Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 167, No. 1 (1993) 169–176

TRACE-ELEMENT DETERMINATIONS IN VERY LARGE SAMPLES: A NEW CHALLENGE FOR NEUTRON ACTIVATION ANALYSIS

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(Received September 22, 1992)

At the Interfaculty Reactor Institute the development of large sample INAA has been started. A facility is being installed in the reactor's thermal column for irradiation of samples with sizes up to 100 cm in length, and 15 cm in diameter and weights up to 50 kg. A gamma-ray spectrometer with a very large semiconductor detector and sample scanning options will be used for measurement of the induced radioactivity. Algorithms are being developed to correct for the neutron self-shielding and gamma-ray attenuation problems.

Introduction

All routine multi-element analysis techniques share the problem that the size of the sample to be analyzed has to be relatively small, varying from a few grams or milliliters to a few milligrams or microliters. There are high demands, therefore, on maintaining representative sampling of the material. Moreover, much effort has to be spent in sample size reduction and homogenization steps, and in minimizing contamination.

Trace element determinations in samples, larger than the usual sizes mentioned above, have received only limited attention in the analytical world. For selected cases such as coal and ore analysis, special bulk analysis procedures have been developed, but normally only for major constituents. However, such procedures are customized for the problems they have been developed for, and their practical features cannot easily be translated into a routinely applicable method for analysis of a large variety of sample types.

It is not difficult to name a variety of problems in chemical analysis which may require by a technique capable of direct analysis of samples with sizes which greatly exceed the usual ones, i.e. up to weights in the orders of kilograms. Maybe one of the most well-known problems is the determination of gold in drill cores. But one may also think of materials difficult to homogenize - such as shredder waste - materials in which knowledge of the inhomogeneity is of primarily importance, e.g. samples from sedimentation studies. Also, for the analysis of high-purity materials, large samples have the advantage, of reducing the effects of external contamination.

It has been mentioned earlier[1,2] that instrumental neutron activation analysis has all the potential to analyze, even with adequate accuracy, large samples in the kilogram range. There are no theoretical or physical limitations to such a form of INAA. This new approach to sample analysis may lead to entirely new fields of application of INAA, where no other analytical technique can compete. In addition, entirely new possibilities may arise,

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since up to now the analysis of very large samples, through desired, has never been practised due to the sample size limitations set by the various techniques.

The tools and methods to be developed for large sample neutron activation analysis, are (i) an irradiation facility, (ii) an adapted gamma-ray spectrometer, and (iii) methods to correct for neutron- and gamma-ray self attenuation phenomena. At the Interfaculty Reactor Institute at Delft such facilities and methods are being developed to facilitate INAA of very large samples. In this paper, the various aspects of large sample INAA are discussed with a presentation of the irradiation facility and gamma-ray spectrometer design, and an introduction to self-attenuation correction methods.

General remarks

It has been anticipated that the types of analytical questions for which large sample analysis may be of interest will generally make no extreme demands on accuracy. This is important to realize since it can be foreseen that the self-absorption phenomena of neutrons and gamma-rays will affect to some degree the accuracy of the analysis, even when correction methods are applied.

Another important starting point for large sample NAA has been that the induced radioactivity in the samples should be of the same order of magnitude, up to one order of magnitude higher than in conventional INAA, independent of the weight and size of the sample. The higher induced activity is required to compensate for both gamma-ray self-attenuation losses and relatively larger sample detector distances. At a given irradiation time, the increase in sample mass can be translated into a lower required neutron flux. A thermal neutron flux in the order of 10^{13} - 10^{14} $s^{-1}.m^{-2}$ is therefore amply adequate to induce the desired radioactivity, if one accept a lower overall effective activation due to neutron self-absorption losses. By keeping the induced radioactivity limited for all sample sizes, the specific radioactivity after completion of the analysis may become so low that no substantial waste problem is generated.

The type and sizes of drill cores being used in soil mechanics and by the mining industry do not exceed the maximum sample dimensions that can be handled in this facility, i.e. a diameter of 15 cm and a length of 100 cm. Such samples would involve sample weights up to 50 kg.

Irradiation facility

Choice of location

The reactors' thermal column was selected for the large sample irradiation facility for the following reasons:

- easy accessibility for installation of a facility without direct interference of the reactor's operation;
- adequate thermal neutron flux;
- opportunity to increase the ratio of thermal over non-thermal neutrons, thus reducing effects possibly introduced by sample self-thermalization;

A 3 mm thick cadmium sheet is placed in front of the column's entrance window to minimize activation of the reactor pool's stainless steel lining. This cadmium sheet also causes the spectrum of neutrons entering the column to be highly energetic. Thermalization is achieved by stacking nuclear grade graphite in the column.

Neutron flux and spectrum

Utilizing the diffusion code "CITATION[3]", the distribution of neutrons over 5 energy groups was calculated. These calculations indicate that an optimum position in the thermal column can be found which shares a high thermal neutron flux and a high ratio of thermal neutrons over non-thermal neutrons. At about 140 cm from the entrance window the thermal neutron flux is about $1 * 10^{14} s^{-1} m^{-2}$, and the ratio between the thermal neutron flux and the total non-thermal neutron flux is about 235. So only 0.4 % of the total neutrons is non-thermal and might eventually be thermalized by the sample itself.

Facility design

A 'wet' facility has been designed, in which water is used as shielding material against neutron and gamma radiation. The facility (see Fig. 1) consists of a water tank, placed on top of the thermal column, an irradiation tube and a by-pass system for water displacement. The water tank serves not only as a reservoir for the water, but also as a shielded storage facility for irradiated samples.

The irradiation container is a simple cylindrical polyethylene canister with an outer diameter of 20 cm and a length of appr. 100 cm. The canister can be closed with a lid. It can house sample containers of different heights and diameters up to maximum sizes of 100 cm in length and 15 cm in diameter. The sample containers must be surrounded with neutron flux monitors.

Samples can be placed in an irradiation container by hand or by using a handling tool. A small crane is used to hook on the irradiation container and to lower it into the irradiation position. In the irradiation position, a water 'film' of only 3 mm thickness surrounds the container. After irradiation, the container can be hoisted to a position about 1 m above the irradiation position for intermediate cooling. Because of the presence of boron carbide in the graphite stack, additional neutron activation at this position can be neglected. After appropriate cooling the container can be positioned back in the tank, and the samples can be taken out for counting.

Counting facility

For large sample INAA a device based upon the same principles as waste barrel scanners was designed (Fig. 2). Samples are being placed on a turntable, which can be moved and positioned in vertical and horizontal direction. The turntable is located in between the gamma-ray detector, and a mount with a ^{152}Eu source for determining mass-attenuation coefficients by transmission measurement.

A very large semiconductor detector (Ortec, 96.3 % ref.eff.), which can eventually be collimated, has been selected. The high efficiency of this detector facilitates both large sample-detector distances and collimation without a too large loss, e.g., in efficiency.

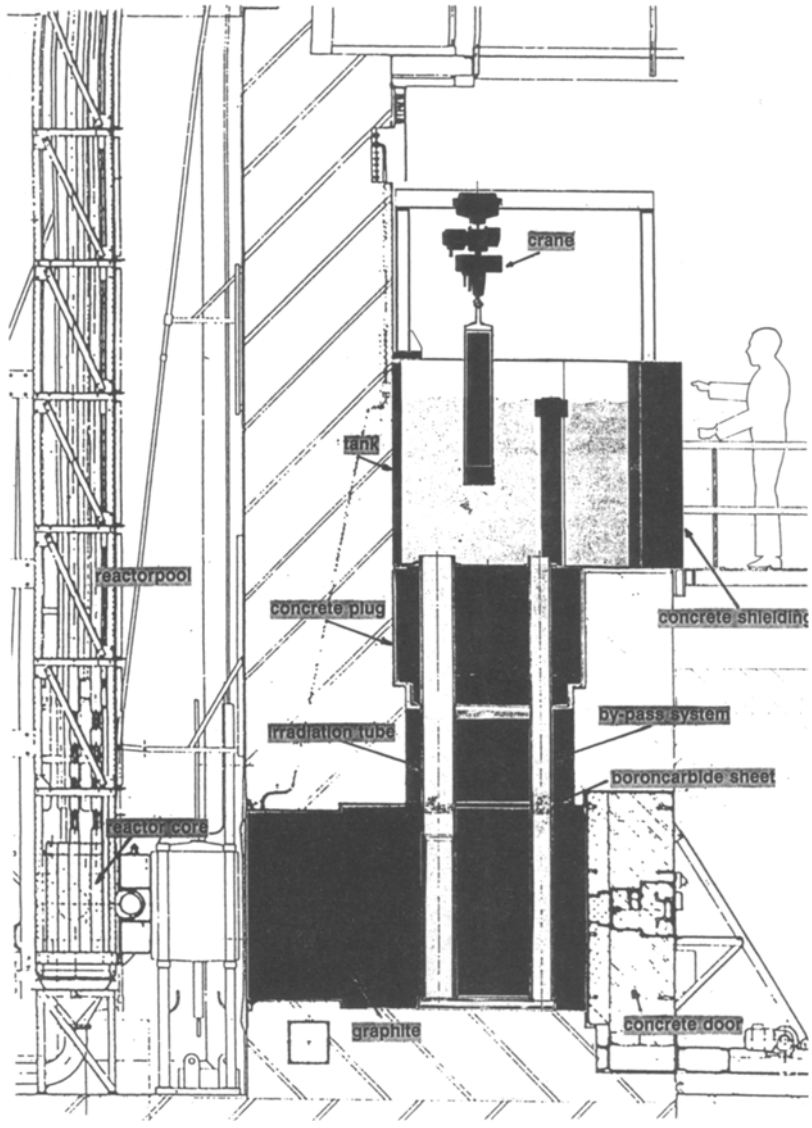

Fig. 1. Vertical cross section of relevant part of IRI reactor, showing the thermal column irrradiation facility

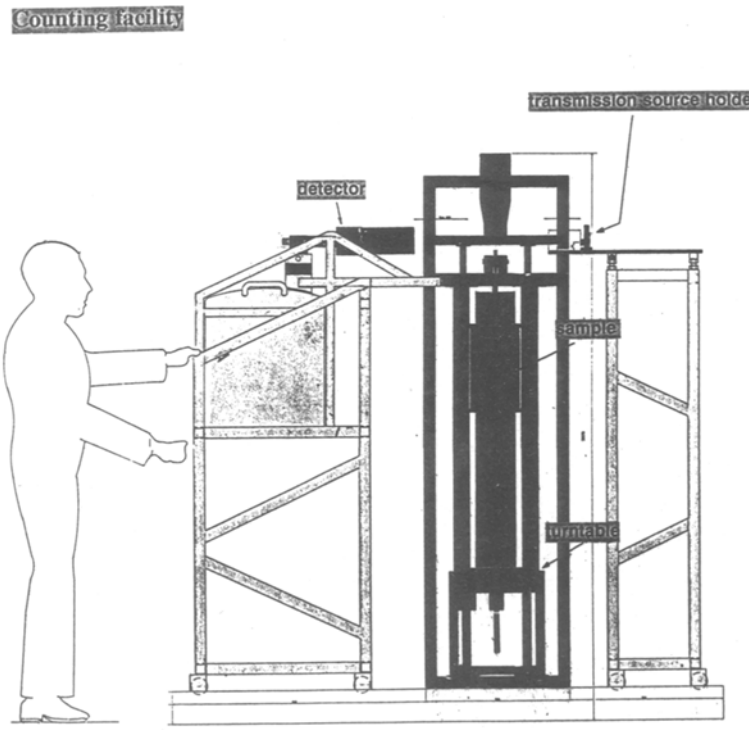

Fig. 2. Counting facility for large samples, showing (from left to right) the detector support, the turntable and sample turntable, and the transmission source support.

Attenuation correction methods

Neutron attenuation

If all the major constituents are known in advance, the macroscopic absorption cross section and diffusion coefficient of the entire sample can be calculated. The attenuation of the thermal neutrons can then be calculated using e.g. the diffusion code CITATION[3]. As an example, Fig. 3, gives a three-dimensional representation of the relative thermal neutron attenuation inside a cylindrical sample assuming water as matrix.

In most cases this essential information on the matrix composition is not available. The attenuation of thermal neutrons in voluminous samples has then to be determined using an approximate analytical solution of the neutron diffusion equation inside a cylindrical sample completely surrounded by a homogeneous medium.[4] This analytical solution still has three free parameters viz. the diffusion length and the diffusion coefficient of the sample, and the absolute thermal neutron flux at an undisturbed reference point. All the parameters can be calculated from neutron fluxes, derived from activated flux monitors just outside the sample.

The analytical solution obtained describes the neutron flux inside the samples; the correction for neutron self-absorption can be carried out in the same way as corrections for gamma-ray attenuation.

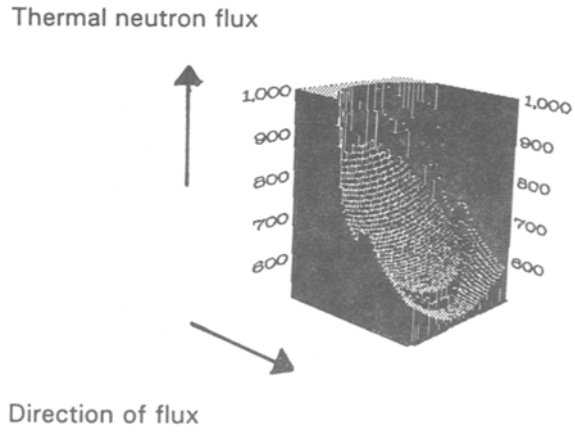

Fig.3. Schematic representation of thermal neutron attenuation in a cylindrical sample of SiO_2 with a 15 cm diameter, surrounded by 0.3 cm water. Thermal neutron intensity in arbitrary units

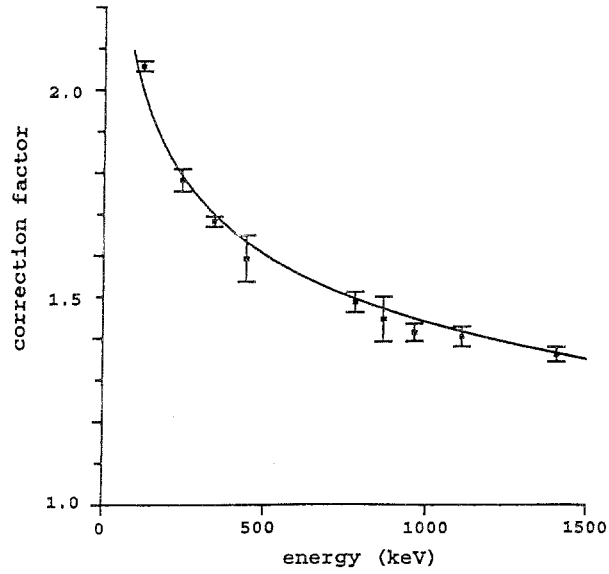

Fig. 4. Calculated (solid line and measured correction factor, representing, in gamma-ray spectrometry, the deviation from an ideal point source by a voluminous water source of 12 cm diameter and 20 cm height

Gamma-ray attenuation

Two effects have to be taken into account when gamma-ray spectrometry is applied to large, neutron activated samples, viz. the detector's spatial energy efficiency, and the gamma-ray self-attenuation. By comparison of radioactivity present in a voluminous source and the same radioactivity present as an ideal mass-less point source, R.M.W. OVERWATER et.al.[5] derived an energy, source-size and distance dependent correction factor. This approach only requires an experimentally determined mass attenuation coefficient, and precise information on sample and detector dimensions. For several large sources of radioactivity (up to 12 cm diameter and 25 cm length) this approach has been experimentally verified.

As as example, Fig. 4, gives the calculated and measured correction factors for large cylindrical sources.

Outlook

Large sample INAA opens possibilities for an entirely new type of chemical analysis. Less or no attention will have to be paid to the usual sample size reduction step. This is obviously of importance for analysis of materials for which it is difficult to obtain representative samples of analyzable size. It also meets the request for rapid answers which do not require an ultimate accuracy. Besides, large sample INAA may be found useful for analyses in which an indication of inhomogeneity is required. Samples with sizes up to 100 cm can be analyzed by segmented scanning, which results in a longitudinal distribution of the results. Moreover, indications of a radial distribution can also be obtained and eventually emission tomography may be considered. Large sample INAA may contribute to a better understanding of sampling and preservation of representability of the sampled material. It may also be found very useful to minimize effects of contamination when analysing e.g. high purity materials.

Sofar, large-sample analytical chemistry is an unexploited field and in order to apply it, one may have to develop another way of facing analytical problems.

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This project has been made possible through special funding by the Delft University of Technology.

The authors express their thanks to DR. J.E. HOOGENBOOM, IR. J.L. KLOOSTERMAN, IR. P.A DE LEEGE (all department of Reactor Physics at IRI), and V. HAVRÁNEK (on leave from the Institute for Nuclear Physics, Czechoslovak Academy of Sciences, Řež, CSFR) for their contribution to the neutron flux calculations and shielding calculations and to PROF. DR. M. DE BRUIN and PROF. DR. IR. J.J.M. DE GOEIJ for their stimulation of this project.

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