to fit within the reactor's activation sample parameters. When using other neutron sources, such as DT generators, some restrictions have to be accounted for: namely low cross sections and insufficient neutron flux, which greatly reduces the efficiency of NAA. Furthermore, not all elements can be detected by NAA. CPAA, which typically employs high energy protons, deuterons, or He-3 atoms, has very high sensitivity, but it has extremely low penetration depth and thus can examine only the surface of the sample.

Photons, on the other hand, can penetrate relatively deep into a medium, so the range of the sampling is not limited to the surface. For the same reason, the range of sizes and the masses of the samples can be quite large (microgram to kilogram). PAA can frequently be carried out non-destructively, which is of particular importance during investigations of antiques, artifacts and any item

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where non-consumptive analysis is required. More than 70% of all elements have properties suitable for measurement by PAA, and many of them cannot be analyzed using other activation analysis techniques. PAA sensitivity greatly depends on the properties of the sample, irradiation parameters, and detection system, but typically can be optimized to reach ng/g levels.

PAA has been established for more than fifty years [1, 2], and became widely used by the 1980s, when high intensity photon sources became available [3]. The goal of this paper is to review numerous applications of PAA in science, art, and industry.

## PAA principles and general analytical procedures

### PAA principles

Photon Activation Analysis is predicated on the physics of an energetic photon interacting with the nucleus [4]. When a photon of high enough energy strikes a nucleus, a neutron or a proton can be liberated (see Fig. 1). In many cases, the produced nuclide is unstable and will decay by  $\beta^+$  emission,  $\beta^-$  emission or electron capture, followed by emission of photons, most of which are in the energy range of  $\sim 8$  keV to several MeV. Photons in this energy range are readily measured with off-the-shelf X-ray and gamma-ray spectrometers.

The yield of the produced radionuclides ( $Y$ ) depends on a number of parameters, including the number of target nuclides that are irradiated ( $N_T$ ), the threshold energy of the nuclear reaction ( $E_{th}$ ), the photon flux density as a function of energy and position ( $\varphi(E, \vec{r})$ ), the cross-section of the photonuclear reaction ( $\sigma(E)$ ), the decay constant of the produced radionuclides ( $\lambda$ ) and irradiation time ( $t$ ):

$$Y = N_T(1 - e^{-\lambda t}) \int_{E_{th}}^{\infty} \varphi(E, \vec{r}) \sigma(E) dE d^3\vec{r}. \quad (1)$$

If both photon flux distribution ( $\varphi(E, \vec{r})$ ) and cross-section ( $\sigma(E)$ ) are known, the integral can be evaluated. Measuring the yield and the time of irradiation allows one to find  $N_T$ , which is directly related to the concentration of the isotope of interest. Such an “absolute” method,

conducted without any reference material, is rarely applied due to the difficulty in measuring or calculating photon flux distribution in the sample. Relative methods, which are performed with the assistance of reference materials, are used much more often (see “[Calibration and reference material](#)”, “[Flux monitoring](#)” sections).

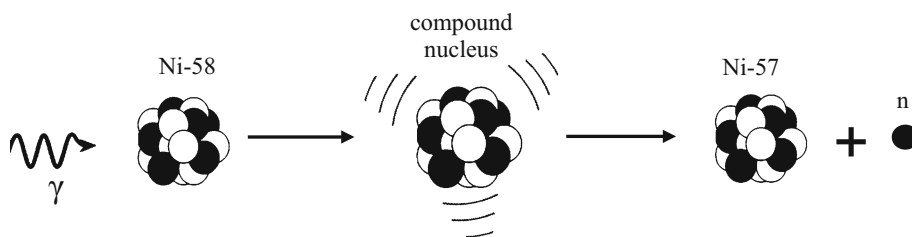
Frequently, photon activation analysis and other radio-analytical techniques, e.g. neutron activation analysis (NAA) and X-ray fluorescence analysis (XRF), are referred to as “non-destructive” methods. However, there are three different basic modes of activation analysis with varying degrees of “non-destructivity” or “non-consumptivity”, independent of the activating particle, but depending upon the nature of the respective product nuclide and the specific requirements of the given analytical task. They are:

*Radiochemical* photon activation analysis (RPAA) involves both taking samples from the item under study (before or after bremsstrahlung exposure) and radiochemical separation of the components to be determined separately using an appropriate radiation spectrometry method. A typical example is the analysis of light elements (C, N, O, F) since their activation products ( $^{11}\text{C}$ ,  $^{13}\text{N}$ ,  $^{15}\text{O}$ ,  $^{18}\text{F}$ , respectively) do not emit  $\gamma$ -radiation, but unspecific annihilation quanta and  $\beta^+$  continua only (see “[Non-standard PAA procedures](#)” section, photon activation analysis using “Non-gamma” spectroscopy).

*Instrumental* PAA (IPAA) allows sampling, but neither separation of the elements under study nor any other chemical treatment; thus, usually high resolution photon spectrometry is required for analytical multi-component evaluation. This method is used most often because high-resolution detectors enable the successful separation of the characteristic photon energies emitted by the activation products, leaving few cases where spectral interference is problematic.

In *non-destructive (aka non-invasive)* PAA the entire item under study (or an area of it, screened out by a collimator during bremsstrahlung exposure) has to be irradiated; no sampling or any other treatment is allowed. Both the exposure and the subsequent spectroscopy and data processing are quite complicated and may require special hardware and software. A typical application case is the analysis of valuable items like antiques and works of art.

**Fig. 1** Schematic representation of a photonuclear reaction. From left to right a photon is absorbed; a compound nucleus is formed; the excitation energy is released in the form of a neutron in this example



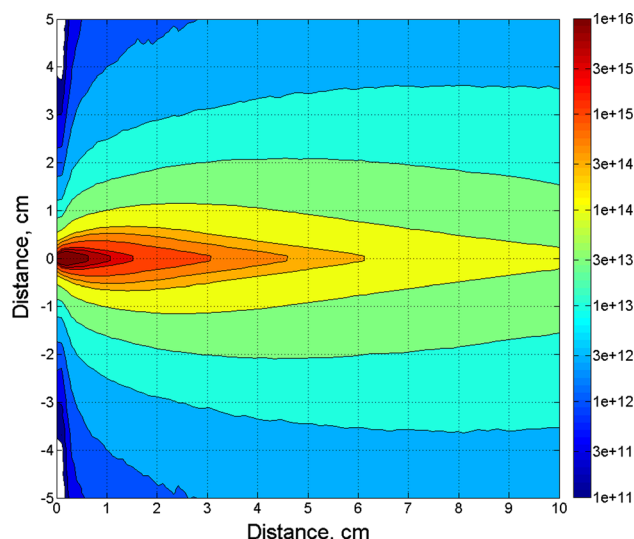
## General considerations

Regarding the literature about instrumental analytical methods including PAA, one finds a significant difference between the different fields of application, e.g., due to the various matrix compositions of the items under study. Consequently, the analyst has to select the appropriate procedure, for each individual analytical task, depending upon the range of variation of the respective matrix compositions within the field of application. For instance, when studying biological material the range of variation of the matrices (and usually the components of interest, too) normally is quite narrow, and its behavior under bremsstrahlung bombardment and during the subsequent photon spectroscopy is quite similar, thus one common procedure typically can be applied for all samples involved. Within limits this also applies to studies of medical material and organic matrices in general, and to a minor extent to environmental analyses, too. In contrast, if PAA is used for investigation of industrial material, archaeological findings, antiques, objects of art, and forensic items, the analyst might be faced with very different matrix compositions. Moreover, the decision about the mode of the analytical procedure (radio-chemical, instrumental or non-destructive approach) is often unique to the application of interest. Thus, a “standard” PAA procedure frequently cannot be applied, but appropriate individual procedures have to be developed.

## Sample preparation and exposure geometry

Proper sample preparation is of prime concern in photon activation analysis for ensuring correct calibration and thus precise and accurate analytical results. Basic preconditions for results of appreciable quality include providing high photon flux of proper energy (10–30 MeV). Unfortunately, direct measurements of photon flux distribution (spatially and in energy) are nearly impossible due to the high rates that would be required ( $\sim 10^{14}$  Hz, or higher). The bremsstrahlung photon beam, which is the most common photon beam used for PAA, is highly inhomogeneous [3], both axially and laterally. For example, photon flux density generated by a 30 MeV electron beam spans several orders of magnitude at a distance of 10 cm in the region of  $10\text{ cm} \times 10\text{ cm}$  behind a tungsten converter (see Fig. 2). One can attain greater uniformity by increasing the distance from the converter, but only at great cost in photon flux density. However, there is another option that offers multiple advantages, namely the use of an electron beam scanner (see “On-site PAA and large volume analysis” section).

Furthermore, the photon energy spectrum strongly depends on the emission angle with respect to the direction



**Fig. 2** Photon flux density ( $\text{cm}^{-2}\text{ s}^{-1}$ ) generated by a 30 MeV, 100  $\mu\text{A}$  electron beam incident on a 2.5 mm thick tungsten converter

of the incident electrons. As the emission angle increases the spectrum becomes “softer”, meaning that the proportion of high energy photons in the spectrum declines as one increases emission angle. While Monte-Carlo simulations can be done to predict the photon flux distribution even for complex setups, it is often easier to monitor photon flux using additional methods (see “Flux monitoring” section).

## Calibration and reference material

In almost all cases, instead of calculating photon flux, the sample under study, a calibration material (CM; also known as a standard or comparator, used to obtain the analytical results) and a reference material (RM, required for quality control) are activated. They should have similar properties (e.g., matrix composition and analyte contents). Typically, the CM contains the desired analytes with the highest possible level of accuracy and precision [5, 6] which is essential for calculation of the analytical result. If available, certified reference materials (CRM) are preferred for quality control. Usually the unknown sample, CM and RM are exposed simultaneously and undergo the same analytical procedure.

Theoretically, the size of the exposed items is not limited. However, several preconditions must be fulfilled [7], the most relevant of which requires equal bremsstrahlung dose received by each item exposed. This also implies the requirement of equal geometry of the items under exposure; a quasi-ideal exposure design would be a geometrically congruent package of very thin sample(s), CM and RM. However, practically this does not completely fulfill the aforementioned precondition because of the extreme inhomogeneity of the activating bremsstrahlung field.

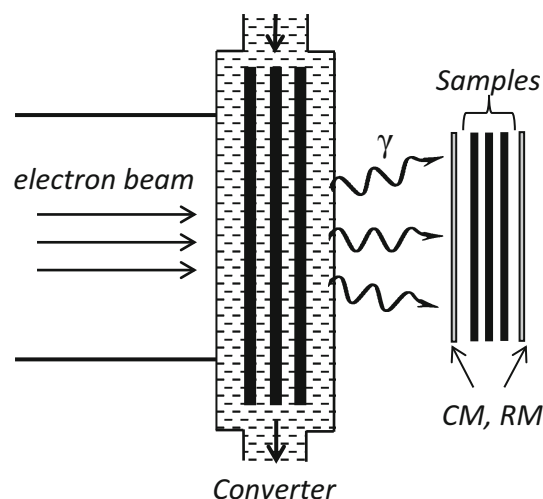
Finally, matrix effects might occur, but due to the high penetration power of the activating power of the activating photon radiation in extreme cases only, e.g. if there are huge differences in the absorption power (due to density and/or the average atomic number) and in the contents of analytes of the sample(s), CM and RM. Thus, normally matrix alignments are not necessary.

### Flux monitoring

The simplest mode of indirect flux monitoring is using external monitors. Any element or compound can be used; however, normally nuclides with a high photonuclear cross-section are chosen. External monitors are typically thin so that they do not perturb photon flux and are inserted between the materials to be exposed. A common example of an external monitor is 10–100  $\mu\text{m}$  thick Ni foil [7]. An alternative to external monitors are internal monitors which can provide much more reliable flux information, if they can be added to the samples. For best results internal monitors should be distributed in the samples at a high level of homogeneity, for example added in form of an aqueous solution, and their contents must be known with high accuracy and precision. Scandium, yttrium, and samarium have been successfully used as *additive* internal monitors [8]. Finally, in some cases, *inherent* internal monitors are present in the materials *à priori*, and no additive internal monitors are necessary. A typical example is the ultra-trace analysis of elements in a high-purity matrix [9], or a matrix with a well-known composition, one component of which can be used as inherent internal monitor [10]. The respective procedures of flux monitoring are described in detail elsewhere [7–10].

### Irradiation

A schematic representation of a typical exposure set-up is shown in Fig. 3. Photon activation analysis requires photons energetic enough to knock out a neutron, a proton, or their combination. For most nuclides, photonuclear cross-section becomes non-zero for  $E > \sim 10$  MeV, peaks at  $\sim 20$  MeV, and drops significantly at  $\sim 40$  MeV. In most cases 20–40 MeV bremsstrahlung is optimal for PAA standard operation procedures and [3]. Using higher energy gammas may result in higher yield of the activation products and thus higher sensitivity of the PAA method. However, it may also open additional reaction channels, such as  $(\gamma, 2n)$ ,  $(\gamma, np)$ ,  $(\gamma, 3n)$  resulting in numerous activation products often with interfering gamma emissions. This will complicate the gamma-spectrum and make elemental analysis challenging. Thus, optimum photon energy should be chosen on case-by-case basis. 20–40 MeV electron accelerators (primarily linacs, or microtrons), equipped with an appropriate bremsstrahlung



**Fig. 3** A typical PAA setup consisting of a water-cooled three-plate tungsten converter and samples sandwiched with CM and RM

converter, are considered to be the most intense, efficient, and convenient photon sources for PAA.

The exposure geometry (in terms of distance downstream from the bremsstrahlung converter) should be selected so that the sample package is located in the bremsstrahlung axis and within the bremsstrahlung cone. The optimal exposure period depends upon several parameters, e.g. half-lives of the activation products under study, behaviour of the sample matrices under bremsstrahlung bombardment and others.

If the bremsstrahlung converter does not have the saturation thickness to absorb nearly all electrons one has to take into account possible overheating and even destruction of the sample material. In this case a light metal filter, e.g. an aluminum layer, can be located between the converter and the sample to stop the electrons. In this case the temperature in the vicinity of the sample remains moderate. However, in any case, the sample experiences an extremely high bremsstrahlung dose which can cause radiolytic reactions which, in turn, can lead to evaporation of some analyte components and other undesired reactions. These are dependent upon various parameters, e.g. bremsstrahlung dose and energy, chemical properties of the sample components and their chemical environment, e.g. organic or inorganic. To obtain knowledge about the volatility behavior of Se, Br, I, Hg and Pb as components in different matrices several experiments were carried out by Segebede [11], particularly focusing on mercury. Efficient countermeasures against Hg evaporation were developed.

### Gamma spectroscopy

After the irradiation it is necessary to measure the induced activity of various radioisotopes in the activated materials (samples, CM, and RM). Depending on the half-lives of the

isotopes of interest (which range from seconds to years) and the activity of the samples, these can be transferred to the gamma-spectroscopy setup manually or using an automated (usually pneumatic tube rabbit or robot-operated [12]) system.

A typical gamma-spectroscopy setup consists of gamma-detectors and signal post-processing electronics including signal amplifiers, analog-to-digital converters (ADC), and multi-channel analyzers (MPA). Among the most common types of detectors used for PAA nowadays are scintillation detectors (primarily thallium-doped sodium iodide NaI(Tl)) and semiconductor detectors (mainly high-purity germanium, or HPGe). NaI detectors typically have very high efficiency due to high photo-fraction and the fact that large crystals can easily be mass produced. In addition, NaI detectors are inexpensive and convenient to use, which makes them popular for field applications. However, because of the poor resolution of NaI-based detectors (5–10% at 662 keV), they are not suitable for the analysis of complicated mixtures of radioactive elements. HPGe detectors have significantly higher resolution (0.1–1% at 662 keV) than that of NaI detectors, which allows accurate and reliable identification of radionuclides, even if their gamma lines are very close in energy. One of the disadvantages of HPGe detectors is their low efficiency in comparison to NaI, which can be partially compensated by drift configuration and crystal shape. In particular, using coaxial and well-type crystals can significantly improve efficiency relative to standard planar ones. However, standard planar HPGe detectors with 100% efficiency or more are not unusual nowadays. Another disadvantage of HPGe detectors is a necessity to keep them at approximately  $-200\text{ }^{\circ}\text{C}$  during operation. This is typically done by connecting a detector to a cryostat with liquid nitrogen, which results in low mobility of the system. Recently electrically cooled compact Ge detectors were developed [13, 14]; however, such detectors are not widely used for PAA as of yet. Alternative materials have been investigated as possible detector crystal including CdTe, CZT, and HgI<sub>2</sub> [15–17]. Among these, cadmium telluride diodes (CdTe) now are widely used for highly efficient low energy photon spectroscopy (LEPS) in different fields including X-ray fluorescence measurement, diode array digital imaging, and other applications [18]. For a good number of analytes, LEP spectra offer significant advantages of the analytical evaluation. The measurement chain of a LEP spectrometer is different from that of the classical gamma device only in so far as a planar germanium diode (typical dimensions: active area  $500\text{ mm}^2$ , active thickness 10 mm) is used. The first application of PAA using LEPS was published by Weise and Segebade in 1977 [19], see also [20, 21].

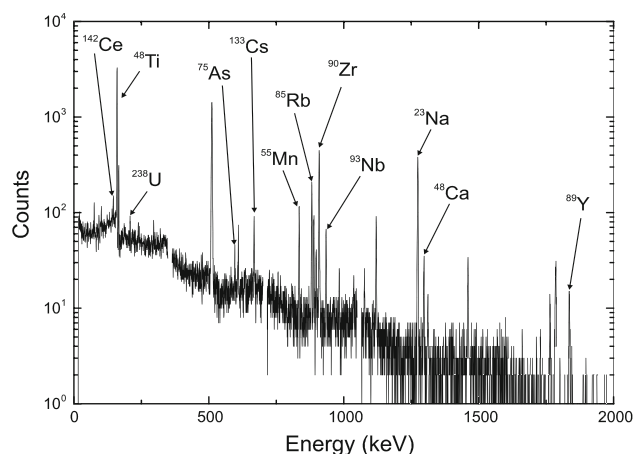
A typical HPGe detector has a built-in preamplifier which converts the electrons produced in the detector crystal by an incoming photon into an analog signal at the same time reducing noise which may degrade the energy resolution of the setup. Further signal amplification is necessary before the signal is processed by a multichannel analyzer. A typical amplifier further reduces noise, restores the signal baseline, optimizes the pulse shape, and rejects the pileup to produce Gaussian shaped, noise-free pulses whose heights are proportional to the respective energies of the photons absorbed by the detector crystal. Once the pulses are received by the MCA they are digitized by an ADC and assigned to a specific channel depending on their pulse height (and correspondingly the energy of the original photon).

### Data processing

The resulting spectrum is stored and may then be displayed and analyzed (see Fig. 4 as an example). MCAs are typically interfaced with via USB or Ethernet, but can also use PCI or RS232. A number of spectrum acquisition and processing software packages currently exist to display gamma-spectra and fit the peaks. Among them are MPANT, Genie-2000, and MAESTRO [22–24].

To calculate the activity of a certain isotope,  $A$ , one needs to measure the decay rate (or count rate) “seen” by the detector,  $dN/dt$ , which corresponds to the area under the peak of interest. This number of counts needs to be corrected by taking into account geometric and intrinsic efficiency of the detector,  $\eta$ , and the branching ratio of the transition,  $I_g$ :

$$A = \frac{dN/dt}{\eta \cdot I_g} \quad (2)$$



**Fig. 4** A typical spectrum obtained with an HPGe detector. The parent nuclides are labeled with each peak

Once the “cooling down” time  $t$  is known, the activity at the end of irradiation,  $A_0$ , can be found:

$$A_0 = \frac{A(t)}{e^{-\lambda t}} = \frac{dN/dt}{\eta \cdot I_g \cdot e^{-\lambda t}} \quad (3)$$

Often, the half-life of the isotope is comparable with the time of measurement and the decay rate drops significantly between  $t_1$  (beginning of measurement) and  $t_2$  (end of measurement). Integrating the left side of Eq. 2:

$$A_0 \cdot \int_{t_1}^{t_2} e^{-\lambda t} dt = \frac{A_0}{\lambda} (e^{-\lambda t_1} - e^{-\lambda t_2}) \quad (4)$$

And the right side of Eq. 2:

$$\int_{t_1}^{t_2} \frac{dN/dt}{\eta \cdot I_g} dt = \frac{N}{\eta \cdot I_g} \quad (5)$$

where  $N$  is the total number of counts. Then the activity at the end of irradiation,  $A_0$ , can be obtained as:

$$A_0 = \frac{N \cdot \lambda}{\eta \cdot I_g \cdot (e^{-\lambda t_1} - e^{-\lambda t_2})} \quad (6)$$

Once the yield of the isotope of interest is known for both the sample and the CM, the ratio of the yields can be found, which must be equal to the ratio of the number of the parent nuclides in the sample and the CM. Since the concentration of all the elements in the CM,  $C_{CM}$ , is well-known, one can easily find the concentration of the element of interest,  $C_{Sample}$ , in the sample using this relative method:

$$C_{Sample} = C_{CM} \frac{A_{Sample}}{A_{CM}} \quad (7)$$

When calculating concentration, the uncertainty from decay constant, detector efficiency, branching ratio, and time parameters usually can be ignored. The primary contributors to the uncertainty are total number of counts, mass of sample, and beam current.

These calculations can be done manually, or with software which would use gamma spectra to find the total number of counts for each peak as well as all necessary time information. AUTOCALC is one of such programs, written originally by the Radioanalytical Group of the Federal Institute for Materials Research and Testing (BAM) of Germany, but widely used by other groups as well. Another program, or rather a database processing system called PAAS, was written by the Idaho Accelerator Center group in 2010 [25]. All the PAAS databases are stored on a server, and a user can run it with a web browser which makes PAAS a convenient cross-platform program. A number of other gamma-spectrum analysis software are available as well [26, 27].

## Detection limits, validation, quality control

Like in all analytical methods, the achievable PAA detection limits depend upon many experimental parameters (bremsstrahlung energy and flux density, exposure geometry and sample mass, exposure and measuring periods and many others). Selected detection limits under standard conditions are listed in Table 1. A complete compilation was published by Segebade et al. [8, 20].

Normally, the different standard PAA versions (see “PAA principles” section) are validated through comparison campaigns using different conventional and radioanalytical methods (ICP-MS, NAA, XRF and others if applicable). However, in rare cases several PAA techniques have not been validated, several non-standard procedures in particular.

Usually, quality control has been carried out by simultaneous PAA of appropriate reference materials (see “Calibration and reference material” section). However, as in validation, in some cases the standard quality control procedure cannot be applied because of non-compatible exposure and measurement geometry if large items with irregular geometry have to be analyzed non-invasively, e.g. antiques and objects of art.

## Non-standard PAA procedures

As to extraordinary analytical applications, the standard PAA operation procedure might not be applicable. A typical example is the analysis of inhomogeneous material. In this case, PAA offers the opportunity to analyse large samples (up to kilogram amounts), thus minimising inhomogeneity problems [28]. Moreover, non-invasive analyses of large-size items of high value, e.g. antiques or objects of art can be carried out [29]. Analyses of liquid and gaseous

**Table 1** PAA detection limits of selected elements

Element	Detection limit ( $\mu\text{g}$ )
Carbon	0.1
Oxygen	0.05
Fluorine	0.001
Sodium	150
Calcium	5
Titanium	0.05
Nickel	0.6
Arsenic	0.5
Zirconium	0.3
Thallium	0.4
Lead	1
Uranium	0.001

samples have been carried out only in rare cases; to the knowledge of the authors the latter has been reported only once [30]. In some of these PAA procedures, simultaneous exposure of the samples/calibration-/reference materials is not possible. In these cases the application of flux monitors is indispensable. However, due to possible inconstancy of the output energy of electron accelerators (linear ones in particular) an increase of the total uncertainty budget of the analytical results is unavoidable. One way out is to use a circular machine for photo-activation, e.g. a high-power microtron [3].

Another non-standard PAA application is the analysis of light elements (mainly C and O) in alkali metals. This cannot be performed instrumentally since the respective analytes do not emit gamma radiation after bremsstrahlung exposure but unspecific annihilation radiation and  $\beta^+$  continua only. Thus, radiochemical separation has to be applied. After irradiation the samples have to be dissolved in water, and the analyte radionuclides ( $^{11}\text{C}$  and  $^{15}\text{O}$ , respectively) are separated from the alkali matrix by fast radiochemical distillation [30–33].

### Photon activation analysis using “non-gamma” spectroscopy

Unlike thermal neutron activation analysis PAA can well be used for determination of Light Elements, e.g. C, N, O, F. Normally, after bremsstrahlung exposure the product nuclides  $^{11}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{O}$  and  $^{18}\text{F}$ , respectively, have to be separated from the sample matrix by a fast radiochemical procedure, and the different fractions have to be counted separately [34, 35]. Instrumental PAA of the light elements can be performed in very few cases only [36]; as described below in Industrial Applications section. However, Segebade and Goerner [37] developed a PAA procedure for instrumental determination of C, N, O, and P in organic matrix using both annihilation radiation and differential  $\beta^+$  continuum counting, for the latter using plastic scintillator spectroscopy. Analysing a BCR Reference Material (“Milk Powder”) excellent accuracy and precision of the result were obtained.

### Environmental analysis

A significant fraction of publications discussing multi-element photon activation analysis deals with environmental applications. One of the reasons might be that several elements of environmental interest (for example Pb or Tl) can be easily analyzed even in trace quantities using PAA. Also, as environmental samples are activated, many matrix elements, quite abundant in nature (for example Na), do not produce isotopes with complex interfering gamma-spectra. Other matrix elements, such as carbon,

oxygen, or silicon, produce rather short-lived radioisotopes, which mostly can be ignored. Most of the environmental applications refer to air (or, rather, air-born particulate filters). The most common air filter materials include polystyrene, polypropylene, quartz fibers, cellulose, and paper. Soil samples have been studied in an environmental context frequently, too.

One of the first papers on instrumental PAA of air particulates was published in 1973 by Aras et al. [38]. Concentration of fourteen elements (including Ca, Ti, Ni, Sr, I, and Pb and other elements which are difficult to determine using NAA) was measured with high quality of results (<5%). It was shown that PAA of air particulates could be used in the systematic study of car emissions. Several thorough detailed investigations of activation analysis of air particulate matter were carried out, e.g. by Alian and Sansoni [39] and Roberts et al. [40].

Analyzing soil samples poses different challenges compared to air filters. Usually much more sample material is available for analysis, so the mass of the elements of interest is significant. However, substantial soil matrix often produces significant interference background after bremsstrahlung exposure, e.g. by calcium ( $^{42}\text{K}$ ,  $^{43}\text{K}$ ,  $^{47}\text{Ca}$ ,  $^{47}\text{Sc}$ ); see also below, Geochemical Analysis. A number of publications presented analysis of soil samples in the vicinity of potential pollution sources such as lead refineries, sewage farms, etc. to investigate toxic element propagation. It was shown that Pb, Cd, Hg, and other toxic elements can be reliably detected in with high sensitivity.

Since the 1970s numerous studies have been performed comparing air and soil quality in urban and rural, industrial and residential areas. Results of airborne particulate were published by Jervis et al. [41], Aras et al. [38], and Segebade et al. [42]. An analytical intercomparison study of air particulate filters using five different instrumental techniques was carried out by Cawse et al. [43]. Soil samples were studied by Chattopadhyay and Jervis [58], Williams and Hislop [44], Chattopadhyay [45] and Segebade et al. [46]. Further studies of various matrices were performed by Jervis et al. [47], Chattopadhyay et al. [48], Jervis et al. [49] and others. Among them it was shown that the trace component pattern of human hair can serve well as an indicator of environmental pollution. Scalp hair was analyzed, e.g. by Jervis et al. [56].

### Analyses of biological and medical materials

The applicability of PAA to biological materials was first investigated in late 1960s. Most of the fundamental biomolecules contain a very limited number of elements: C, H, O, N and S. Some of them, for instance nucleic acids, also contain P. Some trace elements, such as Co, Cr, Cu, B, F,

Fe, I, Mn, Mo, and Zn, are essential for plant and animal life. Others, such as Pb, Tl, Se, Cd, and Hg are of toxicological concern. Since biological matrices generally do not produce high background radiation, they allow identification of numerous trace elements with PAA, both essential and toxic [50–53]. Multielement analysis of such biological samples was an important contributor to expediting studies of the role of trace elements in biological systems.

Both radiochemical and instrumental PAA have been used to study uptake and assimilation of different elements by plants, animals, and humans [54]. Analyses of biological materials have been frequently conducted within an environmental context. Elevated concentrations of toxic elements in plants, animals, and humans have often been used as an indicator of exposure to environmental pollution [55–59].

Many metal species are capable of producing toxic effects in humans, and typically they are removed less effectively from the body than organic chemicals [60]. Analysis of trace elements in human body tissues can reveal accumulation of toxic elements and help with establishing a correlation between trace element distribution and certain disorders. Activation analyses have been used to determine a number of trace elements in hair, blood, urine, serum, teeth, and tumor tissues [52, 61]. Additionally, a number of *in vivo* PAA studies were done to investigate concentration changes of several elements in tissues during radiotherapy of cancer treatment patients [62, 63].

## Geochemical analyses

In comparison to biological samples, rocks and minerals are typically heat resistant and can withstand much higher bremsstrahlung beam power. However, in many cases background activity from rocks or ores is very high. For example, limestone activated with photons with energies greater than 16 MeV produces a very intense and complex gamma ray background ( $^{42}\text{K}$ ,  $^{43}\text{K}$ ,  $^{47}\text{Ca}$  and  $^{47}\text{Sc}$  lines; see also above, Environmental Analysis). Activated copper ores also produce very high background which does not allow measurement of any isotopes with half-lives of up to few hours. Despite these limitations, PAA of rocks and ores has been performed by many analytical groups. Both major and minor components of rock material including Mg, Ca, Ti, Ni, Sr, Rb, Zr, Cs, Ta, and other elements were successfully quantified (see also “PAA in mining” section).

## Analysis of liquids

PAA of liquid matter has been reported relatively rarely; in the most cases water has been analyzed. As far as the

authors know, PAA of “non-water” has been reported only once (determination of halogens in waste oil samples [64]). Analyzing water samples using conventional methods, frequently the analytes, trace components in particular, are pre-concentrated to enhance their detectability, e.g. by precipitation. However, in using such methods one has to bear in mind sources of erroneous analytical results, e.g. due to complexation behavior of some trace analytes, which eludes the pre-concentration process. Moreover, this bears the risk of contamination of the sample under study. Conversely, PAA and other activation analysis methods offer the opportunity of activation of the water sample “as is” and allows subsequent post-concentration followed by radiation spectroscopy. Thereby any contamination is avoided, and complexed species in the sample are destroyed radiolytically, thus enabling concentration with any method [65].

Wilkniss and Linnenboom [66] reported determinations of fluorine and other elements in sea water using photon activation after lyophilisation (freeze drying).  $^{18}\text{F}$  produced by  $^{19}\text{F}(\gamma, n)^{18}\text{F}$  was separated from the sample matrix through distillation since it does not emit any  $\gamma$ -rays, but  $\beta^+$  continua and unspecific annihilation radiation (511 keV) only. Wilkniss et al. [67] developed other methods of  $^{18}\text{F}$  separation, as well. A similar analytical procedure was applied for analysis of strontium in sea water by Gordon and Larson [68]. After bremsstrahlung exposure they separated strontium by precipitation as  $\text{SrCO}_3$ . A separation scheme of fluorine, chlorine, bromine, and iodine in one water sample was also developed by Wilkniss [69]. A thorough evaluation of nuclear interference reactions was published by Wilkniss et al. [67, 69, 70]. In an inter-laboratory test published by Knoechel and Petersen [71] the multi-element analysis results of an Elbe river (Germany) water sample were presented. Thirty-three laboratories participated, using seven different methods in various versions, including PAA.

## Analysis of cosmogenic material

Cosmogenic material is a special type of geochemical sample which is typically very precious due to their unique character and analysis of such samples benefits greatly from non-destructive testing. Meteorites are the most common cosmogenic objects which can be studied to determine the history and origin of their parent bodies. PAA work on meteorites began in 1969, when concentrations of the main constituents of iron meteorites (namely iron and nickel) were measured [72]. Shortly afterward, beryllium content in stony and iron meteorites was determined using PAA [73]. Since then many other meteorites have been analyzed including the Pueblito de Allende,



Kobe, and Moravka H5-6 [74–77]. Concentration of more than 40 elements, including rare earth metals, transition metals, halogens, and lanthanides were measured and found to be in good agreement with the results from other analytical techniques. Libyan Desert glass (LDG), whose origin is considered to be meteoritic, but still uncertain, has also been analyzed [78]. PAA and NAA data confirmed the concept of LDG formation by an impact of an extraterrestrial body into Cretaceous Nubian sandstones.

With plans to resume human exploration of the Moon, it is imperative to fully understand the hazards that dust can cause and to determine ways to minimize these effects. It was shown that lunar rocks and dust samples can be analyzed with PAA quite effectively [38, 79, 80]. Further PAA studies of cosmogenic material from the Solar system will be very interesting if such samples are brought back to earth.

## Archaeology, paleontology, and forensic sciences

### Objects of art

Investigation of antiques, objects of art and archaeology, and other precious items is another application of PAA where its minimal destructiveness plays an important role. These items in general require particular or custom analytical procedures. First and foremost, each operational step, beginning with acquisition, e.g. during excavation of archaeological items, until the successful completion of the analysis, any damage must be avoided (“Non-destructive” analysis). In extreme cases the analysis has to be performed touch-free [81]. Furthermore, the unavoidable radioactivity induced through activation is of concern. In this instance IPAA is advantageous as compared to INAA, since in some cases the generation of undesired long-lived radioactivity can be avoided by making use of the energy thresholds of the different photoreactions [3]. Finally, one has to bear in mind that in some cases damage of the item under study might be induced during exposure to the activating radiation, such as irreversible color change of glass objects.

An excellent example is an investigation of ancient weaponry [82]. In this case a whole medieval sword was irradiated at an electron linear accelerator and the induced activity was measured with a standard radiation spectrometer. The analysis of the elemental composition of the different materials (steel and gold decorations), together with the results of absolute age determination and stylistic studies carried out by weaponry experts, allowed the sword to be attributed to King Edward III of Britain (or his eldest son, the Black Prince) with a high degree of probability. Another attribution example was made during an analytical study of 18th century furniture metallic decorations in

several monasteries in Bavaria, Southern Germany. Analysing the trace impurity patterns of the different metal items using PAA, the location of production (a workshop near Passau, Bavaria) could be clearly stated for most of the objects [83].

### Paleontological and archaeological applications

A similar utility for PAA is the study of paleontology objects, for example fossils, which are a limited and valuable scientific resource. The elemental concentrations found in fossils can be used to study migration patterns [84], diet, trophic level, climate, and can be used for paleoenvironmental reconstruction [85]. In particular, rare earth element concentrations in fossils are often used to study taphonomy [86], depositional environment [87], and provenance [88], as well as to constrain the age range of a species [89]. Rare earth elements increase by orders of magnitude [84] during the diagenesis process in fossilization. This leads to fossils having rare earth element concentrations typically on the order of 10–10,000  $\mu\text{g}$  per gram [90, 91], which are easily detectable with PAA.

At the moment, no published work has been done on the use of PAA with fossils; however, PAA has been used to study sediment profiles of the Jurassic-Cretaceous boundary [92] and it has been used to determine the elemental concentrations in a geochemical history study of the Cenozoic volcanic region of the Bohemian Massif [93].

There are currently no non-destructive techniques for studying the elemental composition of fossils; thus, PAA has a very valuable potential. Similar activation techniques (NAA) are already well established in the palaeontology field; however, the low penetrating power of neutrons requires samples to be ground into a powder if a full elemental composition is desired. This is not ideal, as fossils provide two main pathways for scientific information: the physical characteristics, such as bone structure, morphological, and pathological indications, and the elemental composition. PAA is able to analyse the elemental composition of the entire sample, while maintaining the physical characteristics, unlike other techniques.

Recent work has investigated the use of PAA with fossils [94]. A provenance study was undertaken by using PAA with pairs of fossils and their surrounding rock (matrix). Thirty-one elements were identified in four sample pairs. PAA was used non-destructively, keeping the physical characteristics of the fossils intact. The work was motivated by the need for a reliable method to identify fossils illegally taken from Federal land. PAA has much potential utility as a forensic tool, due to its non-destructive capability.

PAA can contribute to studies of many other archaeological artefacts. For instance, PAA might help to find

evidence of raw material processing techniques in antiquity. In favourable cases entire manufacturing process chains can be traced. Coincidentally, analytical results can help to find evidence of forgery, e.g. through indirect determination of the date of production of an item that had been estimated to be produced in antiquity. For example, in 1979 three hundred ancient Roman copper coins, estimated by experts of numismatics to be produced during the regime of Emperor Augustus (about 2000 years ago), were analysed by IPAA. Two of these coins were identified as forgeries by their trace impurity patterns. First, their total matrix impurity did not exceed 100 µg per g. In contrast, total impurity of unalloyed copper of less than 0.5% could not be produced during this period. Second, it was obvious that their matrices were produced by electrolytic purification, probably obtained from industrial copper scrap.

### Forensic science applications

PAA can also be an excellent tool for match analysis in forensic science. Fibers, hair, soil, wood, gunshot residue and pollen are only a few examples of trace evidence that may be transferred between people, objects or the environment during a crime. It is inevitable that the destruction or alteration of trace evidence negatively impacts preservation, retesting, and further analysis. PAA has been successfully used for match analysis of glass, hair, and stainless steel samples [55, 95, 96]. For example, in [96] it was shown that that PAA can measure concentrations of various impurities in stainless steel knife blades. If suitable elements are selected, PAA can tell the difference not only between different knife brands, but also between individual knives of the same brand. PAA can be successfully used for match analysis and attribution studies while preserving the integrity of the samples.

Quick and reliable trace elemental and isotopic analysis is essential to national defense and security. PAA may be able to provide information on the origin of stolen or diverted nuclear material and attribution (i.e.—tracking back the source of such material to help identify the perpetrators). Additionally, it can help with detecting counterfeit electronics used in US military equipment. A 2012 Government Accounting Office investigation found that the use of counterfeit parts among military-grade electronics was significant, and could seriously disrupt system integrity and endanger troop's lives [97]. PAA can be used to distinguish between the original and the counterfeit parts and thus improve the reliability of military equipment. It could also be used in conjunction with a spikant or taggant (i.e.—intentionally introduced trace elements) that could positively identify genuine parts.

It is also possible to use PAA to assess the relationship between trace elements in illicit drugs and the soils in

which they were grown. Plants originating from different locations have different concentrations of certain trace elements [54]. Thus, activation analysis can serve as a means to “fingerprint” and thereby trace the origins of illicit drugs. Similar applications to detecting and tracing hazardous materials, explosive materials, and other materials of interest might be exploited in the future.

### Industrial applications

#### PAA in mining

One of the most common industrial applications of PAA is in mining. PAA is good for special cases when a concentration of a certain element needs to be quickly known. A particular case is the analysis of noble metals in ores and metallurgical residues of ore processing. Due to large reaction cross sections and favourable spectra of the activation products, PAA allows extremely precise and accurate analyses of small traces of noble metals, gold in particular.

Isomeric state PAA determination of silver, gold, and the PGE, except rhodium and palladium, were reported in a systematic study of all elements having isomeric states with suitable nuclear parameters [98]. Isomeric excitation of gold in ores was also reported by Kapitsa et al. [99]. Ore samples of 100–200 g were exposed to 9 MeV bremsstrahlung from a microtron and gamma spectrometry was carried out using NaI(Tl) detectors. A similar procedure was applied by Bourmistenko [100], Pchelkin et al. [101], and Tickner et al. [102]. Sample masses as large as 500 g were exposed to 8 MeV bremsstrahlung from an electron linac. The common problem of isomer excitation is the comparably short half-life of most of the activation products, e.g. 7.3 s for  $^{197m}\text{Au}$ . Thus, an extremely fast sample transfer facility is indispensable unless the detector (heavily shielded) is placed right next to the sample. In this case the sample transfer time is minimized and the extremely short lived isotopes can be observed as the researchers are limited solely by the detector recovery time (typically tens of milliseconds).

Using longer lived radionuclides for the analysis, for example  $^{196}\text{Au}$  (half-life of s 6.2 days) produced via  $^{197}\text{Au}(\gamma, n) ^{196}\text{Au}$  reaction, makes sample transfer easier, but requires longer irradiation and higher energy electron beam at the same time resulting in lower sensitivity [103].

#### Impurity and trace component analysis

Determination of Pd, Ag, Pt, and Au in high purity copper by PAA was reported in the 1970s [104]. Sets of samples with different noble metal contents had been produced by

the European Community Reference Bureau (BCR). These were analyzed by several qualified laboratories as candidate reference materials. Most of the samples were analyzed instrumentally. Only those with the lowest contents of Pd and Pt (about 1  $\mu\text{g/g}$ , respectively) had to be processed radio-chemically after bremsstrahlung exposure; Pd and Pt were separated from the matrix electrolytically and by co-precipitation, respectively.

Since the properties of many metals are influenced significantly by the contents of non-metals, the light elements: C, N, O, F in particular, the trace determination of these has been reported frequently. In most of the cases, radiochemical separation of these analytes has been reported. For instance, radio-carbon, -nitrogen and -oxygen produced through photo-activation of metal samples have been separated through oxidising or reductive fusion heat extraction and measured sequentially by annihilation spectroscopy [34, 35, 105, 106]. Fluorine has been separated in almost all cases by radio-chemical distillation [107] (see above in 5.1 and [46, 49]). Instrumental analyses of the light elements can be carried out only in rare favourable cases [36, 108].

PAA has been applied frequently to the analysis of coal and coal-related material. Instrumental multi-element procedures have been preferred in almost all cases [109–112]. This is due to the fact that the carbon matrix mostly does not produce any significant background radiation. Thus, extremely small traces of components of interest can be detected and quantified with a high level of accuracy and precision.

### Industrial waste

During the last decade, major attention has been paid to the analytical investigation during recycling processes of different waste materials. Major objectives have been, first and foremost, to find possible sources of materials needed for future re-use, and second, to develop strategies of handling hazardous components, e.g. avoidance of landfill. Different kinds of waste material, such as those of industrial origin in particular, were brought into focus. One example of waste characterization for future segregation is described by Segebade et al. [18]. PAA of material volumes up to several litres, e.g. electronic waste, were performed. Both hazardous and useful components could be determined with good precision. The accuracy of the PAA results was obtained by comparison with values found by high volume INAA [113]. Similar work was done by Tickner et al. [114], who demonstrated that PAA provides a powerful tool for analyzing both valuable and hazardous elements (such as gold, silver, copper, tin, bromine, and lead) in waste materials.

Finally, due to the vast variety of matrices and analytes of industrial relevance a great number of technical reports have been published. Several miscellaneous applications of PAA in this field have also been reported [115–118].

### Comparison of paa with other analysis methods

In Table 2 below, we compare photon and neutron activation analysis techniques with other modern instrumental analytical methods in terms of trace analysis capabilities, hardware costs, effort to process the sample, invasiveness, etc. Normally only elements can be detected; determinations of chemical species are possible in only a few exceptional cases.

We can divide these delineated instrumental analytical methods into three broad categories:

- Nuclear techniques (PAA, NAA, CPAA, PIGE).
- Atomic radioanalytical techniques (PIXE, XRF, TXRF).
- Inactive atomic spectroscopy techniques (AAS, ICP).

These techniques are defined as follows:

PAA	Photon activation analysis; exposure to bremsstrahlung from electron linear accelerators or microtrons; product activities measured using $\gamma$ , low energy photon or $\beta$ -spectrometry
NAA	Neutron activation analysis; exposure to neutrons from nuclear reactors, neutron generators or electron accelerators; product activities measured using $\gamma$ -spectrometry. A variant of NAA is the Prompt Gamma Neutron Activation Analysis (PGNAA) when the spectrum of the promptly emitted gamma radiation is evaluated
CPAA	Activation analysis with particles carrying positive charge; exposure to high-energy positive ions, usually protons, from accelerators with electrostatic or cyclic operation mode; product activities measured using $\gamma$ -spectrometry
PIXE	Particle/proton-induced X-ray emission spectrometry; electron shell excitation and subsequent X-ray fluorescence emission effected by high-energy positive ions from accelerators with electrostatic or cyclic operation mode; fluorescence measurement by low energy photon spectrometry
PIGE	Particle/proton-induced $\gamma$ -ray emission spectrometry; measurement of prompt $\gamma$ -ray emission effected by nuclear reaction induced by exposure to charged particles, usually protons, from accelerators with electrostatic or cyclic operation mode; prompt gamma-ray measurement by $\gamma$ -spectrometry

**Table 2** Comparison of photon activation analysis with other modern instrumental analytical methods, both applied during standard analysis procedures

Feature	PAA	NAA	CPAA	PIXE	PIGE	XRF	TXRF	ICP	AAS/AES
Detectable elements <sup>a</sup>	Many, few exceptions	Many, few exceptions	Mostly light elements	Z > 8	Mostly light elements	Z > 8	Z > 8	Many, few exceptions	Many, few exceptions
Chemical treatment <sup>b</sup>	No	No	No	No	No	No	Yes	Yes	Yes
Trace analysis <sup>c</sup>	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Non-destructive <sup>d</sup>	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	No
Bulk versus Surface analysis	Bulk	Bulk	Surface	Surface	Surface	Surface	Bulk	Bulk	Bulk
Large volume analysis <sup>e</sup>	Yes	Yes	No	No	No	No	No	No	No
Hardware costs <sup>f</sup>	Considerable to very high	Very high	Considerable	Considerable	Considerable	Moderate	Considerable	Considerable	Moderate
Sample processing effort	Moderate	Moderate	Considerable	Considerable	Considerable	Moderate	High	High	High

<sup>a</sup> Detectable at high precision without inordinate effort

<sup>b</sup> All radioanalytical methods except PIXE/PIGE can be used including radiochemical treatment, too. In rare cases, ICP and AAS/AES can be performed without chemical sample processing

<sup>c</sup> Sub-mg amounts

<sup>d</sup> Whole-object analysis without sampling using CPAA or PIGE non-destructive analysis is possible in very few cases only; if performed using ICP (LA-ICP; Laser Ablation ICP) no bulk analysis is possible

<sup>e</sup>  $\geq 0.5$  L, PAA, NAA require large photon/neutron beam facility

<sup>f</sup> PAA: considerable for LINAC activation; very high for microtron activation

XRF	X-ray fluorescence spectrometry; electron shell excitation and subsequent X-ray fluorescence emission effected by high energy photons from X-ray tubes, accelerators or radionuclide sources; fluorescence measurement by low energy photon spectrometry
TXRF	Total reflection X-ray fluorescence spectrometry; Basic principle, excitation mode, spectroscopy see above, XRF; special sample preparation and excitation geometry
ICP	Inductively coupled plasma spectrometry; high temperature atomic electron shell excitation by Noble Gas (usually argon) plasma, followed by either optical emission spectroscopy (ICP-OES) or (currently in the most cases) mass spectrometry (ICP-MS)
AAS/ AES	Atomic absorption/atomic emission spectrometry; high temperature atomic electron shell excitation by acetylene-oxidant torch (flame AAS) or by graphite furnace heating (graphite furnace or flameless AAS) and other operation modes for special procedures; analyte signal obtained by optical (UV/VIS) spectrometry.

## Future steps

PAA is one of the first nuclear analytical techniques and it remained an important role in elemental assays for many years. Other instrumental methods, including radioanalytical techniques, grew in popularity in 1980s and partially supplanted PAA in some areas. Nevertheless, in many situations PAA has advantages over NAA, ICP-MS, and other instrumental methods. Moreover the dramatic development of high power electron accelerators during the last two to three decades has restored interest in photon activation analysis. Other factors also are promoting or could promote a PAA renaissance Perhaps the two most important are:

- (i) the prospect of increased availability of precise photonuclear activation cross sections (or the more fundamental exclusive differential photonuclear cross sections) which are important for many applications in security, non-proliferation, isotope production and PAA
- (ii) the potential for precise bremsstrahlung flux-density information as a result of advances in small accelerators, particularly in the areas of real-time electron beam controls and measurement of beam emittance and energy dispersion.

These and other prospective achievements would open the field for further applications of PAA as well as for significant improvement of PAA results in terms of detection sensitivity, accuracy and precision. Some examples of these expanded PAA applications and opportunities are listed below.

## Quasi calibration-free IPAA

Quasi calibration-free IPAA was developed to conduct PAA without any assistance from calibration materials. According to Eq. 1 the two most critical variables in calculating induced activity  $Y$  are the energy-differential activation cross section  $\sigma(E)$  and the energy-differential activating photon flux density  $\varphi(E)$  whilst all other parameters (timing, number of target nuclides, etc.) can be determined with high precision. By virtue of the aforementioned prospective improved precision and accuracy of  $\sigma(E)$  and  $\varphi(E)$ , the induced activity (and the analytical results thereof) can theoretically be obtained with satisfactory precision. Satisfactory precision, of course, depends entirely upon the application. For some applications that merely require low-precision answers to the presence of certain elements, we may have adequate data today for calibration-free IPAA. In contrast, if high precision and accuracy is required, more and better photonuclear data is needed, as is better information about the bremsstrahlung-producing electron beams.

To the best of the authors' knowledge there are two different approaches to this technique. First, the yield can be calculated purely by using the respective physical basic parameters [120]. Second, an experimentally obtained yield factor  $Y_0$  can be used to calculate the results. This approach has been derived from the  $k_0$  method [119], a technique of the evaluation of data obtained in instrumental neutron activation analysis (INAA). However, both approaches still need further development to improve the overall quality of the results.

## On-site PAA and large volume analysis

Preliminary laboratory experiments using stationary linacs have been carried out [65]. Furthermore, on-site analysis of large material volumes can be performed. Sample amounts of up to several kg were studied by laboratory-scale analyses (see “Non-standard PAA procedures” section). With the availability of small mobile high energy bremsstrahlung sources, particularly S-band and X-band linacs [120], these and other applications of IPAA are potentially possible, with the caveat that current technology in this area generally provides low power electron beams at the beam energies of interest and this, in turn, would limit sensitivity.

## Analysis of fissile material

Photon activation analysis of fissile elements is problematic. The photon spectra after exposure to the activating radiation are quite complex due to the vast number of photofission products. Therefore, a precise isotope speciation is complicated because of multiple spectral interferences, as well as limited photonuclear data for these complex reactions. As far as the authors know, photonuclear reaction of fissile species for traditional PAA application has been applied for the determination of uranium (more exactly:  $^{238}\text{U}$ ) only [118]. However, in non-traditional PAA applications, such as nuclear nonproliferation, nuclear safeguards and similar security applications, extensive work in this area has been done by many, especially Harmon et al. [121]. Nonetheless, there remain many prospective opportunities for which further study of fissile isotope determination by PAA is needed.

## Conclusions

PAA is a powerful analytical tool with potentially dramatic impact on a variety of applications in science, industry, and national security. It is a relatively complex method with each new application introducing a new set of questions concerning subjects such as sample composition and geometry, sensitivity for a particular isotope of interest, interfering reactions, optimum beam energy, sample heating and induced radioactivity, and others. We described a wide spectrum of applications which benefited from use of PAA—from forensic science and anthropology to environmental science and geochemistry. Still, we firmly believe that more uses of PAA are to come. We hope that our review will provide PAA with a rightfully deserved boost of interest from the researchers in many areas of science and industry.

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