Titre: Title:	Application of the k0 method in neutron activation analysis and in prompt gamma activation analysis
Auteurs: Authors:	Zsolt Révay, & Gregory Garth Kennedy
Date:	2012
Type:	Article de revue / Article
Référence: Citation:	Révay, Z., & Kennedy, G. G. (2012). Application of the k0 method in neutron activation analysis and in prompt gamma activation analysis. Radiochimica Acta, 100(8-9), 687-698. https://doi.org/10.1524/ract.2012.1957

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/5111/
Version:	Version officielle de l'éditeur / Published version Révisé par les pairs / Refereed
Conditions d'utilisation: Terms of Use:	CC BY-NC-ND

Titre de la revue: Journal Title:	Radiochimica Acta (vol. 100, no. 8-9)
Maison d'édition: Publisher:	Oldenbourg Wissenschaftsverlag
URL officiel: Official URL:	https://doi.org/10.1524/ract.2012.1957
Mention légale: Legal notice:	

Radiochim. Acta **100**, 687–698 (2012) / **DOI** 10.1524/ract.2012.1957

Application of the k_0 method in neutron activation analysis and in prompt gamma activation analysis

By Zs. Révay[1,*] and G. Kennedy[2]

[1] Technische Universität München, Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), 85747 Garching, Germany
[2] Ecole Polytechnique, Montreal, Quebec, H3C 3A7, Canada

(Received January 31, 2012; accepted in revised form February 17, 2012)

k_0 method / Standardization / Neutron activation analysis / Prompt gamma activation analysis

Summary. The k_0 method is a highly successful standardization method developed for Neutron Activation Analysis (NAA), later also introduced in Prompt Gamma Activation Analysis (PGAA). After the careful calibration of the irradiation and counting facilities, the k_0 method makes the use of elemental standards unnecessary. Masses of the components are determined relative to the flux monitor, or, in the case of PGAA, to other known components of the sample. The development of the method is summarized in this review together with the description of methods implemented at different laboratories. The activities carried out in the laboratories of the authors are described as examples for the successful implementation of the k_0 approach to activation analysis.

1. Introduction

Activation with neutrons results in two distinct reaction processes: immediately after neutron capture, prompt gamma radiation is emitted, and in cases when radioactive nuclides are formed, delayed beta and gamma radiation is also released. The detection of the neutron-induced radioactivity was first recommended for chemical analysis by György Hevesy (in international literature George de Hevesy) in 1936, just a few years after the discovery of neutrons [1]. In the same decade, the prompt activation of nuclei was also discovered [2,3]. From the early 1960s, neutron activation analysis (NAA) was a quickly developing technique at the first generation of research reactors. Since then, NAA has become one of the most reliable methods for trace-element analysis. The first reactor-based prompt gamma activation analytical (PGAA) experiment was performed at the Institut Laue-Langevin (Grenoble, France) using a chopped neutron beam from a reactor and detecting the gamma rays with a NaI(Tl) detector in 1966 [4,5]. In the same year, neutron guides were proposed for neutron capture measurements [6], and in just a few years, the first in-beam PGAA measurements were performed in Garching and Saclay [7,8]. However, the real development of the method started only two decades later. Since the 1970s, high-resolution semiconductor detectors, nowadays high-purity germanium (HPGe) detectors, have been used to acquire gamma spectra.

Though there are now many competitors of the nuclear analytical techniques, both activation-analysis techniques have their advantages, which will ensure their positions in the most important neutron research centers.

At many laboratories, both PGAA and NAA have been performed using the relative method: the gamma spectra of the irradiated samples are compared to those of similarly prepared standards containing the elements in question. For one analysis, several measurements have to be performed, and this may require a huge collection of expensive reference materials. The standardization of the method became increasingly important in order to make the reliability of the method independent of the practices followed at the different laboratories. In this paper, we deal with the most successful standardization technique, the k_0 method, as applied to both techniques.

2. Theory

Both neutrons and gamma photons have a relatively long mean free path in matter (typically of the order of centimeters in H-free matrices), that is why NAA or PGAA provide information on the whole irradiated volume. In practice, the ideal conditions can be approximated well enough when the illumination of the sample can be regarded as uniform and the emitted gamma radiation is detected without significant self-absorption. In other words, the obtained signal is fairly matrix-independent. A method like this is an obvious target for standardization, because the intensity of the measured signal can be derived from physical models: from the well-understood laws of neutron capture (or the (n,γ) reaction), nuclear de-excitation and radioactive decay, as well as the principles of radiation detection. The most complete description of k_0 standardization of NAA can be found in [9]. The equivalent equations for PGAA can be found in [10]. In this paper, we start with the description of PGAA, and then NAA will be discussed, as the first one does not involve the correction for radioactive decay, but otherwise the basic equations are the same for both techniques.

---

[*] Author for correspondence (E-mail: zsolt.revay@frm2.tum.de).

2.1 History

Already before 1970, several researchers had devised standardization techniques for various projects, where calibration factors, sometimes called k factors, were measured for the gamma rays of the desired elements for specific irradiation and counting conditions. It was very convenient to continue using these k factors as long as the conditions did not change [11].

In the early 1970s, András Simonits was conducting research at the laboratory of Julien Hoste in Gent, Belgium. He proposed to Frans De Corte the development of a standardization of NAA using "universal k factors", where the essential information for a gamma ray emitted by any nuclide produced by neutron activation would be contained in a universal constant, the k_0 factor, and all the factors depending on the specific irradiation and counting conditions would be calculated by models. Thus, multi-element analysis could be performed with the same amount of work as was previously needed for single-element analysis [12].

Following the publication where the k_0 method was introduced, the development of the method required many years of hard work. The $k_{0,\mathrm{Au}}$ values relative to the generally used gold flux monitor were accurately measured for the gamma rays of practically all nuclides produced by neutron irradiation, as were the other activation and decay properties mainly at Budapest and Gent [13, 14]. The validated k_0 dataset can be found in [15].

The first datasets proposed for PGAA did not meet the requirements of chemical analysis [16], and the listed elemental cross-sections and emission probabilities were all biased with serious systematic errors [17]. During the 1990s, the k_0 standardization was encouraged by András Simonits in Budapest, when the new PGAA facility started its operation. The k_0 approach was introduced in this technique by Lindstrom *et al.* [18].

In PGAA, first chlorine was used as a comparator because it has a relatively simple prompt gamma spectrum with distinct and strong lines, and many elements have stoichiometric compounds with chlorine. Titanium as a prompt flux monitor was also used at some laboratories. Later, hydrogen became the ultimate comparator for PGAA, as many elements could be standardized to it directly when using stoichiometric compounds or water solutions. Hydrogen has one characteristic line, its natural form can practically be regarded as a monoisotopic element, and its cross-section as well as its characteristic energy has been determined very accurately. The first analytical datasets still listed $k_{0,\mathrm{Cl}}$ or $k_{0,\mathrm{H}}$ values. The final convention uses another composite nuclear constant, the so-called partial gamma-ray production cross-section. This cross-section is still determined relative to a comparator (ultimately to hydrogen), and the whole method is still based on the k_0 principle, but using cross-sections instead of the ratios of cross-sections, *i.e.* the k_0 factors.

A systematic series of measurements was performed in Budapest from 1997 to 2000, in which the energies and partial cross-sections of the most important characteristic gamma lines for all naturally occurring elements were determined. After an evaluation, the data are now available for users [19, 20].

2.2 Activation

The basic equation of activation is very simple: the reaction rate (R) induced by mono-energetic neutrons is as follows [10]:

$$R = N\sigma\Phi \tag{1}$$

where N is the number of atoms of the irradiated nuclide, Φ is the neutron flux, and σ is its neutron capture cross-section at the given energy of the neutrons. Eq. (1) is valid at any neutron energy, but in neutron capture, the basis is always the thermal energy: 0.0253 eV. For cross-sections measured at this energy, we use the name thermal cross-section, denoted by σ_0. Most of the nuclides follow the so-called $1/v$ law for thermal neutrons, thus their cross-sections will change equally in different-temperature neutron fields.

In the case of prompt gamma activation, R is the induced activity during the irradiation, while the activity of radioactive nuclides depends on their half-lives (see later).

In activation analysis, gamma spectra are always collected using multi-channel analyzers (MCA-s). First, the gamma detection has to be calibrated by measuring calibration sources with accurately known activities. Once we have the count-rate-to-activity function, we can determine the activity of the sample from the areas of characteristic gamma peaks:

$$\frac{A}{\varepsilon t} = \frac{m}{M} N_{\mathrm{A}} \theta \sigma P_{\gamma} \Phi \tag{2}$$

where A is the net peak area of the given gamma line, t is the measurement time (live time, see below), and ε is the counting efficiency at the measured gamma energy; the number of atoms of interest is the product of the mass of the irradiated element m over its molar mass M, the Avogadro constant N_{A}, and the abundance of the target isotope θ; σ is the neutron capture cross-section and P_{γ} is the emission probability from the transition resulting in the given gamma photon. The expression on the left-hand side equals the number of given energy photons emitted per unit time, which we will call gamma activity for short in our explanations.

Note that it is assumed that the peak areas have already been corrected for count-rate dependent random counting losses, whether they are caused by pulse pile-up or analog-to-digital converter (ADC) dead-time. Since modern spectrometers have quite accurate live-time clocks, this correction is usually achieved simply by using the live-time in the factor A/t. In the case of highly varying count rate and significant decay of the nuclide during the counting period, typical in certain NAA measurements, it may be more accurately done by a real-time correction method, such as loss-free counting, or zero dead-time [21].

The neutron flux depends on the neutron energy, and so does the capture cross-section. In principle, the product of the flux and the cross-section in the above equations has to be replaced by the integral of the energy dependent cross-section multiplied by the flux distribution:

$$\int\limits_{\text{thermal}} \sigma(E_{\mathrm{n}})\Phi(E_{\mathrm{n}})\,\mathrm{d}E_{\mathrm{n}} = \Phi_0\sigma_0 \tag{3}$$

where E_{n} is the neutron energy. In the case of pure thermal neutron fields the integral simplifies to the product of an average quantity, the so-called thermal flux (Φ_0) and the thermal cross-section (σ_0), introduced already above. This convention can be extended to irradiations with cold neutron beams, too, where all reaction rates are higher thanks to the increased cross-sections (due to the $1/v$ law). If we use thermal cross-sections (σ_0) in our calculations, with an increased thermal flux (also called thermal equivalent flux, Φ_0) we get the proper reaction rates.

It is advantageous to introduce the so-called partial gamma-ray production cross-section, the product of the abundance, the capture cross-section, and the emission probability:

$$\sigma_\gamma = \theta \sigma_0 P_\gamma \tag{4}$$

In thermal beams, we still can use Eq. (1) with thermal cross-section and flux [10].

2.3 PGAA

In PGAA, the sample irradiation and the counting of the gamma spectrum take place at the same time. At research reactors, the sample is placed in a directed neutron beam, and the gamma radiation is detected perpendicular to that beam. In pure thermal or cold neutron beams, the following equation can be used:

$$\frac{A}{\varepsilon t} = \frac{m}{M} N_\mathrm{A} \sigma_\gamma \Phi_0 \tag{5}$$

where σ_γ is the partial gamma-ray production cross-section (at thermal neutron energy). This equation can be used for the determination of m, σ_γ, or Φ_0, if the detector is calibrated, *i.e.* its counting efficiency (ε) is known. First, using a monitor with a known mass and cross-section, the thermal flux can be determined. Then using a standard with a known mass, the partial cross-section for the studied element can be measured. Finally, one can perform the analysis, *i.e.* determine the mass using the flux and the cross-section.

In collimated beams, higher-energy neutron components from the reactor may also appear. They are generally attenuated with sapphire or bismuth single-crystal filters, so that their contribution to activation is regarded as negligible. Curved neutron guides provide pure thermal or cold neutron beams.

The actual flux inside the sample may not always be accurately known due to the possibly inhomogeneous beam profile and neutron scattering, especially when measuring bulk samples. Instead of using a flux monitor, in the case of homogeneous samples one can compare the peak area to that of another component in the same material:

$$\frac{A_1/\varepsilon_1}{A_2/\varepsilon_2} = \frac{m_1}{m_2}\frac{M_2}{M_1}\frac{\sigma_{\gamma,1}}{\sigma_{\gamma,2}} = \frac{n_1}{n_2}\frac{\sigma_{\gamma,1}}{\sigma_{\gamma,2}} \tag{6}$$

Other quantities (measurement time, flux, and the Avogadro constant) cancel. The mass ratio weighted by the molar masses can also be replaced with the ratio of the stoichiometric coefficients (n). In other words, the ratio of the gamma activities equals the ratio of partial cross-section times the ratio of the stoichiometric coefficients. This equation is the basis of the accurate quantitative analysis in PGAA, following the k_0 approach [10, 22].

In PGAA, it often can be assumed that all major and minor components emit detectable prompt gamma radiations, which allows their determination with reasonable accuracies. Using the above approach, the composition of such samples can be determined in one measurement without the use of standards or monitors [22].

When irradiating in beam, radioactive nuclides are also activated, whose delayed gamma radiation certainly can be used for elemental analysis. It is especially true for quasi-prompt gamma lines, *i.e.* those with half-lives in the range of seconds or less. Longer-lived nuclides can also have significant peaks in the spectra. The peak areas of such decay lines have to be corrected for saturation using the following factor:

$$B = 1 - \frac{1-\mathrm{e}^{-\lambda t}}{\lambda t} \tag{7}$$

where λ is the decay constant, t is the measurement time (true time). Nuclear data for short-lived nuclides can be determined more accurately in neutron beams than with delayed radioactivity measurements when the half-life is very short [23, 24].

The cross-sections of certain nuclides (^{133}Cd, ^{157}Gd, ^{149}Sm, ^{176}Lu) do not follow the $1/v$ law in the thermal energy region. This irregular behavior disappears in cold neutron beams and is mostly insignificant in guided beams, too. The increased activation of the irregular nuclides can be corrected for using the so-called Westcott g factors, which can be as high as 2–3, when irradiating in collimated thermal beams [25].

Gamma-ray self-absorption and neutron self-shielding may play an important role in PGAA, especially when bulk samples are analyzed. In the case of homogeneous samples, neutron self-shielding will lower the induced activity of all elements to the same extent, so it does not affect the calculation of the mass ratios. The gamma self-absorption, on the other hand, has to be corrected for, because the lower-energy gamma rays which are absorbed more strongly would yield lower masses in the calculation. An analytical formula can be found for a homogeneous slab sample with thickness d, and with an angle α between the beam and the slab:

$$\frac{A}{A_0} = \int_0^d \mathrm{e}^{-x\left(\frac{\mu_\gamma}{\cos\alpha}+\frac{\mu_\mathrm{n}}{\sin\alpha}\right)} = \frac{1-e^{-d\left(\frac{\mu_\gamma}{\cos\alpha}+\frac{\mu_\mathrm{n}}{\sin\alpha}\right)}}{\frac{\mu_\gamma}{\cos\alpha}+\frac{\mu_\mathrm{n}}{\sin\alpha}} \tag{8}$$

where A_0 would be the ideal peak area with no self-shielding and self-absorption, μ_γ is the linear absorption coefficient for gamma rays, which can be found in publicly available databases [26], μ_n is the same for neutrons, and it can be calculated from the density, the Avogadro constant, the capture cross-section, and the molar mass as: $\mu_\mathrm{n} = \rho N_\mathrm{A} \sigma / M$. Note that in this case one has to use the real cross-section, which can be calculated from the thermal value based on the $1/v$ law, *e.g.* from the effective beam temperature $\sigma_0 (T_\mathrm{eff}/T_0)^{1/2}$. The actual linear absorption coefficients are sums of those of the elements weighted with concentration (mass fractions), *i.e.* they depend on the result of the analysis. The correction factor thus can be determined in an iterative way. Normally, one step of iteration is enough [22].

2.4 NAA

In the case of NAA, the irradiation takes place in the nearly isotropic field of neutrons in an irradiation channel inside a research reactor, where the other components of the neutron spectrum also take part in the activation. Activation by thermal neutrons is usually the most important process. With the capture of epithermal neutrons, the same radioactive nuclides are formed, which emit the same decay gamma rays. Fast neutrons open other reaction channels. The nuclide produced by an (n, p) reaction may be the same as the one produced by an (n, γ) reaction on an isotope of a different element, resulting in an interference; the correction for these interferences is not discussed here.

When irradiating in research reactors, the increased activities due to the epithermal activation have to be taken into account. The Høgdahl convention [27], used in k_0 standardization, separates the neutron spectrum into two regions, above and below the cadmium cut-off energy, 0.55 eV: a cadmium cover of 0.5 mm absorbs almost all the neutrons below this energy. In reactor activation, Eqs. (1) and (3) can be modified like this:

$$\begin{aligned} R &= N \int\limits_{\text{thermal+epithermal}} \sigma(E_\text{n})\Phi(E_\text{n})\,\text{d}E_\text{n} = N\left(\Phi_\text{s}\sigma_0 + \Phi_\text{e} I_0\right) \\ &= N\Phi_\text{s}\sigma_0\left(1 + \frac{Q_0}{f}\right) , \\ R_\text{e} &= N \int\limits_{\text{epithermal}} \sigma(E_\text{n})\Phi(E_\text{n})\,\text{d}E_\text{n} = N\Phi_\text{e} I_0 = N\Phi_\text{s}\sigma_0 \frac{Q_0}{f} \end{aligned} \tag{9}$$

Φ_s (practically equals Φ_0) and Φ_e are the sub-cadmium and the epi-cadmium flux, usually simply called the thermal and epithermal flux, while σ_0 and I_0 are the thermal cross-section and the so-called resonance integral, respectively. I_0 is the average cross-section weighted with a neutron spectrum following the theoretical $1/E_\text{n}$ function between the cadmium cut-off and the fast neutrons. In this region, many nuclides have a huge number of resonances, all contributing to I_0. Q_0 is the ratio of the resonance integral to the thermal cross-section, and f is the ratio of thermal to epithermal flux for the irradiation channel. Based on the above equations, one can calculate the activation of the samples in reactors.

After the irradiation, the sample is transferred to a low-background counting facility, where the gamma radiation is collected by a spectrometer in an energy spectrum. The electronic pulses from the gamma ray detector are sorted by their amplitudes into the typically 8192 channels of a multichannel analyzer (MCA). The net areas of the peaks have to be divided by the product of the saturation, the decay, and the counting factors below, to correct for the radioactive decay during the irradiation, the cooling, and the counting, respectively:

$$S = 1 - \text{e}^{-\lambda t_\text{irr}} , \quad D = \text{e}^{-\lambda t_\text{d}} , \quad C = \frac{1 - \text{e}^{-\lambda t_\text{c}}}{\lambda t_\text{c}} \tag{10}$$

where t_irr, t_d, t_c are the irradiation, the decay (cooling), and the counting times (true times), respectively, and λ is the decay constant. These factors have also been formalized by the developers of the k_0 method for all the more complicated cases of decay [15]. Thus the detected peak areas, measured bare and cadmium-covered, can be expressed as:

$$\begin{aligned} \frac{A}{\varepsilon tSDC} &= \frac{mN_\text{A}}{M}\theta P_\gamma \sigma_0 \Phi_\text{s}\left(1 + \frac{Q_0}{f}\right) , \\ \frac{(A)_\text{Cd}}{\varepsilon tSDC} &= \frac{mN_\text{A}}{M}\theta P_\gamma \sigma_0 \Phi_\text{s}\frac{Q_0}{f} \end{aligned} \tag{11}$$

On the left-hand side, the gamma activities are given, as calculated from the peak area and corrected for decay. This equation can be directly used for quantitative analysis (determination of m) if the flux-related quantities (Φ_s, f), as well as the cross-section-related and other physical data (M, θ, P_γ, σ_0, Q_0) are known. These physical data can be found in the literature, but their accuracies do not meet the requirements of chemical analysis. The intention of the inventors of the k_0 method was to avoid these inaccuracies when performing activation analysis.

A composite nuclear constant, the k_0 factor, was introduced in the standardization of NAA:

$$k_{0,c}(x) = \frac{M_c}{M_x}\frac{\theta_x \sigma_{0,x} P_{\gamma,x}}{\theta_c \sigma_{0,c} P_{\gamma,c}} \tag{12}$$

where x denotes the investigated element, and c the comparator (the cross-section standard, which is ^{198}Au, as will be discussed later). It can be seen that the k_0 is the ratio of the partial gamma-ray production cross-section (Eq. 4) divided by the molar mass. Using Eqs. (9) and (11), the k_0 factor can be expressed in another way, too:

$$k_{0,c}(x) = \frac{\left(\dfrac{A}{m\varepsilon tSDC}\right)_x - \left(\dfrac{A}{m\varepsilon tSDC}\right)_{\text{Cd},x}}{\left(\dfrac{A}{m\varepsilon tSDC}\right)_\text{c} - \left(\dfrac{A}{m\varepsilon tSDC}\right)_{\text{Cd,c}}} \tag{13}$$

This expression does not contain physical constants, but experimental data: peak areas, measurement times and other time-related quantities, counting efficiency and sample masses. The four terms in parentheses are the gamma activities divided by the mass of the irradiated element, what is called specific activity in the k_0 literature. The terms with Cd subscript subtract the epithermal contribution from the specific activity measured without cadmium cover; thus the k_0 factor is the ratio of specific activities calculated for thermal activation. The k_0 value can thus be thought of as the number of gamma rays emitted per unit mass of the element, activated in unit thermal neutron fluence, relative to the similar quantity of the flux monitor.

The k_0 factor is a nuclear constant, which can also be determined from measured quantities and other experimental data. While deriving it from other nuclear data would result in a rather inaccurate number, its derivation from areas of spectral peaks and samples masses may be performed very accurately, meeting the requirements of chemical analysis.

Q_0 values can be determined using the cadmium-ratio method, derived from Eq. (11):

$$Q_0 = \frac{f}{\dfrac{\left(\dfrac{A}{mtSDC}\right)}{\left(\dfrac{A}{mtSDC}\right)_\text{Cd}} - 1} \tag{14}$$

where f is the thermal-to-epithermal flux ratio, predetermined during the calibration of the irradiation channel, and in the denominator the ratio of the specific activities measured bare and with cadmium-cover can be seen. (Since we count the same gamma line in both cases, the efficiency cancels from the ratio).

A cadmium cover does not perfectly separate the activation in the two energy regions. When resonances of the investigated nuclide coincide with those of cadmium at certain energies, then the cadmium cover will not transmit 100% of epithermal neutrons. The specific activities determined with cadmium cover must be corrected for this using the cadmium transmission factors F_{Cd}. Since some of the F_{Cd} factors are not known with the required accuracy, some researchers feel that it is preferable not to use Cd covers.

Q_0 values can be determined without the use of cadmium covers by irradiating in two different channels with highly differing f values [28], *i.e.* using the so-called two-channel method. The accuracy attainable is comparable to that of the cadmium-ratio method.

The k_0 factor can also be determined without the use of cadmium covers, once the irradiation channel is calibrated, and if the Q_0 value is also known:

$$k_{0,\mathrm{c}}(x) = \frac{\left(\dfrac{A}{m\varepsilon tSDC}\right)_x}{\left(\dfrac{A}{m\varepsilon tSDC}\right)_\mathrm{c}} \, \frac{1+\dfrac{Q_{0,\mathrm{c}}}{f}}{1+\dfrac{Q_{0,x}}{f}} \tag{15}$$

The developers of the k_0 method decided to use gold (^{198}Au) as the comparator, because it has been widely used as a flux monitor, and its nuclear data are known with a high accuracy ($\sigma_0 = 98.65 \pm 0.9$ barn, $I_0 = 1550 \pm 28$ barn, $Q_0 = 15.71 \pm 0.28$ [29, 30]). Over the years, accurate $k_{0,\mathrm{Au}}$ and Q_0 values have been measured relative to the 64-h half-life, 411-keV gamma line of ^{198}Au for more than 400 gamma rays emitted by more than 122 nuclides, essentially all the gamma rays used in NAA. (In this convention, $k_{0,\mathrm{Au}}(\mathrm{Au}) = 1$ [13–15].)

The Høgdahl convention also assumes that in the epithermal neutron region, the neutron spectrum varies with energy as $1/E_\mathrm{n}$. This might not be strictly true from thermal energies up to fast-neutron energies, and even small deviations from this model result in significant systematic errors when the nuclide has a high Q_0 value. Thus a modification became necessary to keep the universality of the method. The neutron spectrum proved to be described satisfactorily with the model function $1/E^{1+\alpha}$. The shape parameter α can be determined with nuclides having greatly differing resonance energies, which are thus highly sensitive to the variation of the spectrum shape [31].

The resonance integral, and thus the Q_0 value, varies with α. It varies most for the reactions which have resonances at high neutron energies. In the k_0 method, the calculation of $Q_0(\alpha)$ is simplified by using the concept of mean resonance energy, where the contribution to the resonance integral of all the resonances is approximated by one resonance situated at the effective mean energy. Then, knowing α, one can calculate $Q_0(\alpha)$ by a theoretical formula:

$$Q_0\,(\alpha) = (Q_0 - 0.429)\;E_\mathrm{r}^{-\alpha} + \frac{0.429}{(2\alpha+1)0.55^{\alpha}} \tag{16}$$

The mean resonance energies have been calculated by Jovanovic, by integrating over all the resonances available in the literature for all the (n,γ) reactions used in neutron activation analysis [32].

When performing k_0 NAA, one has to calibrate carefully the irradiation and counting facilities first, which means the determination of Φ_s, f, α, and ε. In fact, the thermal flux may change from irradiation to irradiation, so a flux monitor should be co-irradiated with the sample(s). The masses of the elements in the sample can then be determined using this equation:

$$m_x = \frac{\left(\dfrac{A}{tSDC}\right)_x}{\left(\dfrac{A}{mtSDC}\right)_\mathrm{c}} \, \frac{1}{k_{0,x}} \, \frac{1+\dfrac{Q_{0,\mathrm{c}}(\alpha)}{f}}{1+\dfrac{Q_{0,x}(\alpha)}{f}} \tag{17}$$

The subscripts x and c refer to the unknown and the comparator, respectively.

The developers of the k_0 method emphasized the need to take into account neutron self-shielding, both for thermal and epithermal neutrons. With the self-shielding correction factors, the above equation becomes:

$$m_x = \frac{\left(\dfrac{A}{tSDC}\right)_x}{\left(\dfrac{A}{mtSDC}\right)_\mathrm{c}} \, \frac{1}{k_{0,x}} \, \frac{G_{\mathrm{th,c}} + G_{\mathrm{epi,c}}\frac{Q_{0,\mathrm{c}}(\alpha)}{f}}{G_{\mathrm{th},x} + G_{\mathrm{epi},x}\frac{Q_{0,x}(\alpha)}{f}} \tag{18}$$

The thermal and epithermal self-shielding factors, G_th and G_epi, are very close to unity for most activation reactions in most samples, such as biological materials, and can be ignored. But the self-shielding effect is important for samples containing large amounts of nuclides with high neutron capture cross sections. Historically, the calculation of G_th and G_epi was extremely difficult, and it was recommended to dilute the samples to avoid self-shielding. Now, G_th and G_epi can be calculated easily and accurately with an analytical formula (see later) [33].

The cross-sections of certain nuclides (like ^{176}Lu and ^{151}Eu) do not strictly follow the $1/v$ law due to low-energy resonances. These nuclides will be activated somewhat differently in different reactors, depending on the temperatures of the irradiation channels. In this paper we do not discuss this in detail.

3. Methods

3.1 PGAA

3.1.1 Getting started, spectrum evaluation

PGAA can be best performed in neutron beams. When the k_0 approach of PGAA is applied, the composition can be determined without knowing the flux or the mass of the sample. In this case, the calibration of the facility means the determination of the counting efficiency only. The sensitivities, however, are affected by the neutron flux and the sample mass.

After the acquisition of the spectra, one needs spectrum-evaluation software that can fit asymmetric peaks and multiplets from several overlapping peaks. There are not too many software packages that can do that well. One of them is Hypermet [34], which used to be available in many nuclear laboratories since the 1970s. Its further developed version with a graphical interface and with calibration routines, Hypermet-PC, became available in 1994, and is still being used in many laboratories [35, 36].

For the analysis, one needs the spectroscopic database. The most complete and most accurate one has been established for analytical purposes in Budapest [19]. It is also available through the IAEA [20].

3.1.2 Flux and flux profile

If the beam is collimated, then the neutron spectrum originally is the same as that inside the reactor. To lower undesired reactions, epithermal and fast neutrons are attenuated with filters. The neutron spectrum will thus consist of a dominant thermal component (Maxwellian with a temperature of about 300–320 K) and a much lower epithermal component with an f of the order of several hundred.

In the case of guided neutron beams, the thermal spectrum is strongly distorted, as neutron guides transmit lower-energy neutrons much better. As a result of that, the originally nearly-Maxwellian thermal component becomes significantly colder (the effective temperature will be typically below 100 K), but the distribution covers a much broader energy range from thermal to cold neutrons. Epithermal neutrons are not guided; thus f increases with the length of the guide, and it is typically above 1000. Curved neutron guides transmit pure slow (thermal or cold) neutrons.

The performance of the neutron beam can be best characterized by the thermal flux. The f value is used for checking if the epithermal activation is really insignificant. The inhomogeneity of the beam may be interesting, especially when inhomogeneous samples are measured. The beam profile can be studied with an x-ray film, or by mapping the flux across the beam using a small piece of monitor material. When analyzing homogeneous samples using the k_0 approach, neither the flux, nor its inhomogeneity is important, as they cancel in the calculation.

3.1.3 Efficiency and energy calibration

The most important part of the calibration is the determination of the detector efficiency. The samples are counted during the irradiation, which can only be performed using a relatively large sample-to-detector distance. That is why corrections for coincidence summing are not necessary.

The prompt gamma peaks cover a very broad range of energies, typically between 50 keV up to 11 MeV, so the efficiency cannot be determined using a single calibration source. Standard radioactive sources are used at lower energies, while above the energies of radioactive decay, prompt gamma lines have to be applied. The efficiency calibration routine of Hypermet-PC is capable of combining datasets from several measurements and normalizing them together, fitting a 6^{th}–8^{th}-order polynomial to sometimes more than a hundred points [37].

In PGAA, a lower amplifier gain is used than in NAA: one channel in the spectrum equals about 0.7 keV. Any non-linearity in the channel-to-energy function or a slight change in the gain may result in significant deviations when peak energies are determined. The nonlinearity is an inherent characteristic of the spectrometer, which does not change considerably with time. Using a nonlinearity correction, together with a two-point energy calibration of each spectrum, reliable energy data can be obtained. At low energies, accuracies are typically near 0.01 keV, while at the highest prompt gamma energies about 0.1 keV can be achieved, which is enough for the identification of peaks. The non-linearity function can be determined by comparing peak positions to those calculated from a two-point energy calibration. This calibration can also be performed using Hypermet-PC in a similar routine to that of the efficiency calibration [35].

3.1.4 Analysis

The analysis in PGAA, in principle, is the following: in a carefully calibrated spectrum, the identification of the emitter elements can be performed based on the energies, while the qualitative analysis uses the peak areas. In a typical prompt gamma spectrum, hundreds, sometimes more than a thousand characteristic peaks appear. So, the chance of peak overlaps is rather high. In such a spectrum, the energy cannot be the only criterion for qualitative analysis. Hence, a method is needed that examines the energies and the relative intensities of the peaks at the same time. An element can be regarded as detected only when the matching peaks show a similar intensity pattern as that in the spectrum of the pure element. The best way to do that is the statistical analysis of peak energies and areas.

The ProSpeRo program, developed in Budapest and also used in Garching lists all possible matches with the database of prompt gamma lines [22] and calculates the masses of the elements. The selection of elements is done automatically (based on statistical qualifiers like Z scores and χ^2 values), but it can be corrected manually. The program also corrects for interferences from other components, neutron self-shielding and gamma-ray self-absorption (according to Eq. 8), as well as radioactive decay (Eq. 7).

The final mass values and their uncertainties are determined as weighted averages from the individual mass values, calculated for the selected peaks. The major and minor components in most cases are detected with PGAA, so the composition of the sample can be directly calculated from the peak area ratios.

Oxygen, one of the most abundant components of many natural materials, has a very low cross-section. Though it can be analyzed with PGAA, its uncertainty calculated from the peak areas is too large, so it may destroy the accuracy of the other components. That is why it is advantageous to calculate the oxygen content from the stoichiometry, assuming all possible elements as oxides.

The accuracy of the mass values is mainly determined by those of the peak areas and of the spectroscopy data. For the most abundant elements, uncertainties of about 1% can be reached [22].

3.2 NAA

3.2.1 Getting started, software issues

The essentials of the k_0 method are: knowledge of the thermal neutron flux, f and α, and detection efficiencies for all counting geometries used. Since the calculations for the derivation and the use of these parameters are extensive, a software package is needed. One can begin a collaboration with one of the many laboratories using the k_0 method and adopt their method of calculation and their software. Two software packages are now readily available to all potential users. The KAYZERO Software [37] performs the calculations in the well-understood classical manner. It is widely used and has been well tested over many years. The k_0-IAEA Software [38] uses a holistic approach, making the best possible use of all available information, and benefits from the support of the IAEA. The maintainers of both packages also provide training.

The instructions with the software package usually indicate how to determine f and α, how to measure the parameters of the efficiency calibration of the detector and how to convert it to specific counting geometries, and how to convert the peak areas into the concentrations of the elements. These software packages have a library of all the k_0, Q_0 values, mean resonance energies, half-lives, decay types and the details of the decay schemes needed for true coincidence summing calculations.

3.2.2 Measuring f and α

Many methods have been developed to determine f and α. They all involve the activation and counting of a number of nuclides having a range of Q_0 values and mean resonance energies. The most accurate measurements of α use irradiations under cadmium cover to activate with epithermal neutrons only. Most laboratories do not require such high accuracy or may not be permitted to irradiate under cadmium cover. Bare irradiations have been shown to give sufficient accuracy if done carefully. Since the parameters are determined by subtraction of the thermal-neutron-induced activity from the total activity, two possibly similar quantities, accurate element masses, peak areas and detection efficiencies are needed. The minimum number of monitors which need to be irradiated for the simultaneous determination of the Φ_s, f and α is three. One of the most convenient trios of monitor elements is Cr, Au and Mo [39]. Earlier, the trio consisting of two isotopes of natural Zr and Au was recommended [40].

3.2.3 Detection efficiency ε

Detection efficiencies appear to play only a minor role in the activation equations, but in fact, their determination is by far the most difficult aspect of k_0 NAA. When using the relative standardization method, the counting geometry for the unknown is maintained almost identical to that of the standard, and only a small correction factor needs to be calculated. But with the k_0 method, for greater flexibility, the counting geometry for the unknown may be completely different from that of the monitor, and the comparison is between two different nuclides. It may be straightforward to determine a relative efficiency curve, efficiency vs. gamma-ray energy, for a point source far from the germanium detector, but essentially required are efficiencies for small or large samples, most often counted very close to the detector.

The efficiency-calculation routine, a major part of any k_0 software package, may use a physical or parametric model, which calculates the gamma ray detection probability as a function of the position of the emitting nuclide relative to the centre of the face of the detector. This is integrated over the volume of the sample, taking into account gamma attenuation in the sample and its support. Using calibrated and uncalibrated sources, for absolute and relative efficiencies, the user will perform the measurements necessary to determine the parameters of the model; the measured dimensions of the detector may also be used. Then the parameters of the model are fine-tuned, using further measurements in typical counting geometries.

A huge complication is coincidence summing of gamma rays. This is negligible when using the relative method, because the standard and the unknown are the same nuclide and the effect is the same for both. With the k_0 method, the software must have the decay schemes of all the nuclides used, to determine the probability of each decay path involving the gamma ray of interest, and the probability, for each counting geometry, of summing with the gamma rays emitted simultaneously along each decay path. Many routines have been developed to perform coincidence summing calculations. Three of the routines used with the k_0 method were compared for the case of a small sample counted close to the detector [41]. The reduction in detection efficiency due to summing-out was as high as 30% for some nuclides. Discrepancies between the three routines were as high as 10% in some cases and they were corrected.

Not all the routines correct for coincidence summing with x-rays. This may be important, especially for heavy nuclides, but it is difficult to correct accurately because it varies greatly with detector window thickness and sample thickness. For this reason, detectors with thin beryllium windows should not be used with k_0 NAA, unless samples are counted at distances of 10 cm or more. None of the routines correct for coincidence summing with beta rays. This may be important for some short-lived light nuclides which emit high energy betas in coincidence with the gamma rays. In these cases a 4 mm thick plastic absorber should be placed between sample and detector.

3.2.4 Accuracy

In 1987, the developers of the k_0 method estimated that the accuracy was typically 3.8% [42]. Since then, several expert labs have made a considerable effort to understand the method completely, to determine the causes of their inaccuracies and to eliminate them. These labs now routinely achieve 2% accuracy under favorable conditions, such as counting the samples far from the detector. However, for new labs adopting the method, a large number of papers comparing results with the accurately known concentrations in certified reference materials show many deviations between 5 and 10%. These papers did not identify the likely causes of these deviations and it is unlikely that these labs will ever have the resources necessary to find the causes. Thus, it must be concluded that new labs adopting the method should expect accuracies of the order of 5%.

An important step towards improved quality assurance is the development of the SMELS material [43]. There are three types, SMELS I, II and III, which when activated produce nuclides with short, medium and long half-lives. In each of the three spectra one obtains many clear gamma ray peaks over the entire energy range, emitted by at least a dozen nuclides produced by (n, γ) reactions with low and high Q_0 values. These stable, homogeneous materials with well known concentrations of all the elements are very useful in verifying the method. In spite of their popularity, the three materials are still available from the developer. SMELS I and II can be recycled after the decay of the nuclides. The intended use of this material is to verify if the k_0 method is being carried out correctly. If discrepancies with the expected concentrations are observed, the user should determine the cause and correct it. Since the SMELS material was originally characterized using mainly the k_0 method, it can not be used as an absolute confirmation of the accuracy of measured concentrations, nor to verify the accuracy of published k_0 values.

There is a continuing effort to improve the nuclear data base, containing k_0 values, Q_0 values, mean resonance energies and half-lives. This will make a difference for a few nuclides for which the currently used k_0 and Q_0 values may be in error by as much as 10% [28, 44]. The international committee updating the database hopes to recommend new k_0 values for all the nuclides for which there is a doubt whether the current values are accurate to better than 2% [45].

4. Experimental

4.1 Installation of a PGAA laboratory

A PGAA facility has the simplest equipment among the instruments installed at a neutron beam. The simplest facilities consist of a beam shutter, a sample holder, a beam stop, and a high-purity germanium detector. Since the irradiation and the counting are performed simultaneously, the most important task is the proper arrangement of the shielding against neutrons and gamma rays. Against fast neutrons, boron-loaded polyethylene (or paraffin) can be used; thermal or cold neutrons can be stopped efficiently with boron-, or lithium-containing materials. Boron produces 478-keV gamma rays, which can be shielded much easier than the high-energy prompt gamma radiation from high-cross-section metals like Cd or Gd. Lithium was considered to be the ideal shielding material against slow neutrons; however, the fast neutron production due to secondary reactions may cause detector damage. Hence, in high-flux beams, the use of lithium has to be avoided, and a combination of boron and lead has to be applied instead. Against gamma radiation, a massive lead shielding has to be built. The most efficient shielding arrangement is when the different components (sample, beam stop, and detector) of the instrument are covered with almost closed lead chambers lined with the proper neutron shielding sheets, with the smallest possible apertures in the directions of the beam and detector [46–48].

The sample holder and other structural components around the sample have to be as light as possible, and be made of low-cross-section materials. Teflon or FEP (consisting of carbon and fluorine), aluminum, and lead are preferred. Plastic because of its hydrogen content or steel has to be avoided. Samples may be held in the beam using Teflon strings, and, if necessary, they can be sealed in bags made of FEP foil. The samples can also be changed manually. In high-flux beams, the sample chamber has to be evacuated to minimize the count rate from the nitrogen content of the air [49].

The detector has to be surrounded with lead shielding with a thickness of 10–20 cm to obtain the lowest possible spectral background. Active background reduction techniques are also preferred. The best Compton-suppressed detector system consists of a 25–50-% relative-efficiency HPGe detector surrounded by a bismuth germanate (BGO) scintillator annulus. Whenever scattered photons are detected by the BGO, their signal in the HPGe detector is rejected; thus the characteristic peaks collected without any energy loss are detected with a much higher probability, which results in a significant reduction of the spectral background [49].

4.2 Applications of PGAA

PGAA is usually used for the determination of the average composition of the irradiated sample. It is more sensitive than NAA to the major elements of the matrix; however, certain trace elements can be analyzed with reasonable sensitivity. Thus, it is complementary to NAA, which can be regarded as a trace-element analytical technique.

This technique is mainly used for the analysis of samples with light-element matrices, and provides a unique opportunity for the determination of hydrogen and boron. Minerals, cement, concrete, glass, and ceramic are ideal samples for PGAA, but metals can also be analyzed.

A comprehensive summary of applications is given in [50]. Here, a few typical measurements will be mentioned mainly performed at Budapest and Garching.

k_0-PGAA has been used for the analysis of all types of geological samples. For instance, boron was analyzed in volcanic rocks together with the determination of the composition [51]. PGAA has been used extensively in archeology in Budapest. Various types of prehistoric and polished stone tools were analyzed and classified based on the results [52, 53]. Inka-period ceramics from the Paria Basin (Dept. Oruro, Bolivia) were also studied [54]. Roman silver-copper coins were analyzed with PGAA, and based on the bulk composition; it was shown that the silver content gradually decreased during the period 119–194 AD [55].

PGAA proved to be efficient in the analysis of different materials in containers with wall thicknesses of several millimeters. Nuclear materials were successfully detected in lead containers [56]. When placing a tube-enclosed chemical reactor in the beam, the composition of the reactants inside the irradiated volume can be monitored. The amount of hydrogen during the hydrogenation of n-pentynes on palladium catalysts, varying in the range of 5–50 ppm was measured in situ [57–59].

In Garching, archeology is also a major field of application. Two gilded bronze reliefs from the Florence Baptistery were analyzed at the Garching PGAA facility [60]. See the Garching PGAA facility in Fig. 1.

4.3 Installation in a small NAA laboratory

The NAA Laboratory at Ecole Polytechnique Montreal had been doing NAA from 1976 to 1997 using what was called

Fig. 1. The PGAA facility at Garching. Lower right corner: shielding of the beam stop, left side: shielding and dewar of the detector, in the middle: sample chamber tube.

the Improved Relative Method with the EPAA software [44]. Since the gamma-ray detection efficiencies and the neutron flux of the SLOWPOKE reactor were reproducible to about 1 or 2%, it was decided to standardize once and for all for the gamma-rays of all the nuclides used and for a small number of sample sizes and counting geometries. This approach was very convenient as it eliminated the need to prepare new standards for every batch of samples analyzed, but it had two drawbacks. First, many of the standards prepared and used at that time were of questionable quality and the sensitivity constants which were determined from them sometimes had errors greater than 10%. Second, the method lacked flexibility. Measurements were limited to the sample sizes and densities and counting geometries already standardized and a complete re-standardization was necessary for every reactor fuel change (done in 1997), new irradiation channel (two were installed in 1997) and new germanium detector (typically one every five years).

Thus, in 1997, it was decided to install and adopt the k_0 method at the NAA Laboratory. There were several things to do: acquire k_0 software and the k_0 database, measure the neutron spectrum parameters and measure the parameters needed for the germanium detector efficiency model. Two major decisions were made. First, it was decided not to use the k_0 method in the classical manner, irradiating flux monitors with every batch of samples and performing the neutron spectrum calculation and detector efficiency calculation for every sample. Instead, it was decided to retain the advantages of the convenient Improved Relative Method and calculate sensitivity constants for each nuclide and for a small number of irradiation channels and counting geometries [61]. A simple spreadsheet was used for this; it used k_0 values and other data collected from the published literature.

The second major decision was not to adopt the detector efficiency software which was readily available: KAYZERO/SOLCOI Software [44]. The reason was that we were using small and large cylindrical irradiation/counting vials placed on their sides usually very close to the detector, dictated by the relatively low neutron flux of the SLOWPOKE reactor. This was not the counting geometry envisaged when the SOLCOI Software was developed. Our own detector efficiency model was therefore developed [61]. It was found to work well for our purposes. However, the necessary coincidence summing calculations for all nuclides were found to be extremely complex and long to program. They were finally verified and validated [28].

The measurement of the neutron spectrum parameters was relatively easy. The bare-triple-monitor method using ^{197}Au, ^{94}Zr and ^{96}Zr gave reasonable and reproducible values for f and α. Later, using the more accurate cadmium ratio for multi-monitor method, it was found that the values of f obtained with the Au-Zr trio were always about 10% high. The recently developed trio of monitor elements Cr, Au and Mo [39] was found to be very convenient and gave essentially the same values of f and α as the cadmium ratio for multi-monitor method.

Our earliest experience with the use of the k_0 method (1997–2001) was very satisfying. For the first time it was possible to analyze any material for any element without having the need for a standard of each element which matched the unknown samples. We were able to offer users an analysis service guaranteeing fast, accurate results.

The development of the k_0 method did not cease. When good standards became available they were used to verify the accuracy of the results obtained with the k_0 method [41] and in a few cases new k_0 and Q_0 values were proposed [28].

With the k_0 method now working extremely well, it was found the analysis results were almost always of high accuracy, usually between 2 and 5%, for small and large samples of all types of materials, except for those which contained severe neutron absorbers causing significant neutron self-shielding. Methods were available for estimating and correcting thermal neutron self-shielding but none for epithermal neutron self-shielding except very difficult Monte-Carlo calculations. Then it was discovered that other researchers had an idea [62] for an analytical formula for epithermal self-shielding with only one nuclear constant to be determined for each nuclide. This was developed at Montreal by Chilian *et al.* [33] and now the effective self-shielding factor, G_{eff}, which is a combination of the thermal and epithermal self-shielding factors, G_{th} and G_{ep}, can be calculated for cylindrical samples easily and accurately with the following formula:

$$G_{\mathrm{eff}} = \frac{f}{f+Q_0(\alpha)}\left(\frac{1.00}{1+\left(\dfrac{N_{\mathrm{A}}k_{\mathrm{th}}}{r(r+h)}\displaystyle\sum_i \frac{m_i\sigma_{\mathrm{abs},i}}{M_i}\right)^{0.964}}\right) + \frac{Q_0(\alpha)}{f+Q_0(\alpha)}\left(\frac{0.94}{1+\left(\dfrac{mN_{\mathrm{A}}k_{\mathrm{ep}}\sigma_{\mathrm{abs,ep}}}{r(r+h)M}\right)^{0.82}}+0.06\right) \qquad (19)$$

with N_{A} Avogadro constant, k_{th} thermal self-shielding constant, r and h radius and height of the cylinder, m_i mass of element i, $\sigma_{\mathrm{abs},i}$ thermal neutron absorption cross-section for element i, M_i molar mass of element i, m mass of the element, k_{ep} epithermal self-shielding constant, $\sigma_{\mathrm{abs,ep}}$ epithermal neutron absorption cross-section, M molar mass of the element.

The thermal neutron absorption cross-sections are well known and the recently defined epithermal neutron absorption cross-sections have now been determined for all nuclides used in NAA [33]. For the analysis of unknown samples, the normal situation in NAA, the amounts of the elements are not known in advance. Therefore, G_{eff} is calculated with the above formula using first the uncorrected measured amounts, and the final values of G_{eff} and the amounts of the elements are obtained by an iterative procedure [33].

Another often overlooked benefit of the k_0 method is that it forces the user to understand the models for the neutron irradiation and gamma-ray detection processes. This understanding, besides making NAA more interesting, is of great benefit when analyzing difficult or unusual samples. The user better understands what is happening and can make the key measurements or corrections necessary to achieve accurate results.

4.4 Application of k_0 NAA at Ecole Polytechnique Montreal

The k_0 method is most useful for multi-element NAA, but also for single-element NAA when it is inconvenient to prepare a good standard of that element that matches the samples in terms of size, density and chemical composition.

At Ecole Polytechnique Montreal, the staff of two or three performs approximately 1000 multi-element analyses and 3000 single-element analyses per year for researchers and for industry, which enabled the NAA Laboratory to become financially self-sufficient. It should be mentioned that one of the main reasons for this success was the use of the very convenient EPAA software. EPAA does the peak area calculations from the gamma-ray spectrum and also the calculation of the concentrations of the elements of interest using sensitivity constants derived from k_0 and Q_0 values, as well as f and α and detection efficiencies for the counting geometry used. Combining the two steps, peak area calculation and concentration calculation, allows the analyst to focus only on the peaks needed for the analysis at hand and eliminates the need to weed through a lot of unwanted calculated results. To always ensure the best possible peak area determinations, the analyst inspects the peak fit of every peak used and can easily improve the fit interactively if needed.

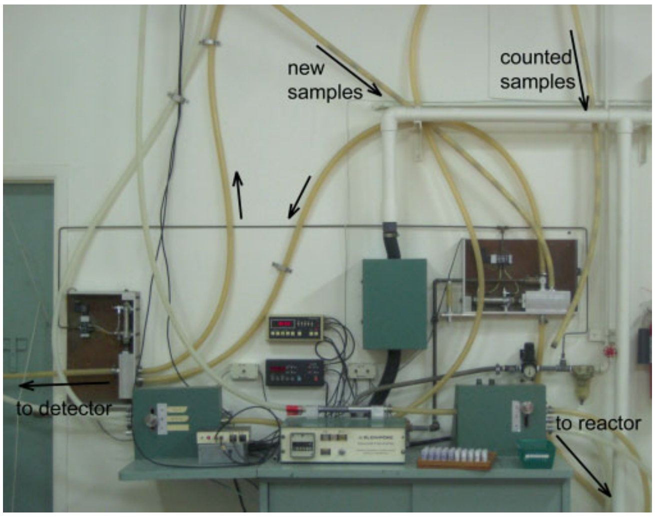

Fig. 2. The automated pneumatic irradiation system at Ecole Polytechnique Montreal.

The NAA work is accelerated by the use of three mechanical sample changers for overnight counting and an automated pneumatic irradiation system, shown in Fig. 2, used two or three times a week for batches of samples analyzed with short-lived radionuclides.

Some of the types of materials analyzed by the k_0 method are listed here.

- Improved materials for fuel cells are being developed with catalysts containing Ru, Pt and Ir. Their composition is verified by NAA.
- Fabric used for medical bandages may contain Ag for antibacterial protection and to promote wound healing. The amount is verified by NAA.
- There is a great demand by the petrochemical industry for the analysis of polymer products for quality assurance and for product development. They are usually analyzed for catalyst residues or additives and on occasion to verify the low levels of toxic heavy metals. The catalysts themselves are also analyzed. Sometimes plastic products which have failed or which contain visible inclusions are analyzed to determine the cause of the problem. Plastics manufacturers also analyze their competitors' products to learn about their production methods.
- The Cl level in the catalyst of an oil refinery is regularly measured to determine if it is time for regeneration.
- Wood, paper, canvas, and vinyl used in humid environments are treated with chemicals to prevent mould. They are analyzed for active elements such as As, I, Cu and Sn [63].
- Refined rare-earth products are analyzed for traces of other rare-earths.
- Silicon for the semiconductor industry is analyzed for impurities.
- Insulation on electrical wires is analyzed for fire-retardant elements Sb and Br.
- Soil samples are analyzed for uranium contamination.
- Rocks, coal and soil are analyzed for heavy metals, rare-earths and platinum group elements.
- For medical studies, human hair and toenails are analyzed for Se and As [64, 65].
- The end products of chemically treated toxic waste are analyzed to determine the pathways of various heavy metals.
- Materials collected from crime scenes are analyzed to establish chemical signatures as an aid in determining the possible origin.
- Archaeological artifacts (ceramics, lithics and metal objects) are analyzed to determine their provenance.

Many of these applications illustrate the great advantage of k_0-NAA over other analysis techniques. It can be applied immediately to the sample of solid material; there is no need for dissolution or other difficult sample preparation. This makes possible fast and accurate analyses even for unusual materials.

5. Conclusion

The k_0 approach has proved to be a successful method of standardization of both prompt gamma activation analysis and neutron activation analysis. During the standardization, the physical processes of neutron capture, de-excitation, and detection have been studied thoroughly, and the results were implemented in the methods. Reliable spectroscopy databases have been established, which are available and can now be used for chemical analysis. The k_0 method has been introduced at many NAA and also PGAA laboratories, providing an important step towards laboratory-independent, highly reliable analytical results.

Acknowledgment. The shared knowledge of András Simonits on the history of the k_0 method is appreciated. The help by Zsolt Kasztovszky in the compilation of the archeological applications of PGAA is also acknowledged.

References

1. Hevesy, Gy., Levi, H.: Det. Kgl. Dan. Vidensk. Selskab. Math.-Fys. Medd. Ser. **14**, 3 (1936).
2. Amaldi, E., d. Agostino, O., Pontecorvo, B., Segré, E.: Recerca Sci. **2**, 467 (1934).
3. Lea, D. E.: Nature **133**, 24 (1934).
4. Isenhour, T. L., Morrison, G. H.: Anal. Chem. **38**, 162 (1966).
5. Isenhour, T. L., Morrison, G. H.: Anal. Chem. **38**, 167 (1966).
6. Maier-Leibnitz, H.: Nukleonik **8**, 61 (1966).
7. Comar, D., Crouzel, C., Chasteland, Riviere, R., Kellershohn, C.: Nucl. Appl. **6**, 344 (1969).
8. Henkelmann, R., Born, H. J.: Angew. Chem. **81**, 921 (1969).
9. De Corte, F.: The k_0-standardization method, a move to the optimization of neutron activation analysis. Habilitation Thesis, University of Gent, Belgium (1987).
10. Révay, Zs., Belgya, T.: Principles of PGAA. In: *Prompt Gamma Activation Analysis with Neutron Beams*. (Molnár, G. L., ed.) Kluwer Academic Publishers, Dordrecht (2004), p. 1.
11. Girardi, F., Guzzi, G., Pauly, J.: Anal. Chem. **36**, 1588 (1964).
12. Simonits, A., De Corte, F., Hoste, J.: J. Radioanal. Chem. **24**, 31 (1975).
13. De Corte, F., Simonits, A., De Wispelaere, A., Elek, A.: J. Radioanal. Nucl. Chem. Art. **133**, 3 (1989).
14. De Corte, F., Simonits, A.: J. Radioanal. Nucl. Chem. Art. **133**, 43 (1989).
15. De Corte, F., Simonits, A.: At. Data Nucl. Data Tables **85**, 47 (2003).
16. Lone, M. A., Leavitt, R. A., Harrison, D. A.: At. Data Nucl. Data Tables **26**, 511 (1981).
17. Molnár, G. L.: J. Radioanal. Nucl. Chem. **244**, 27 (2000).
18. Lindstrom, R. M., Fleming, R. F., Paul, R. L., Mackey, E. A.: The k_0 Approach in Cold-neutron Prompt-gamma Activation Analysis. In: Proc. Int. k_0 Users Workshop (De Corte, F., ed.) Universiteit Gent, Gent (1992), p. 121.
19. Choi, H. D., Firestone, R. B., Lindstrom, R. M., Molnár, G. L., Mughabghab, S. F., Paviotti-Corcuera, R., Révay, Zs., Trkov, A., Zerkin, V., Chunmei, Z.: Database of prompt gamma rays from slow neutron capture for elemental analysis. International Atomic Energy Agency, Vienna (2007).
20. Révay, Zs., Firestone, R. B., Molnár, G. L., Belgya, T.: Catalog and atlas of prompt gamma rays. In: *Prompt Gamma Activation Analysis with Neutron Beams*. (Molnár, G. L., ed.) Kluwer Academic Publishers, Dordrecht (2004), p. 173.
21. Pommé, S.: Nucl. Instrum. Methods Phys. Res. A **474**, 245 (2001).
22. Révay, Zs.: Anal. Chem. **81**, 6851 (2009).
23. Szentmiklósi, L., Révay, Zs., Belgya, T.: Nucl. Instrum. Methods Phys. Res. **564**, 655 (2006).
24. Révay, Zs., Molnár, G. L., Belgya, T., Kasztovszky, Zs.: J. Radioanal. Nucl. Chem. **257**, 561 (2003).
25. Révay, Zs.: Nucl. Instrum. Methods Phys. Res. B **263**, 79 (2007).
26. Hubbell, J. H.: Appl. Radiat. Isot. **33**, 1269 (1982), available at: http://www.nist.gov/pml/data/xraycoef/.
27. Høgdahl, O. T.: In: Proceed. Symp. Radiochemical Methods of Analysis, Salzburg, 19–23 October 1964, IAEA, Vienna (1965), p. 23.
28. St-Pierre, J., Kennedy, G.: Nucl. Instrum. Methods Phys. Res. A **564**, 669 (2006).
29. Mughabghab, S. F.: *Neutron Cross Sections, Part B:* $Z = 61–100$. Acad. Press, New York (1984).
30. Holden, N. E.: Report BNL-NCS-36965. Brookhaven National Laboratory, Brookhaven (1985).
31. de Corte, F., Moens, L., Simonits, A., de Wispelaere, A., Hoste, J.: J. Radioanal. Nucl. Chem. **52**, 295 (1979).
32. Jovanovic, S., de Corte, F., Simonits, A., Moens, L., Vukotic, P., Hoste, J.: J. Radioanal. Nucl. Chem. **113**, 177 (1987).
33. Chilian, C., St-Pierre, J., Kennedy, G.: J. Radioanal. Nucl. Chem. **278**, 745 (2008).
34. Phillips, G. W., Marlow, K. W.: Nucl. Instrum. Methods **137**, 525 (1976).
35. Fazekas, B., Östör, J., Kis, Z., Molnár, G. L., Simonits, A.: The new features of Hypermet-PC. (Molnár, G., Belgya, T., Révay, Zs., eds.) in: Proc. 9th International Symposium on Capture Gamma-Ray Spectroscopy and Related Topics, Budapest, Hungary, 8–12 October 1997, Springer Verlag, Budapest/Berlin/Heidelberg (1997), p. 774.
36. Révay, Zs., Belgya, T., Molnár, G. L.: J. Radioanal. Nucl. Chem. **265**, 261 (2005).
37. KAYZERO/SOLCOI: PC software package. DSM Research, POB 18, 6160 MD Geleen, The Netherlands (1996).
38. Rossbach, M., Blaauw, M., Bacchi, M. A., Xilei, L.: J. Radioanal. Nucl. Chem. **274**, 657 (2007).
39. Koster-Ammerlaan, M. J. J., Bacchi, M. A., Bode, P., Fernandes, E. A. D. N.: Appl. Radiat. Isot. **66**, 1964 (2008).
40. de Corte, F., Moens, L., Sordo-El Hammami, K., Simonits, A., Hoste, J.: J. Radioanal. Nucl. Chem. **52**, 305 (1979).
41. van Sluijs, R., Bossus, D., Blaauw, M., Kennedy, G., De Wispelaere, A., van Lierde, S., De Corte, F., J. Radioanal. Nucl. Chem. **244**, 675 (2000).
42. De Corte, F., Simonits, A., De Wispelaere, A., Hoste, J.: J. Radioanal. Nucl. Chem. Art. **113**, 145 (1987).
43. Vermaercke, P., Robouch, P., Eguskiza, M., De Corte, F., Kennedy, G., Smodis, B., Jacimovic, R., Yonezawa, C., Matsue, H., Lin, X., Blaauw, M., Kucera, J.: Nucl. Instrum. Methods Phys. Res. A **564**, 675 (2006).
44. Kennedy, G., St-Pierre, J.: J. Radioanal. Nucl. Chem. **257**, 475 (2003).
45. http://www.kayzero.com/k0naa/k0naa/k0-International_Scientific_Committee.html.
46. Révay, Zs., Harrison, R. K., Alvarez, E., Biegalski, S. R., Landsberger, S.: Nucl. Instrum. Methods Phys. Res. A **577**, 611 (2007).
47. Molnar, G. L., Révay, Zs., Belgya, T.: Nucl. Instrum. Methods Phys. Res. A **489**, 140 (2002).
48. Révay, Zs., Belgya, T., Kasztovszky, Zs., Weil, J. L., Molnár, G. L.: Nucl. Instrum. Methods Phys. Res. B **213**, 385 (2004).
49. Lindstrom, R. M., Révay, Zs.: Beams and facilities.. In: *Handbook of Prompt Gamma Activation Analysis with Neutron Beams*. (Molnár, G. L., ed.) Kluwer Academic Publishers, Dordrecht (2004), p. 31.
50. Anderson, D. L., Kasztovszky, Zs.: Applications of PGAA with neutron beams. In: *Handbook of Prompt Gamma Activation Analysis with Neutron Beams*. (Molnár, G. L., ed.) Kluwer Academic Publishers, Dordrecht (2004), p. 137.
51. Gméling, K., Harangi, Sz., Kasztovszky, Zs.: J. Radioanal. Nucl. Chem. **265**, 201 (2005).
52. Kasztovszky, Zs., Biró, K. T., Markó, A., Dobosi, V.: Archaeometry **50**, 12 (2008).
53. Szakmány, Gy., Kasztovszky, Zs., Szilágyi, V., Starnini, E., Friedel, O., Biró, K. T.: Eur. J. Mineral. **23**, 883 (2011).
54. Szilágyi, V., Gyarmati, J., Tóth, M., Taubald, H., Balla, M., Kasztovszky, Zs., Szakmány, Gy.: J. South Am. Earth Sci. **36**, 1 (2012).
55. Kasztovszky, Zs., Panczyk, E., Fedorowicz, W., Révay, Zs., Sartowska, B.: J. Radioanal. Nucl. Chem **265**, 193 (2005).
56. Révay, Zs.: J. Radioanal. Nucl. Chem. **276**, 825 (2008).

57. Teschner, D., Borsodi, J., Wootsch, A., Revay, Zs., Havecker, M., Knop-Gericke, A., Jackson, S. D., Schlogl, R.: Science **320**, 86 (2008).
58. Teschner, D., Revay, Zs., Borsodi, J., Havecker, M., Knop-Gericke, A., Schlogl, R., Milroy, D., Jackson, S. D., Torres, D., Sautet, P.: Angew. Chem. Int. Ed. **47**, 9274 (2008).
59. Revay, Zs., Belgya, T., Szentmiklosi, L., Kis, Z., Wootsch, A., Teschner, D., Swoboda, M., Schlogl, R., Borsodi, J., Zepernick, R.: Anal. Chem. **80**, 6066 (2008).
60. Festa, G., Andreani, C., De Pascale, M. P., Senesi, R., Vitali, G., Porcinai, S., Giusti, A. M., Schulze, R., Canella, L., Kudejova, P., Muhlbauer, M., Schillinger, B.: J. Appl. Phys. **106**, 074909 (2009).
61. Kennedy, G., St-Pierre, J., Wang, K., Zhang, Y., Preston, J., Grant, C., Vutchkov, M.: J. Radioanal. Nucl. Chem. **245**, 167 (2000).
62. Martinho, E., Gonçalves, I. F., Salgado, J.: Appl. Radiat. Isot. **58**, 371 (2003).
63. Kennedy, G.: Treating wood with chemical preservatives. In: *Analytical Applications of Nuclear Techniques*. (Rossbach, M., ed.), IAEA Publications, Vienna (2004), p. 123.
64. Foster, H., Kennedy, G., Maisonneuve, P., Krewski, D., Ghadirian, P.: Trends Cancer Res. **4**, 15 (2008).
65. Noisel, N., Bouchard, M., Carrier, G.: Environ. Toxicol. Pharmacol. **29**, 252 (2010).