INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF
KILOGRAM-SIZE SAMPLES

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ABSTRACT

Instrumental neutron activation analysis (INAA) can now directly be applied to samples with masses in the kilogram range. It enables the analysis of material which is considered to be not representative at the scale of the traditional analytical portion, but representative at much larger scale. The irradiation facility is located in the reactor's thermal column and allows for the irradiation of samples with a maximum size of 1 m length and 15 cm diameter. Large sample INAA circumspases therefore various problems associated with sample size-reduction and homogenization. Several feasibility studies have been carried-out as with contaminated soil, mineral deposits, waste rocks from mining and recyclable material. Except for trace element data, also information is obtained on the natural radioactivity of the samples. The counting facility allows for segmented scanning of the activated samples which can be applied to obtain e.g. information on depth profile of trace elements in cores of river sediment. Methods are being developed to inspect for the presence of extreme inhomogeneities and to account for them in the uncertainty of the results.

I. INTRODUCTION

All routine multi-element analysis techniques employ rather small amounts of material varying from microliters and milligrams to a few grams. For technical and fundamental reasons, larger quantities are not being handled. In AAS and ICP only small portions can be introduced; since in XRF information is derived from the surface layers, the usage of quantities larger than required to prepare the target is meaningless. In INAA the situation is somewhat ambivalent: in many (university) research institutes the size of the analytical portion is kept limited - often not larger than 1 gram- to limit effects of neutron and gamma-ray self-shielding and deviations from the point-source geometry in counting. In some commercial service laboratories much larger sample masses are handled -up to 10 - 30 grams- to facilitate automated sample weighing, to reduce effects of contamination and, because of the proportional shorter irradiation time, to limit reactor costs. In these laboratories a high degree of accuracy is not always the prime objective in the analysis.

The limitation to the size of the analytical portion can face the analyst with problems when the amount of material collected is larger. Which is often the case since e.g. soils, rocks and plant material can easier and more representative be sampled at quantities in the order of hundreds of grams to kilograms than at quantities less than 1 gram. A mixture of minerals may be inhomogeneous at the molecular or atomic level but homogenous at the particle level. In chemical analysis this unit is obviously correlated with its effect to the execution of the analysis (e.g. differences in solubility) or to its interpretation. Thus, both for practical and sampling considerations often more material is collected and presented for analysis than can be handled.

Irrespective of the analysis technique selected, attention has to be paid to representative sub-sampling to obtain a relevant final analytical portion from the originally collected material. Testing the degree of homogeneity is a common practice in the preparation of reference materials, but for routine operations the requirement of analysis and statistical evaluation of at least 5 test portions of each sample to be analyzed would raise the cost of an analysis considerably. When restricting the discussion to the analysis of solid materials this sub-sampling may imply sample size reduction techniques and other processing such as sieving, crushing, milling or blending. Problems arise when
Homogenization is impossible, or extremely expensive due to material properties. Examples are electronic circuits on printed boards, household waste, scrap from recycled electronics, automobiles, plastics. A solution to this problem is to sort the material and to perform individual homogenization and, subsequently, analyses, thereby increasing the total project costs.

- The homogenization step results at contamination of the sample. Often the contamination due to crushing or milling is not controlled on every sample type. When processing large series of samples careful interim cleaning may get the less attention since it is time-consuming and thus expensive.

The considerations from the above indicate that for some applications, direct analysis of the voluminous solid sample as it has been collected might have advantages, both analytical and economical.

Instrumental neutron activation analysis (INAA) has all the potentials to analyze, even with adequate accuracy, large samples in the kilogram range. Both the neutrons as incoming radiation for activation and the gamma-rays as outgoing radiation to be measured have sufficiently high penetrating powers to facilitate NAA of samples of kilogram weights.

A method for large sample INAA has been developed at the Interfaculty Reactor Institute in Delft, The Netherlands. The method does not require any a-priori knowledge on the composition of the sample and does not imply any disturbance of the collected material. The facilities allow for the processing of samples with maximum sizes of 15 cm diameter and 1 m length, which corresponds for e.g. a geological material with masses of approximately 50 kg.

In this paper the facilities and methods are briefly described. Examples of studies in which large sample INAA could be applied are given and some quality aspects are discussed.

**II. MATERIALS AND METHODS**

**Irradiation facility.** The large sample irradiation facility [1,2] is located in the thermal column of the Institute’s 2 MW swimming pool reactor. The thermal column has been customized to obtain a well-thermalized neutron flux. In the irradiation facility, water is used as a shielding against neutrons and gamma-rays. The large sample - surrounded by flux monitors - is packed in a polyethylene container.

The sample can be rotated around its vertical axis during the irradiation. The neutron flux is approximately $3 \times 10^{12}$ m$^{-2}$ s$^{-1}$, which is a factor $10^4$ - $10^5$ lower than in the other irradiation facilities of the reactor. However, the product of neutron flux and sample mass is about the same as in conventional INAA.

**Measuring facility.** The measurement of the induced gamma activity is performed with a gamma-ray spectrometer integrated in a scanning device [1,2]. The detector is a side looking (horizontal dipstick) 96 % HPGe detector. Both the spectrometer and the scanner are operated via a workstation of the laboratory's local area network. The scanner allows for rotation around the vertical axis of the sample during counting. Vertical displacement with respect to the detector is also possible e.g. for longitudinal scanning.

**Methods to correct for neutron- and gamma-ray self attenuation phenomena.** Correction for neutron self-attenuation is based on the neutron flux depression as measured just outside the large sample. From measurements at three positions around the sample the parameters can be derived (neutron diffusion length, neutron diffusion coefficient and undisturbed neutron flux) which are needed to describe the neutron flux inside the sample [3]. Correction for gamma-ray self-attenuation is based on the effective linear attenuation coefficients determined via the transmission of gamma-rays from a reference source [4]. The gamma-ray self-attenuation correction is integrated with the calculation of the detector’s photopeak efficiency for a voluminous sample. Combination of both correction algorithms yield an ‘overall correction factor’, which reflects the difference in actual detector response for a given gamma energy compared to the theoretical detector response if the sample would have been a massless point-source located in the large sample’s centre, without any neutron and gamma attenuation [5].

**Additional corrections.** Since quite a few large samples also display gamma lines originating from natural radioactivity, a spectrum of this natural radioactivity is recorded prior to irradiation for correct interpretation of the gamma spectrum after activation.

**Quantitative analysis.** Quantitative analysis is carried-out via the $k_0$ single comparator approach, using a zinc metal foil as neutron flux monitor and comparator element. Using activation of zirconium foil and aluminium (0.1 % gold) wire and measuring the $^{95,97}$Zr and $^{199}$Au activities, the $k_0$ relevant irradiation parameters in the facility were determined. Whereas in the conventional pneumatic irradiation systems typically $f(\Phi_{\text{sw}}/\Phi_{\text{epi}}) = 55$ and $\times = 0.04$, in the large sample facility, as expected, it was found that $f = 10^4$. It indicates a pure thermal neutron flux rendering the $\times$-parameter superfluous. The flux parameters, in conjunction with the $k_0$-related neutron capture cross sections, have been used to convert the effective cross sections [6] experimentally determined at IRI in the pneumatic facility, into effective cross sections for the large sample facility. The $k_0$ method enables the determination of concentrations and detection limits of approximately 60 elements, many of them simultaneously.

**Validation.** Validation of the method for large sample
INAA has been done by the analysis of four homogeneous materials, strongly different in neutron and gamma-ray attenuation characteristics. Gamma-ray spectra of both the large samples and small samples of each of the four materials were taken [3]. The results indicated good agreement between the concentrations found in the large and small samples as can be seen from Fig.1 in which the difference, \( z \), between the concentrations is given, weighted by the uncertainty of this difference. \( z \)-Values between -2 and +2 , respectively -3 and + 3 indicate no statistical significant difference at the \( \alpha = 0.05 \) level respectively \( \alpha = 0.01 \) level.

![Diagram](image)

**Figure 1.** Comparison of Results of Small Sample (200 mg) and Large Sample Analysis (1.3 kg) of Phosphate Ore via z-Chart representation.

### III. FEASIBILITY STUDIES

**Soil and rock.** Contaminated soil. Contamination of soil with heavy metals not always results in a homogeneous distribution of the contaminant and sampling problems may be expected. The analytical problem increases when the contaminant is volatile, and when it cannot be excluded that element losses might occur during sample size reduction, homogenization and preparation of the analytical portion. Analysis of a large sample -as it was collected- may contribute to a more realistic assessment of the contamination. In the case of a Hg contamination is soil, two samples of approximately 1.7 kg each were analyzed. After the analysis, subsamples of approximately 40 g were taken from each of these large portions, homogenized and analyzed via 200 mg sub-portions. In Fig.2 the Hg-concentrations are given for the small samples and the large sample.

Harbour sediment. In another study, large sample INAA was applied to harbour sediment which, after sampling, is expected to be inhomogeneous with respect to trace element concentrations and water content. Large sample analysis was applied to a 2 kg sample and again after the analysis, the large sample was homogenized using a ball-mill, and small sub-samples were taken and conventionally processed (incl. drying) for routine INAA. The calculated neutron diffusion parameters reflect the high degree of inhomogeneity with respect to the water content. Towards the top of the bottle, the parameters resemble the values for water; towards the bottom of the bottle those of soil, as can be seen in Fig. 3. As such, the neutron flux depression inside the sample is inhomogeneous as well. However, the comparison of the concentrations of the small samples and the large sample show good agreement (Fig.4), indicating that the correction algorithms behave adequate for such material, and that the presence of water is accounted for.

![Diagram](image)

**Figure 2.** Comparison of Results of Sub-Sample Analysis of Soil, Contaminated with Hg, with Result of Large Sample Analysis (indicated at 91 mg.kg\(^{-1}\))

**Figure 3.** Neutron Diffusion Parameters at Several Levels in Sample of Harbour Sediment, and Reference Values for Water and Dry Soil.

Mineral deposits. The inhomogeneous distribution of Au in deposits is well known. A mining company had samples from an outcrop where gold was reported at g/t (mg.kg\(^{-1}\)) levels via conventional fire assay. It was suspected that there was an analytical problem. Non-representative subsampling or contamination could have been amongst the possible causes. Therefore, large sample INAA on 1.5 kg samples was applied to clarify the dispute. In none of
the samples Au was observed; a limit of detection of 30 mg.kg⁻¹ was found. As a consequence, the exploration was not longer continued.

Figure 4. Comparison of Results of 200 mg and 2 kg Samples of Harbour Sediment via z-Chart Representation.

**Recyclable waste.** The major stream of domestic waste is incinerated in The Netherlands. The residues of this process, i.e. aerosol, fly-ash and bottom-ash may contain high concentrations of potential (eco)toxic elements. In addition to this, there is an increasing effort in the recycling of waste. Economical and environmental considerations require insight in, amongst others, trace element levels.

Domestic waste incineration. Using INAA it has been possible to demonstrate that plastics are the major source of cadmium in domestic waste [7,8]. Presently attention focuses on the high metal concentrations in the residual ashes, which are suspected to be related to the ferrous and non-ferrous fraction of the waste. Mass balance studies require the determination of many elements in such fractions. However, after sorting and crushing, the average 'particle' size is approximately 3 * 3 cm. As such, the material is unsuitable for conventional analysis since it is not possible to take a 200 mg sample, representative for the entire selected fraction. However, when taking a 1 - 2 kg sample a better representativeness may be expected. Therefore, two samples of approximately 1 kg of each fraction were analysed. Results are presented in Table 1.

### TABLE 1. Results (Rounded-Off Data, in % or mg.kg⁻¹)

<table>
<thead>
<tr>
<th>Elements determined</th>
<th>Ferrous</th>
<th>Non-Ferrous</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
<td>70 %</td>
<td>0.9</td>
</tr>
<tr>
<td>Ti</td>
<td>0.2 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td>V</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
<td>0.2 %</td>
<td>265</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2 %</td>
<td>0.2 %</td>
</tr>
<tr>
<td>Fe</td>
<td>4 %</td>
<td>80 %</td>
</tr>
<tr>
<td>Co</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;1.5 %</td>
<td>&lt;1 %</td>
</tr>
</tbody>
</table>

### TABLE 2. Results (Rounded-Off Data, in % or mg.kg⁻¹) and Detection Limits as Found in Shredded Electronics

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Br</th>
<th>Th</th>
<th>Co</th>
<th>Sr</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>5.5 %</td>
<td>&lt; 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>5.2 %</td>
<td>Fe 680</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>4.5 %</td>
<td>La 130</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>4.5 %</td>
<td>Gd 120</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>3.5 %</td>
<td>Nd 75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>2 %</td>
<td>As 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.3 %</td>
<td>Cr 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>0.2 %</td>
<td>Hf 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.2 %</td>
<td>Rb 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.1 %</td>
<td>Ag 25</td>
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</tbody>
</table>

Recycled plastics. Because of the environmental effects, the use of cadmium as pigment in plastics has been restricted by law in The Netherlands, and should not exceed 50 mg.kg⁻¹. Obviously, the recycling industry has to assess the Cd concentration if the 'input' raw materials with a high degree of reliability. This raw material consists of pieces of plastic of approximately 0.5 * 0.5 cm, usually of different colours and composition. For conventional analysis, the pieces should be reduced further in size, and a thorough homogenization should be applied to get a representative sample of e.g. 200 mg. The alternative is large sample INAA. This was applied to several batches, supplied by companies recycling plastic.

Recycled electronic components. Abandoned electronics (radios, televisions, computers) containing high amounts of valuable elements (Au, Hg, Cu, Sn but also Rare Earth Elements) which may be regained by recycling. The economics of this is partly dependent on the concentrations. After crushing and milling the components are grossly separated, e.g. via magnetic techniques. The fraction related to the electronic printed boards is still highly inhomogeneous at the scale of the conventional analytical portion due to the structure of this fraction which contains pieces of printed circuit boards, wires, solder, IC's, transistors, metal joints but also glass fragments. Further processing to a fine grain size is difficult and expensive. The feasibility of large sample INAA was tested on a sample of shredded electronics. Typical results are given in Table 4. The same type of material was also sorted by hand on typical components like plastic, rubber, printed circuit boards and metals. The metal copper fraction can easily be separated in this way, and a gross indication of approximately 5 % has been obtained. The Cu-concentration found by large sample INAA, 5.5 %, agrees well with this indicative value.

### IV. DISCUSSION
Technical aspects. In contrast to routine INAA, large-sample INAA presently requires still more human actions: analysis of more gamma-ray spectra (natural radioactivity, transmission measurement, more flux monitors), and the use of programs for calculating the overall correction factor. In addition, the measurement of the large samples is not (yet) done with sample-changers, which limits the throughput capacity since the nightly and weekend hours are inefficiently used.

At IRI, the irradiation facility has been realized in the reactor’s thermal column. What are the prospects to implement large sample INAA at reactors without a thermal column? Two types of difficulties will be encountered when irradiating large samples in e.g. the water reflector of a reactor, viz. (i) neutron self-thermalization (except for heavy water moderated reactors) and (ii) a much steeper ‘natural’ neutron flux gradient in the diameter of the sample compared to the gradient in the (graphite packed) thermal column. In such a case, the inner layers of the sample are considerably less activated than the outermost layer, so that the ‘bulk’ analysis is less effective.

Analytical aspects. Internal quality control (IQC) in large sample INAA requires a new reflection on the use of control samples. Even when a suitable quality control sample would be available, it is questionable if the accuracy of the results of such a sample reflects the quality of the results of the real sample. In conventional analysis, the degree of accuracy of the results of the control sample may indicate systematic errors, also applicable to the results of the real sample. An underlying implicit assumption is that the homogeneity in both trace elements and matrix composition is the same for control and real sample. But this may be not the case when analyzing large samples because sample inhomogeneity is one of the reasons for applying the technique. The correction algorithms for neutron and gamma-ray self-attenuation assume that the sample can be considered macroscopically homogeneous; however it can often not be predicted if this assumption is fulfilled. Therefore, the degree of accuracy of the results of a large control sample does not necessary reflect the degree of accuracy for the real sample. Additionally, taking into account the definition of ‘accuracy’, viz.: ‘...the closeness of agreement between the result of a measurement and the true value of the quantity being measured.’ the question arises if the accuracy ever can be assessed for large samples via conventional ways.

Fortunately, some indications on the quality of the analysis can be obtained from the calculated values of the neutron diffusion length and -coefficient and of the linear attenuation coefficient for gamma-radiation. These parameters should all have physically realistic values, with constraints which can be derived from tabulated values of the pure elements. For instance, the calculated neutron diffusion length and diffusion coefficient should be within certain intervals; typically, $4 \text{ cm} < L < 20 \text{ cm}$ and $0.5 \text{ cm} < D < 30 \text{ cm}$. Another indication is obtained from the spectrum analysis: many gamma-ray lines and their intensity ratios are used. When a strong local absorption hasn’t been ‘seen’ in the transmission measurement the fit in the interpretation will be wriggling, resulting in an unacceptable high reduced Chi-squared value.

The elaboration in the above asks for a reflection on the analytical consequences of extreme inhomogeneities. The inhomogeneities may affect the assumptions with respect to the neutron- and gamma-ray self-attenuation. Via modelling the role of extreme inhomogeneities has been studied. It was found that false concentrations may primarily be expected due to inhomogeneities which affect the gamma-ray attenuation. Such inhomogeneities are largely accommodated for by rotating the sample during counting in front of the side-looking detector. Alternatively, the sample can be counted in fragments of the total measuring time in fixed positions but under different rotational angles to the detector. The concentrations found in the individual measurements reveal inhomogeneities as well, and the standard deviation of their mean serves as an additional component of uncertainty in the combined uncertainty of the concentration(s) of the respected element(s).

Future prospects. The low neutron fluxes required for large sample INAA also may lead to new impulses in the use of isotopic neutron sources; particularly $^{252}\text{Cf}$ since its fission neutron spectrum is relatively much easier to thermalize than the spectra of e.g. $^{241}\text{Am}/\text{Be}$ or $\text{Pu}/\text{Be}$ sources.

Except for producing multi-element concentration data, the direct analysis of large samples has attractive aspects from a methodology point-of-view. At IRI a study has started for experimental verification of theories on sampling, aspects of representativeness, and sampling factors.

Additionally, research has started at IRI to locate inhomogeneities in large samples. The counting facility makes possible to scan the activated sample in three dimensions. As an example, a study has started to investigate the sedimentation profile in a pond to which excess coppersulphate has been added to reduce algal-formation. To this end, drill cores of $1 \text{ m}$ length and $6 \text{ cm}$ diameter are irradiated as collected so that neither the layer structure nor equilibria between sediment and water are disturbed. The activated sample will be scanned in longitudinal direction.

It also has been studied if information on the depth distribution of activated elements could be derived from the shape of the Compton continuum since this is mainly arising from scattered photons in the sample itself. So far this approach seems to be feasible when dealing with spectra resulting from single photon emitting radionuclides [9].

V. CONCLUSIONS
Large sample INAA offers the possibility to analyze materials of which the sample size reduction step, sub-sampling and/or preparation of the analytical portion raise difficulties. Since the neutron and gamma-ray doses in the irradiation position are a factor of $10^4$ lower than in the irradiation facilities for conventional INAA, the radiolysis of water can be neglected and pressure build-up is not a matter of concern. This enables direct analysis of materials which contain water and in which drying raises difficulties with respect to volatile components to be determined, like presented in the example of a mercury contamination in soil.

The pilot-studies have made clear that with the availability of a method for trace-element determinations in large samples, a different approach may have to be developed with respect to the analytical aspects of the related project or study. In contrast to conventional approaches -sampling, subsampling, combining subsamples, homogenization - a direct analysis of the large sample requires attention for, answers on and interpretation of the degree of inhomogeneity of the material.

Parallel to further exploration of the possibilities and spin-offs of large-sample NAA, additional research has to be carried out for better understanding of the analytical fundamentals of the large sample analysis, to further optimization of the method and to the development of methods for internal quality control.

It should be kept in mind though that large sample analysis is not a panacea, but a unique extension of the scope of methods for elemental analysis. It will contribute to enforce the position of INAA in this respect.

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