

METHODOLOGY FOR QUANTITATIVE ANALYSIS OF LARGE LIQUID SAMPLES WITH PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS USING Am-Be SOURCE

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Abstract

An optimized set-up for prompt gamma neutron activation analysis (PGNAA) with Am-Be source is described and used for large liquid samples analysis. A methodology for quantitative analysis is proposed: it consists on normalizing the prompt gamma count rates with thermal neutron flux measurements carried out with He-3 detector and gamma attenuation factors calculated using MCNP-5. The relative and absolute methods are considered. This methodology is then applied to the determination of cadmium in industrial phosphoric acid. The same sample is then analyzed by inductively coupled plasma (ICP) method. Our results are in good agreement with those obtained with ICP method.

Keywords : *PGNAA, quantitative, analysis, liquid, effluents*

INTRODUCTION

Prompt gamma neutron activation analysis (PGNAA) is a powerful analytical technique applied for on-line and in-situ analysis in industry [1,2], non destructive testing [3-5] and environment [6]. This technique is based upon the detection of prompt gamma-rays emitted in a very short time ($< 10^{-13}$ s) through thermal neutron capture reactions which happen after moderation and thermalization of the fast neutrons emitted by the source either in a moderator before reaching the sample or in the sample itself. The prompt gammas emitted, after neutron capture by the elements constituting the sample, have characteristic energies. The gamma detection is then generally carried out in a transmission or backscatter

mode and the number of detected prompt gammas is proportional to the masses of the correspondent elements present in the sample.

As mean free path of neutrons in matter is high, the main advantage of PGNAA over conventional analytical techniques is that, large volume samples can be interrogated and therefore, data that are more representative may be provided.

Nowadays, there is a growing concern of the environmental pollution problems. In this context, an optimized PGNAA set-up has been built [7] for liquid effluents analysis and may be seen on figure 1.

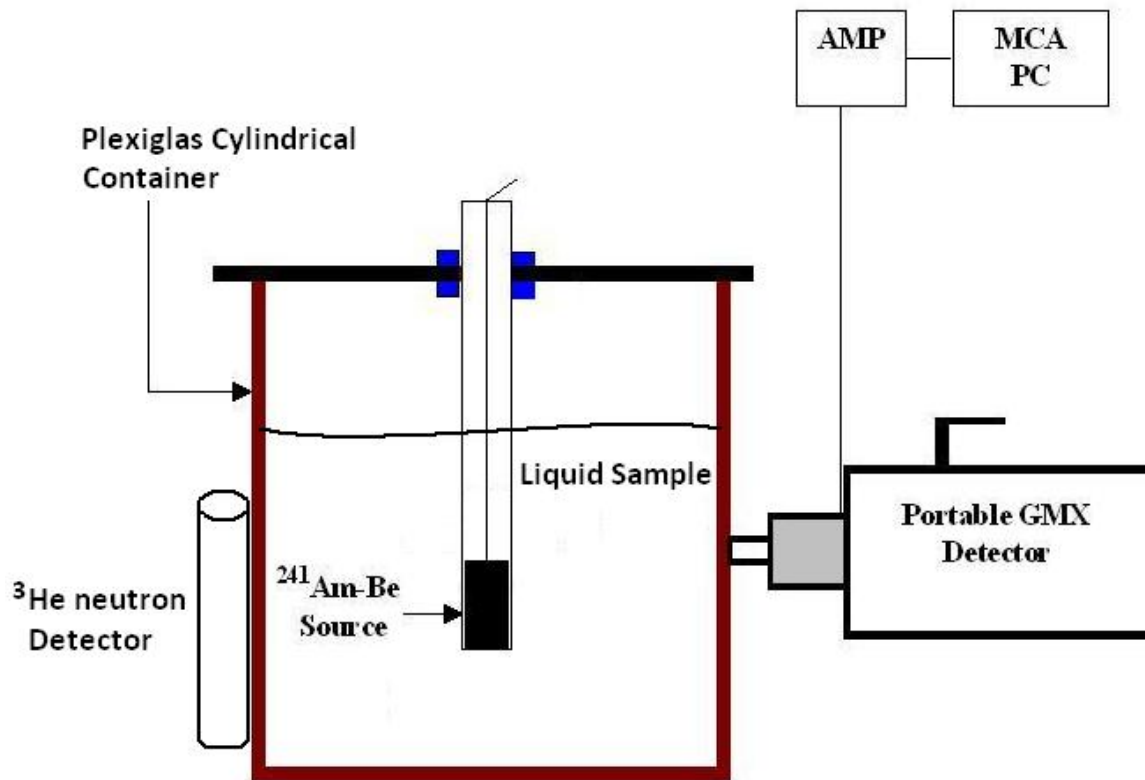


Fig.1. Drawing of the PGNAA set-up devoted to large liquid sample analysis

The optimal sample dimensions are: 40 cm for the diameter and 20 cm for the height. To detect the emitted prompt gamma rays, a portable high purity germanium detector is placed at the surface of the Perspex sample container. A Perspex tube containing the Am-Be source is immersed in the sample with its end situated exactly at the center of the sample. In this work, the absolute and relative methods are considered. In the absolute method, the average thermal flux inside the liquid sample and the average absolute gamma ray efficiency must be known. The average thermal flux is determined knowing the average thermal flux inside a pure water sample obtained by MCNP5 calculations and flux monitoring measurements using an He-3 neutron detector at the surface samples (water and unknown liquid sample). The absolute gamma efficiency was determined using the prompt gamma rays of chlorine dissolved in pure water. Concerning the relative method, the prompt gamma counts of the unknown sample were compared to those obtained with known quantities of the elements dissolved in pure water. When analyzing unknown liquid samples, one must know exactly how average thermal neutron flux and average absolute gamma efficiency are varying

compared to observed values of the same physical quantities in pure water, which is the standard in this work. For thermal neutron flux, we decided to monitor the flux using ^3He neutron detector placed at the surface of the sample. For variations of the average absolute gamma efficiency, this was treated with calculations of average gamma attenuation factors using MCNP5 code. This methodology was then used for industrial phosphoric acid and the validity of the method was checked with cadmium determination in industrial phosphoric acid.

EXPERIMENTAL

The emitted prompt gamma rays are detected with an ORTEC portable high purity germanium (HpGe) detector having 20% relative efficiency and 2 keV resolution at 1332.5 keV of Co^{60} . The detector is placed in the center of the sample container and against the external surface of the latter. On the other side of the sample container and in order to monitor the thermal neutron flux inside the sample, a ^3He neutron detector is lying on the external surface of the cylindrical sample container and parallel to its axis. The center of the ^3He neutron detector is adjacent to the plane perpendicular to the sample axis and passing by the center of the sample. The portable ORTEC HpGe gamma detector is connected to a Canberra Model inspector 2000 portable integrated digital signal processing electronic unit. In this unit, the signal coming from the preamplifier of the detector is digitized, amplified and then processed in a multichannel analyzer. All the functions are controlled through a portable computer and the obtained gamma spectra are treated by Canberra gamma software Genie 2000. The inspector 2000 is working with a lithium battery allowing at least 4 hours autonomy. The Set-up as described above may be used for field analysis.

METHODOLOGY FOR PGNA QUANTITATIVE ANALYSIS

The measured count rate A of a prompt gamma ray of energy E_γ emitted from a capturing nuclide in a sample of volume V is given by [8]:

$$A = \frac{1}{V} \frac{m}{M} N_A \theta \int_V \varepsilon(r, E_\gamma) P(E_\gamma, v) n(r, v) \sigma(v) v dv \quad (1)$$

where m is the element mass, M - atomic mass, N_A - Avogadro number, θ - isotopic abundance, $\varepsilon(r, E_\gamma)$ - the detection efficiency for the prompt gamma ray of energy E_γ emitted at the location r , $P(E_\gamma, v)$ - the absolute gamma ray emission probability (gammas emitted per capture) of the prompt gamma of energy E_γ emitted from the nucleus capturing a neutron of speed v , $\sigma(v)$ - speed dependent neutron capture cross section for the nucleus, and $n(r, v)$ - speed dependent neutron density at the location r .

For a well thermalized neutron flux, the counting rate given in Eq.1 may be written as follows:

$$A = \frac{m}{M} N_A \theta P(E_\gamma) \bar{\varepsilon}(E_\gamma) \bar{\Phi}_0 g \sigma_0 \quad (2)$$

where:

$\bar{\Phi}_0$ is the conventional thermal neutron flux averaged over the whole volume sample,

σ_0 is the capture cross section at the speed of 2200 m/s,

$\bar{\epsilon}(E_\gamma)$ is the detection efficiency for the gamma prompt of energy E_γ averaged over the whole sample volume.

g is the Westcott factor for the element of interest.

In this work, $\bar{\phi}_0$ has been taken as the value of the average thermal neutron flux in pure water calculated by Monte Carlo MCNP5 code and then corrected using flux measurements carried out with He-3 detector on pure water and water reject. For the average gamma detection efficiency, it has been derived experimentally using the prompt gamma rays of chlorine dissolved in pure water and equation (2). The average thermal neutron flux values used in equation (2) were those derived from the fit function of average thermal neutron flux against chlorine concentration determined in our previous work [7] and given by:

$$\bar{\phi}_0 = 1780.04 - 372.98C + 53.67C^2 \quad (3)$$

where C is the chlorine concentration given in %.

For the nuclear parameters like, neutron capture cross section, prompt gamma energies and emission probabilities, they were taken from ref. and are given in table 1. The determined curve of average prompt gamma detection efficiency is shown in fig. 2 with a first order decay exponential fit function.

Table 1. Prompt nuclear data table for chlorine.

Isotope=³⁵Cl,$\theta=75.78\pm0.04(\%)$,$\sigma_0=33.2\pm0.3$,$g(293^\circ\text{K})=1.000$	
Prompt gamma energy (keV)	Absolute intensities P(E_γ) per 100 captures
517.07	24.3±1.4
786.30	10.5±0.4
788.42	16.3±0.4
1164.86	27.2±0.7
1951.14	19.4±0.6
1959.35	12.6±0.3
2863.81	5.77±0.11
3061.86	3.52±0.07
4979.71	3.6±0.1
6110.84	20.6±0.7
6619.63	7.83±0.16
7413.95	10.52±0.24
7790.32	8.31±0.19
8578.59	2.74±0.06

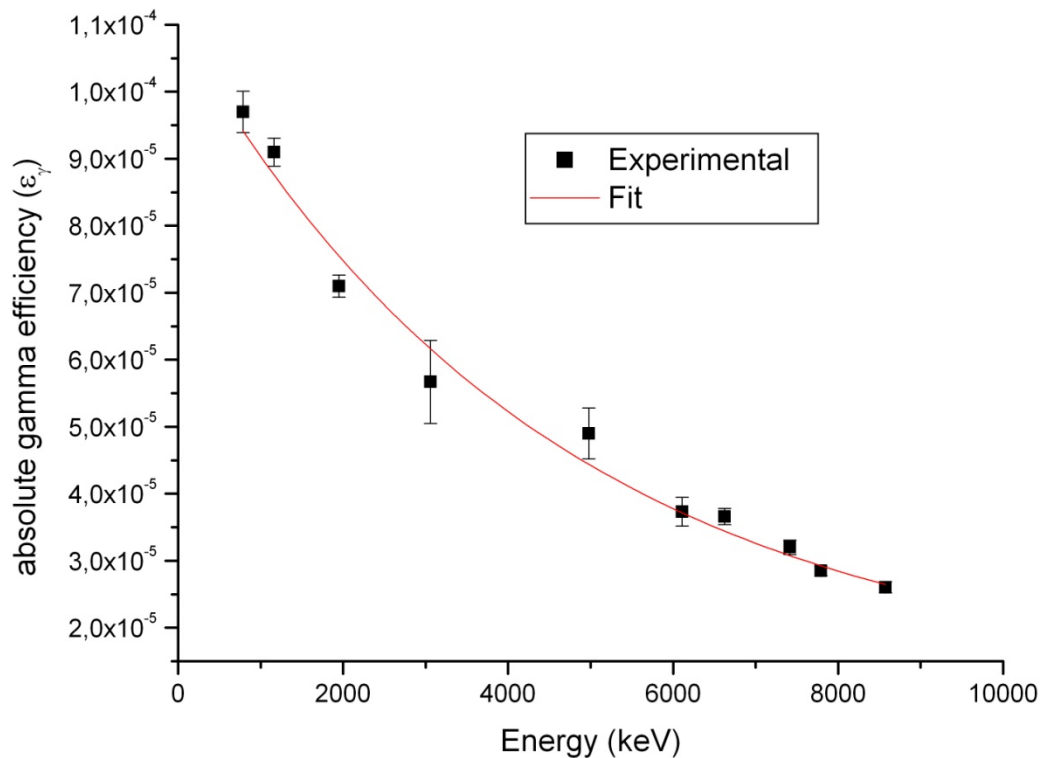


Fig 2. Absolute gamma efficiency for pure water sample

There exists two known methodologies to perform quantitative analysis with isotopic neutron source PGNAA : the Monte Carlo Linear Least Square method (MCLLS) [9] and the fixed point iterative method [10,11] These methods have been developed for use in-situ and on-line in industry, geology,... The linear least square approach is based on the assumption that any unknown sample spectrum is the sum of the products of the elemental amount and the library spectrum of each element for every channel. In applying this approach, the elemental library spectra must be available. However, these elemental libraries are problem-dependant and highly non-linear.

The non-linearity problem is well treated by the fixed point iteration method. A general formulation of the non-linear problem of determining the composition of large homogeneous sample from a prompt gamma measurement is given by Holloway et al.[10]. From this formulation, an iterative method is developed which solves the problem using minimal number of gamma measurements. With a neutron-gamma transport code, it is tried to find the composition of a sample material from the measured photo peak areas. Required data the measured ratios of photo peak areas, sample density, geometry of the experimental set-up, the neutron spectrum, the efficiency of the detector and cross-sections data. However, it uses also a boundary condition is that the mass fraction of all elements determined in the sample material add-up to 1. This condition is difficult to fulfill since in many cases not all elements can be detected.

In our work, the thermal neutron flux was monitored using measurements carried out with He-3 detector placed on sample holder (see fig.1). For The gamma attenuation problem, we define a gamma self attenuation factor F_{att} and the average prompt gamma efficiency $\bar{\epsilon}(E_\gamma)$ in equation (2) can be replaced by the following formula:

$$\bar{\epsilon}(E_\gamma) = \bar{\epsilon}_0(E_\gamma) \cdot F_{att} \quad , \quad (4)$$

where $\bar{\epsilon}_0(E_\gamma)$ is the average absolute efficiency for the PGNAA set-up without sample,

F_{att} is the average attenuation factor which corresponds only to the gamma attenuation in the sample

Relative and absolute methods will be considered in this work. For the absolute method, the absolute thermal flux in water and calculated with MCNP is normalized using the flux measurements of thermal flux carried out with He-3 detector on surface sample holder respectively for water as reference sample and unknown sample. Equation (2) is then used with the normalization of absolute gamma efficiency determined with water for gamma attenuation problem. For the relative method using calibration curve, the calibration factor is normalized for thermal flux and gamma attenuation.

If we know the raw composition of the sample to analyze, the gamma attenuation factors may be calculated using MCNP5 which is a well known Monte Carlo code for the calculation of photon and neutron transport. As we need only an average value of the attenuation factor, in the calculations, we suppose that the source is distributed homogeneously in the sample and we calculate the probability of the gamma to reach the detector volume .To determine the attenuation factor, we calculate the precedent probability with and without the sample and it follows that:

$$F_{att} = \frac{P_{\gamma,s}}{P_{\gamma,ws}} \quad (5)$$

where $P_{\gamma,s}$ is the probability that a gamma originating from the sample reaches the detector,

$P_{\gamma,ws}$ is the probability that a gamma originating from the container (without sample) reaches the detector

To test the validity of the proposed method, cadmium was determined in industrial phosphoric acid using the relative and absolute method. In the relative method , the quantitative analysis was performed using calibration curve obtained with different concentrations of cadmium dissolved in water .When dealing with the relative method, we used the average absolute gamma efficiency (fig.1) obtained with the prompt gamma rays emitted after neutron capture by chlorine dissolved in water. Even if phosphoric acid is mainly composed of light elements like hydrogen and phosphorus, its density (1.3) is higher than that of water (1) therefore the gamma attenuation in the two samples differs largely. To apply the quantitative analysis proposed in this work, the attenuation factors defined by equation (5) were calculated using MCNP5 code for the two samples .For industrial phosphoric acid, the elemental composition was taken as that of H_3PO_4 . .The calculated gamma attenuation factors as function of gamma energy are shown in figure 3.

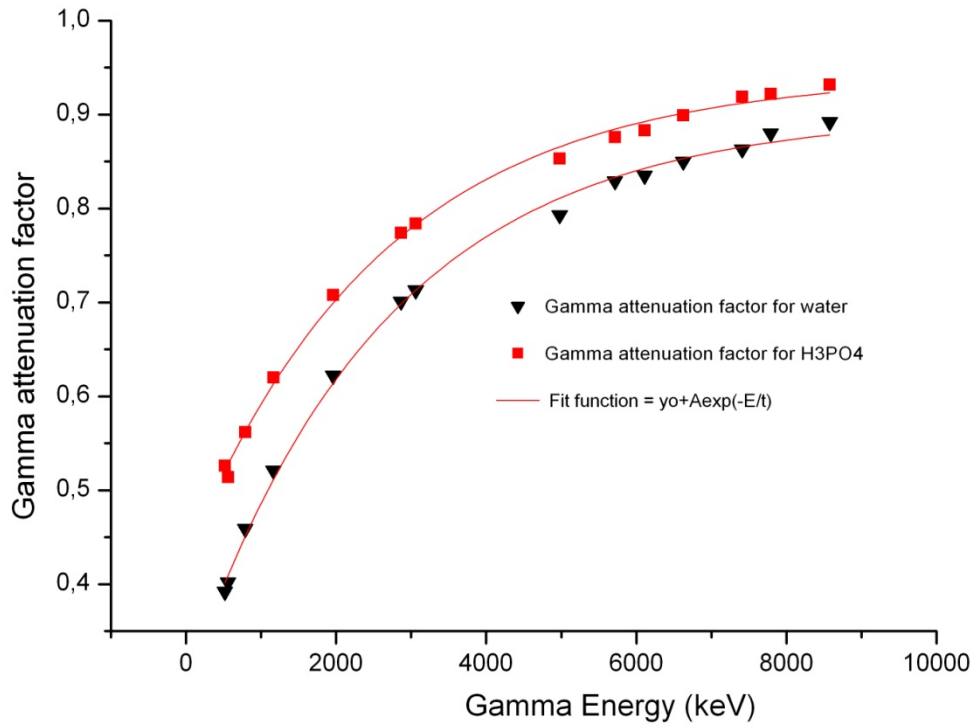


Fig.3. Gamma attenuation factors for Water and phosphoric acid samples

According to equation (4), the relationship between the averaged absolute gamma efficiencies for water and phosphoric acid samples is given by:

$$\bar{\epsilon}_a(E_\gamma) = \bar{\epsilon}_w(E_\gamma) \cdot \left(\frac{F_{att,a}}{F_{att,w}} \right), \quad (6)$$

where

$\bar{\epsilon}_a$ and $\bar{\epsilon}_w$ are averaged absolute gamma efficiencies respectively for phosphoric acid and water samples

$F_{att,a}$ and $F_{att,w}$ are respectively the gamma attenuation factors of phosphoric acid and water samples

For the absolute method, one can use equation (2) where the average thermal neutron flux in phosphoric acid is taken as that of water sample normalized with the values measured with He-3 neutron detector and the average absolute gamma efficiency is determined using equation (6).

In the case of relative method, the calibration factor in the calibration curve must be normalized for flux using measurements carried out with He-3 neutron detector and corrected for gamma attenuation using the gamma attenuation factors calculated at the prompt gamma energy of 558 keV emitted by cadmium in water and phosphoric acid. The results of cadmium determination in industrial phosphoric acid are summarized in table 2. In order to

check the validity of our method developed in this work, the precedent results were compared to those obtained with the inductively coupled plasma (ICP) technique which is often used for environmental sample analysis. The ICP technique is based on atomic spectrometry. Most specifically, it is an emission spectrometric technique that exploits the fact that excited atoms emit energy at a given wavelength as the electrons return to their ground state. A given element emits energy at specific wavelengths peculiar to its chemical character. Although each element emits at many wavelengths, it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at that wavelength is proportional to the amount (concentration) of the element in the analyzed sample. The analysis was done on a Jobin Yvon 32 ICP apparatus and the result is an average on three determinations which is shown in table 2.

Table2. Analysis results concerning the determination of Cadmium in phosphoric using different methods: absolute method, relative method and ICP.

<i>Method</i>	<i>Count rate at 558keV (cps)</i>	<i>Correction Factor for pile-up losses ^{*,1}</i>	<i>Normalization factor for flux ^{*,2}</i>	<i>Normalization Factor for gamma attenuation ^{*,3}</i>	<i>Corrected and normalized count rate (cps)</i>	<i>$\bar{\epsilon}(558 keV)$</i>	<i>Concentration ($\mu\text{g/ml}$)</i>
<i>PGNAA Relative method</i>	0.32±0.05	1.24	1.47	1.23	0.71±0.11	9.82 10 ⁻⁵	17.78±2.84
<i>PGNAA Absolute method</i>	0.32±0.05	1.24	1.47	1.23	0.71±0.11	9.82 10 ⁻⁵	17.25±2.76
<i>ICP method</i>	—	—	—	—	—	—	17.46±0.3

**,1* Correction factor for pulse pile-up is the ratio of count rate delivered by the pulser to that of the pulser peak

**,2* The normalization factor is the ratio of measured flux with He-3 detector for water sample to that of phosphoric acid sample

**,3* The normalization factor is the ratio of gamma attenuation factor of water sample to that of phosphoric acid sample

As it can be observed, there is a good agreement between the results determined by PGNAA and ICP technique. The results obtained by the two methods seem to be in the same magnitude order with results find in the literature for industrial phosphoric acid [12].

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