


On neutron activation analysis with $\gamma\gamma$ coincidence spectrometry

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Abstract A new $\gamma\gamma$ coincidence system has been set up at NIST. It is operated with a digital data finder supported by new software developed at NIST. The system is used to explore possible enhancements in instrumental neutron activation analysis (INAA) and study applicability to neutron capture prompt gamma activation analysis (PGAA). The performance of the system is tested with certified reference materials for efficiency calibration and quantitative performance. Comparisons of INAA results based on conventional gamma-ray spectrometry data with INAA results based on coincidence data obtained from the same samples show improvements in the counting uncertainties and demonstrates the quantitative accuracy of the new system.

Keywords Gamma–gamma coincidence spectrometry · Neutron activation analysis · qpx gamma software · Quantitative assay · Reference materials · Trace elements

Introduction

Neutron activation analysis (NAA) is an important technique for the accurate and precise determination of trace and ultra-trace elemental compositions. The technique is widely used at the National Institute of Standard and Technology (NIST) in the value assignment process for Standard Reference Materials (SRMs) and other projects involving elemental characterization of materials. Its widely acknowledged properties include, among others, independence of matrix and chemical form of the analyte, capability for direct non-destructive assay, and the important metrological characteristics of a definitive technique [1]. However, NAA may be limited in its specificity as well as sensitivity by interference to the characteristic gamma rays and/or high background from other trace elements or matrix elements. Means to minimize these restrictions include radiochemical separation as well as special counting arrangements for the gamma-ray spectrometry. The special measurement method considered for this evaluation is $\gamma\gamma$ coincidence spectrometry.

In instrumental NAA (INAA) most elements form radionuclides that decay with characteristic gamma transitions to a ground state. Many nuclides have γ -ray cascades that may be considered for this measurement method, but often the β -branch feeding is weak or the γ -ray absolute intensities are small. Also, there are several isotopes (e.g. ^{203}Hg , and ^{51}Cr) important for INAA that emit only one β -delayed single γ -ray [2]. In prompt gamma NAA (PGAA) neutron capture reactions lead to highly-excited nuclear states that immediately de-excite via multiple γ -ray emissions in cascade (with some exceptions, e.g., ^1H and $^{10}\text{B}(n, \alpha)^7\text{Li}$). For both techniques, an improvement of selectivity and sensitivity is envisioned with the use of $\gamma\gamma$ coincidence spectrometry.

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Gamma–gamma coincidence counting employs at least two γ -ray detectors to measure the coincident γ -ray emitted in each decay event. In principle, $\gamma\gamma$ coincidence counting can achieve a higher degree of discrimination than non-coincidence (“singles”) spectrometry since it applies a more stringent definition of what constitutes a valid event, namely the observation of two decay-correlated γ -rays within a specified time window. This requirement is useful in separating events of interest from the much larger number of uncorrelated events in a counting period.

The use of the technique for identifying and/or quantifying nuclear decay events based on the observation of unique multiple γ -ray signatures in NAA was reported more than 50 years ago [3]. Despite subsequent early work [4, 5], only occasional applications have been reported in analytical chemistry [6–9]. In contrast coincidence counting is well established in nuclear structure studies where it is routinely used by nuclear spectroscopists to elucidate complex decay schemes. The limited use in NAA has been confined to very special cases that were only resolved with complex and expensive instrumentation instead of classical radiochemistry, and the available counting and data processing equipment NAA specialists normally are familiar with. However, new digital spectrometry equipment, fast-processor desktop computers, and dedicated software developments that are now available may allow the reintroduction of coincidence spectrometry to take full advantage of its sensitivity and selectivity. This study explores the potential advantages in INAA of biological materials where some very low levels of trace elements are difficult to determine because of high background in the gamma-ray spectra. In particular the Bremsstrahlung continuum from phosphorus β^- decay will be suppressed in the coincidence counting.

Experimental section

Detector array

The initial approach at NIST with two detectors has illustrated the feasibility of $\gamma\gamma$ coincidence spectrometry in a modern NAA laboratory [10, 11]. The further development has two goals, high coincidence efficiency for INAA and a possible configuration to be located at the NIST cold neutron PGAA station [12]. An array of two, and alternately of four, high-volume high purity germanium (HPGe) detectors was assembled; Table 1 lists the detectors. The two-detector array for highest coincidence efficiency is shown in Fig. 1a and the four-detector configuration is shown in Fig. 1b. Sample holders are 3D printed frames for detector alignment and guides for Petri Slides[®] as sample containers thus placing the sample at 50 mm distance to the

detectors in the center of the 1000 cm³ four-detector “sample box” or at 5 mm distance to the detectors with the 1 cm \times 10 cm diameter two-detector spacer. The construction of a shielding structure was omitted since there is practically no chance for coincidence events recorded in the background. Each detector is supplied with preamplifier power and high voltage bias through conventional nuclear instrumentation modules (NIM), two liquid nitrogen auto fill modules support the respective 3 L dewars.

Data processing

The data-acquisition system for the spectrometer utilizes all-digital electronics, based on the Pixie-4 module (XIA LLC, 31057 Genstar Road, Hayward, CA 94544) [13]. The Pixie-4 is a four-channel digital pulse-processing module deployed in compact peripheral component interconnect (PCI) for instrumentation (PXI) architecture. The waveform of an input signal, taken directly from an HPGe preamplifier output, is continuously sampled and digitized by a flash analog to digital converter (ADC). The signal pulse height is determined by a programmable, digital trapezoidal filter implemented in a field-programmable gate array (FPGA). Preamplifier pulse heights are determined to 16-bit resolution. Event timing and pulse-pileup inspection is also carried out in the FPGA by a programmable trapezoidal filter. Events are time-stamped at the full ADC rate of 75 MHz. In the present system, the Pixie-4 resides in a 3U PXI crate, and a host desktop PC controls the pulse processing module and performs data readout via a PCI-PXI fiber-optic bridge. All operating parameters, including the filter values, are user-adjustable in software on the host PC. The coincidence time window is also set in software with a granularity of 13.33 ns; a window of ≈ 50 ns is presently employed.

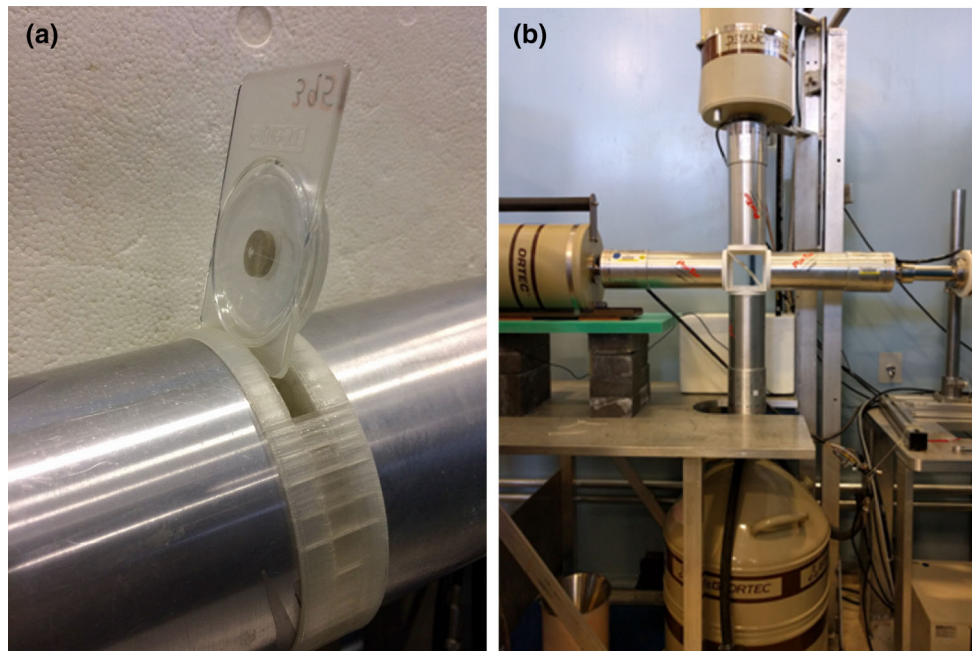
The novel NIST software *qpx-gamma* [14] controls the data recording and provides a graphical user interface (GUI) between the Pixie-4 features and the real-time output of the live acquisition of data [15]. Depending on the parameters of the spectra requested prior to acquisition, individual gamma events are clustered into coincident blocks, tested against the defined coincidence requirements, and binned to the respective spectra in near-real time. List mode output to file is also supported in parallel.

The software supports the critical gain matching of the detectors, however in the current experiments the gain was manually matched for all detectors. This is aided by the Pixie-4 supported automatic baseline adjustment for all selected detectors. The gain stability is excellent over the duration of the experiments. The *qpx-gamma* software supports user selection of simultaneous display and output of single detector, multi-detector coincidence, as well as sum spectra. A typical display of an activated biological

Table 1 Detectors used in the coincidence array

Name	Type ortec	Cryostat	Relative efficiency (%)	FWHM @1332 keV
Sophia*	GEM 80P4	30 L dewar upright	87	1.81
Daphne	GEM 60P4-95	X-Cooler II	64	1.82
Linda*	GEM 65200-P	3 L portable dewar	66	1.79
Meike	GEM 80P4	3 L portable dewar	77	2.20

* Used in the 2-detector array

**Fig. 1** **a** Two-detector array with 1 cm spacer/sample position guide and PetriSlide® sample container about to be inserted. **b** Four-detector array with 10 cm spacer and sample container guide

material counted with the 2-detector array is shown in Fig. 2. Data are saved as one file or exported to commonly used formats (Toolkit tka, ANSI Standard Data Format n42, RadWare spe) that can be accessed by conventional gamma spectroscopy packages.

Samples

Reference materials prepared from mussel tissue (*Perna perna*) [16] and edible tissues of the whitemouth croaker fish (*Micropogonias furnieri*) [17] from IPEN-CNEN/SP, certified reference material (CRM) Infant Formula from KRISS, and Standard Reference Materials (SRMs) 1577b and 1577c Bovine Liver and SRM 1849 Infant Formula from NIST were first subjected to conventional INAA following established NIST procedures [18]. Briefly the powder samples are converted to ≈ 200 mg pellets with a hydraulic press and die, packaged in polyethylene bags and irradiated together with element standards in a pneumatic rabbit system for 8 h or 16 h at a neutron flux of

$2.4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ at the NIST Center for Neutron Research [19]. Correction factors for dry mass were determined on separate samples according to the CRM and SRM instructions. Two quantitative INAA assays were done after 5 days decay and approximately 20 days decay. After these measurements, the samples and standards were counted with the coincidence system, initially with the four-detector array, later solely with the two-detector array for higher efficiency achieved with the close sample to detector distance.

Results and discussion

System performance

Three parameters are critical for the delivery of quantitative data and the expected INAA performance enhancements: the efficiency for the registration of the coincidence events, the system energy resolution, and the corrections for system dead time and pulse pile-up.

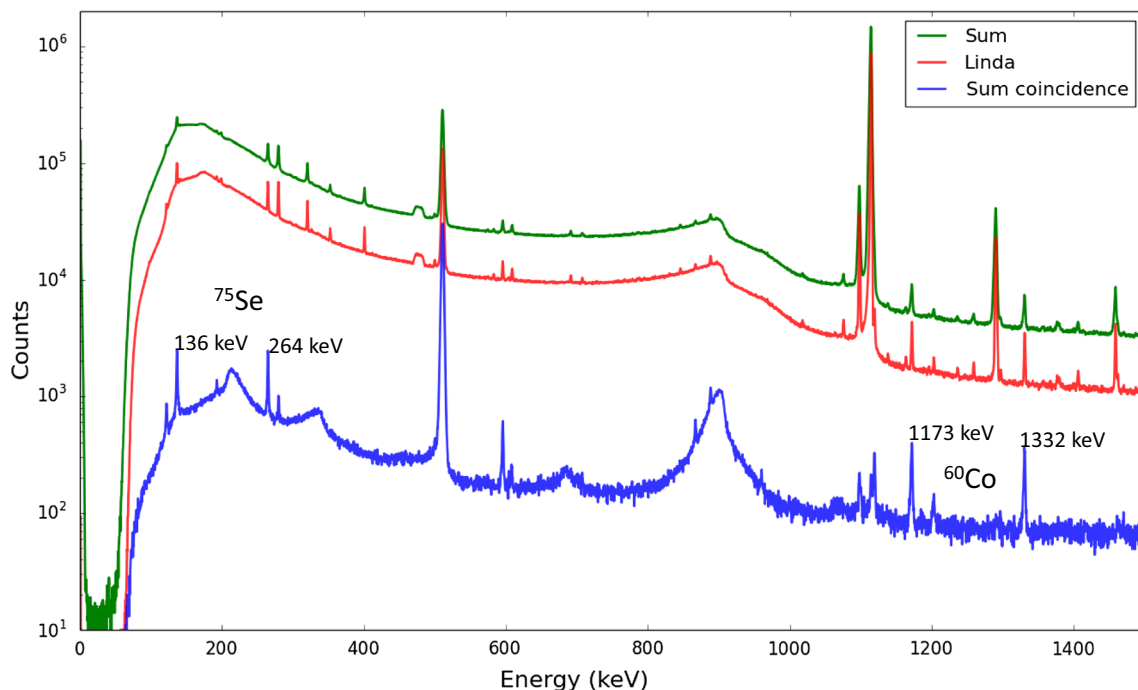


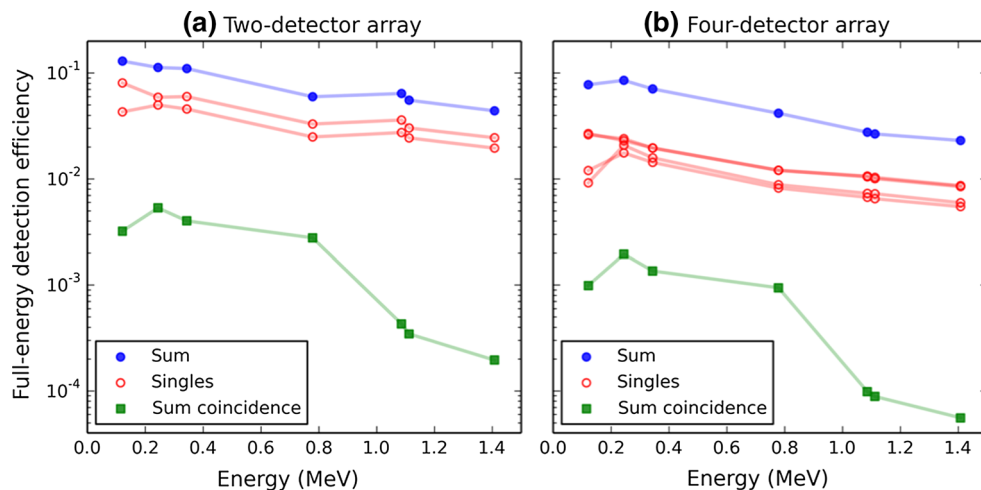
Fig. 2 Example 2-detector array spectrum display of KRISS infant formula with (*from top*) sum of all events, single detector (Linda), and sum of coincidence events

The efficiencies of the two-detector and four-detector arrays are measured with a calibrated ^{152}Eu source (SRM 4218 E) placed in the sample position. This means that the source-to-detector endcap distance is either 5 mm or 50 mm respectively. All individual detector data (singles) as well as the sum of all data are registered without any requirements applied, while all coincidence events are registered for all available detector pairs and are also registered in a sum coincidence spectrum. All singles data points, the sum and each individual detector as well as the sum coincidence data are plotted in Fig. 3a (two-detector array) and 3b (four-detector array). The results show

excellent efficiency for the singles sum data approaching the 10% absolute efficiency margin in the 100–300 keV region and sum coincidence efficiencies nearly equivalent to a standard 25% relative efficiency HPGGe detector. As the data for the four-detector array show lower efficiencies for all data and about a factor 4 lower efficiency for the sum coincidence, the bulk of the samples were measured with the two-detector array.

The system energy resolution, while concurrent with the detectors' solo performance in the singles spectra, degrades somewhat in the sum spectra. Next to slight offsets encountered in the manual adjustment of the gain, the

Fig. 3 Sum, singles, and coincidence absolute efficiency for ^{152}Eu source



detector with the worst resolution performance controls the overall sum spectrum resolution. However, this fact is much less critical in the coincidence sum spectra because of the discrimination from potentially interfering singles.

The overall system dead time is currently registered as the value of the detector with the highest dead time. This is not a correct value for each individual detector’s spectrum or for the sum spectra. A solution is not available in the software since the Pixie-4 provides only an individual value for each detector. In addition, as detailed in the Pixie-4 manual [20], a certain percentage of loss remains unaccounted in the live time extension depending on the input count rates. This has been tested for a dead time range up to 25% with a dual source experiment. The measured losses of the constant source count rate were proportional to the dead time and usable for a loss calibration. The resulting calibration factors are different for the singles sum and the coincidence sum and are also different in the two arrays. The loss factors are applied like commonly known pile-up factors to all gamma-ray data for the results reported here.

Quantitative determinations

Two sets of samples, the two IPEN-CNEN/SP candidate reference materials and SRM control samples and the KRISS CRM and SRM control samples are evaluated. Data for both sample sets were obtained from the standard INAA assay as well as the $\gamma\gamma$ coincidence assay with the two-detector array. Table 2 shows results for selected elements from the first set while selenium results from the second set are shown in Table 3. Table 2 illustrates that depending on the decay properties of the element and other properties of the gamma-ray spectra a slight to significant advantage can be achieved in the counting uncertainty. This however is not the case for Se; this is discussed further below. In particular Ag must be mentioned here since for several matrices no valid peak areas can be obtained with the standard INAA assay. The current results for Ag in SRM 1577c, (5.6 ± 1.2) $\mu\text{g}/\text{kg}$, are equivalent to the previously reported ones in the value assignment campaign for this SRM when considering the limited number of samples in this test. The previous value, (5.48 ± 0.30) $\mu\text{g}/\text{kg}$ from the assay of twelve samples, was obtained by off-line processing of time-stamped list-mode data [10]. This agreement illustrates that the on-line coincidence processing by the *qpx gamma* software is equal to the previous evaluation of coincidence data that were registered in list-mode with subsequent off-line evaluation.

The most significant aspect of this work is the demonstration that *qpx gamma* delivers reliable and reproducible results with an improvement of the counting uncertainties (Table 2). Agreement of the coincidence data with the

Table 2 Selected results from two IPEN candidate CRMs and three NIST SRMs with $\gamma\gamma$ coincidence counting in the two-detector array compared to the regular INAA assay of the same samples; values are average \pm standard deviation of 3 samples and % counting uncertainty in parenthesis

Sample	Ag @ 657 keV (mg/kg)		Co @ 1173 keV (mg/kg)		Cs @ 796 keV ($\mu\text{g}/\text{kg}$)		Se @ 264 keV (mg/kg)	
	$\gamma\gamma$	INAA	$\gamma\gamma$	INAA	$\gamma\gamma$	INAA	$\gamma\gamma$	INAA
IPEN Mussel	2.173 ± 0.024 (0.86)	2.124 ± 0.056 (1.6)	0.781 ± 0.013 (0.66)	0.783 ± 0.053 (0.93)	97.1 ± 3.5 (4.0)	96.4 ± 4.4 (7.2)	4.274 ± 0.045 (1.8)	4.09 ± 0.14 (1.6)
IPEN Fish	0.014 ± 0.03 (24)	ND ^a	0.133 ± 0.013 (1.6)	0.132 ± 0.010 (1.9)	45.3 ± 3.7 (4.7)	43.5 ± 2.6 (7.2)	2.69 ± 0.18 (2.1)	2.64 ± 0.12 (1.7)
SRM 1566	0.620 ± 0.033 (1.7)	0.638 ± 0.020 (5.2)	0.357 ± 0.010 (0.9)	0.360 ± 0.008 (1.1)	29.8 ± 6.1 (15)	28.9 ± 8.1 (34)	1.96 ± 0.15 (6.3)	1.93 ± 0.07 (3.0)
COA	0.666 ± 0.009		0.371 ± 0.009		–		2.06 ± 0.15	
SRM 1577b	0.0376 ± 0.0039 (8.1)	ND	0.235 ± 0.002 (1.0)	0.242 ± 0.004 (1.4)	13.4 ± 1.2 (10)	12.1 ± 3.5 (29)	0.701 ± 0.020 (5.4)	0.684 ± 0.028 (6.7)
COA	0.039 ± 0.007		(0.25) ^b		–		0.73 ± 0.06	
SRM 1577c	0.0056 ± 0.0012 (16)	ND	0.3015 ± 0.0020 (0.52)	0.3031 ± 0.0012 (1.3)	22.8 ± 1.5 (6.8)	17.2 ± 2.6 (25)	1.974 ± 0.034 (2.1)	1.928 ± 0.034 (3.0)
COA	0.0059 ± 0.0016		0.300 ± 0.018		21.7 ± 1.4		2.031 ± 0.045	

Certificate of analysis (COA) data are value \pm expanded uncertainty (approximately 95% confidence) [21]

^a No peak detected

^b Information value

Table 3 Comparison of counting uncertainties for selenium results @ 264 keV in KRISSE infant formula, NIST SRM 1849 control material and candidate SRM 1869 for 8 h counting of each sample in standard INAA assay and in the two detector array

Sample	INAA count			Two-detector $\gamma\gamma$ coincidence	Two-detector sum
	Mass fraction (mg/kg)	U (mg/kg)	U_{count} (%)	U_{count} (%)	U_{count} (%)
KRISSE-A1	0.098	0.017	17.6	15.8	7.4
KRISSE-A2	0.074	0.016	21.7	17.8	7.1
KRISSE-A3	0.092	0.016	17.5	18.1	8.6
KRISSE-B4	0.101	0.018	18.1	16.8	8.5
KRISSE-B5	0.070	0.018	26.0	13.5	6.2
KRISSE-B6	0.101	0.018	17.6	12.2	5.4
Average	0.089*	0.014			
SRM 1849	0.824*	0.026	3.2	1.9	0.6
SRM 1869	0.742	0.025	3.3	3.7	1.3

* Comparable values: KRISSE: 0.0905 ± 0.0029 ; COA SRM 1849: 0.812 ± 0.029

certified values is achieved in the three control materials included in these measurements. The fact that most coincidence results in the control materials are trending to the lower side of the certified range may raise concern about the accuracy of the loss correction, but aging of the materials, i.e., oxidation, may have led to smaller dry mass correction factors than encountered during the certification, and overall one cannot observe a trend in the comparison of the coincidence results with the INAA results. An additional element with a coincidence decaying nuclide, Sc has advantage factors like Ag in the coincidence counting but is not included in the discussion since no certified values are available.

The determination of Se at or below the 0.1 $\mu\text{g}/\text{kg}$ level in biological materials has been difficult in INAA because of Compton and β^- Bremsstrahlung background in the low energy region of the gamma spectra. A common solution has been long counting times after long decay periods. Based on the initial experiments with the IPEN materials it was expected to improve the determination of Se over the INAA assay with coincidence counting that simultaneously would also suppress background events from β^- Bremsstrahlung in high phosphorus containing biological matrices such as the infant formula. Table 3 illustrates that the very low Se mass fractions in the KRISSE infant formula can be determined with both the standard single detector counting and coincidence counting, albeit with large statistical uncertainty in the standard assay as well as in the coincidence assay. Figure 2 illustrates that a reduction of β^- Bremsstrahlung background occurs in the sum coincidence counts when compared to the singles and sum of singles, but still showing the significant component from Compton scatter; the peak uncertainties in the sum coincidence spectra did not improve in this material. However

qpx gamma offered a better approach by simultaneously recording the summed data from the two detectors. The high detection efficiency of the two-detector array provides the significance to the data that is suitable for value assignment.

Conclusions

Setting up a $\gamma\gamma$ coincidence spectrometry system in an NAA laboratory is no longer a trying task thanks to modern digital signal processors and data acquisition software. The two-detector and four-detector array configurations used in this work are operational in practically exchangeable modes; the two-detector array offering better performance in the studied samples due to the highly efficient counting geometry. The NIST *qpx gamma* software supports flexibility in detector arrangements. In addition, it allows visualizing and analyzing the parts of the spectral data that are essential for the particular element in real time and after the experiment, may it be the “singles” spectrum, the sum spectrum of all coincidence events, or the sum spectrum of all detectors. Next to these conveniences for the spectroscopists using the *qpx gamma* software, it is shown that coincidence counting allows determinations that are not feasible in standard INAA counting and that the quantitative relationship of the spectral data to the mass fraction of elements is given in all cases. Therefore advantages exist in the applications of $\gamma\gamma$ coincidence counting to the INAA of the biological materials, albeit these are different for the applicable elements and limited to elements with nuclides that have suitable decay chains.

For future NAA applications we look forward to the possibility of changing detectors and their geometric

arrangement. It is clear that the current standard detector end cap geometries allow only the sample geometries used here; differently constructed detectors could provide even higher efficiencies. Further, an installation of a detector system like the four-detector array in a neutron-beam configuration for PGAA appears to be promising: most neutron-capture products decay with coincident cascade gamma rays. However, considerable challenges for the protection of the HPGe detectors from neutron damage lay ahead.

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