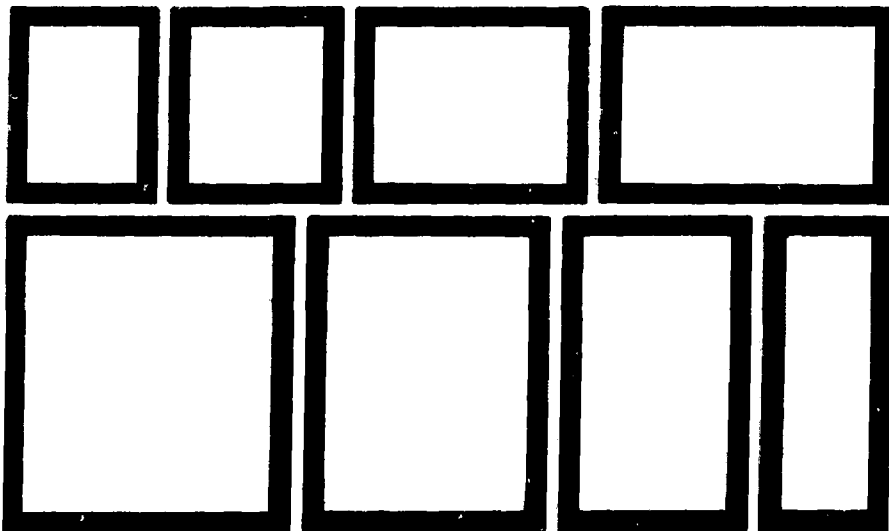
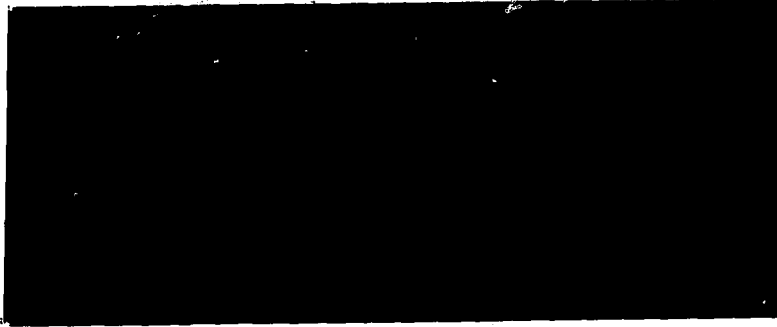


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INITIAL TESTING OF A NEUTRON ACTIVATION
ANALYSIS SYSTEM BY ANALYSING STANDARD
REFERENCE MATERIALS

BY

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INITIAL TESTING OF A NEUTRON ACTIVATION ANALYSIS SYSTEM BY
ANALYSING STANDARD REFERENCE MATERIALS

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Abstract

This paper describes the data acquisition and processing system in our laboratories (ND6600), the methods of activation analysis and the results obtained from our analysis of IAEA standard reference material (SL-1 lake sediments and NBS coal ash 1632a). These standards were analysed in order to check the capability of the system, which was designed in such a way as to enable the user to independently collect and process data from multiple radiation detectors.

1. INTRODUCTION

The capability of neutron activation analysis (NAA) technique in the determination of multielements in various type of sample is wellknown. It is a very sensitive, selective and precise method. Currently the NAA method is being widely used for multielemental analysis in many areas including biomedical, geochemical, agricultural and environmental studies.

In PUSPATI the NAA activity was initiated in late 1982, with the installation of the spectrometers and the data acquisition and processing systems. The main objective of setting up the NAA facilities was to provide the analytical services for various department and research programs in PUSPATI.

The paper presents the neutron activation analysis system in PUSPATI and the evaluation of the system for routine analysis.

BACKGROUND THEORY OF THE NAA METHODS

Neutron activation analysis (NAA) is a method of quantitative elemental analysis based upon the nuclear activation of chemical elements present in samples, followed by detection, identification and quantitative measurement of the induced nuclide. When a sample containing various amount of elements is irradiated with neutron, some of the elements become active. The radioactive elements decay and give off their characteristic radiations such as gamma rays which can be detected with the radiation detector. The energies of gamma rays identify the elements present in the sample and their activities define the quantities of the elements.

The basic equation for NAA for an element x is as follows

$$W = \frac{mDx^*}{\phi_{TH} \times N \times F \times (1 - e^{-0.693T/t_{1/2}}) \left(\sigma_{TH} + \frac{RI \times \phi_{EPI}}{\phi_{TH}} \right)} \dots\dots(1)$$

$$D_{x^*} = kA_{x^*} \dots\dots(2)$$

Where

W = weight of an element x (gram).

D_{x^*} = disintegration/s of a radionuclide x^* at the end of irradiation.

A_{x^*} = activity (conts/s) of a radionuclide x^* .

k = proportionality constant - including detection efficiency and nuclear decay scheme of x^* .

N = avogadro's number.

m = atomic weight of the element x.

F = fractional isotopic abundance of target element.

T = irradiation time.

$t_{1/2}$ = half life of a radionuclid x^* .

ϕ_{TH} = flux of thermal neutron ($cm^{-2}g^{-1}$).

ϕ_{EPI} = flux of epithermal neutron ($cm^{-2}g^{-1}$).

σ_{TH} = thermal neutron reaction cross section (cm^2).

RI = resonance integral of the element x.

The concentration of element x in sample can be calculated from the NAA equation 1 and 2 with the knowledge of the numerical values $k, m, F, \text{TH}^*, \text{EPI}^*, \text{TH}^*, \text{RI}, T$ and $t_{1/2}$. However if a comparative method is used it is not necessary to know the numerical values of any of those parameters. In this method a sample and standard are irradiated together and both sample and standard are counted under exactly the same condition by the same detector. The NAA equation for the comparative method is as follows:

$$\frac{\text{weight of element x in sample}}{\text{weight of element x in standard}} = \frac{A_{x^*} \text{ in sample}}{A_{x^*} \text{ in standard}}$$

THE NAA SYSTEM

The basis of the analysis system is the comparative INAA method. Samples to be analysed are sealed in prewashed (HNO_3 - distilled water - acetone) polyethylene vials which are then loaded into special irradiation tubes.

Irradiations are performed in the irradiation facilities of the RUSPATI Triga reactor. In normal procedure, the determination involves two irradiation periods and four counting intervals as shown in table 1. For short irradiation, samples and standards are individually irradiated for 2-5 minutes, delayed for 20 minutes and counted for 5 minutes. Gamma ray analysis is repeated after 24 hours. Long irradiation is performed simultaneously for samples and standards. Maximum irradiation time is limited to 6 hours. The samples and standards are counted after 4 to 7 days and 30 to 40 days.

Samples are counted in their vials at an appropriate geometry to limit the dead time less than 15 percent on a germanium detector. The vial has no significant amount of elements that analysis are made with no blank subtraction.

Spectral data are stored in magnetic tape and then analysed by a computer.

Irradiation Facilities

The PUSPATI Triga MK.II reactor has a rotating rack with x_0 tube sample positions and the rack revolves around the core to ensure that all the samples receive the average flux during irradiation. The facility is used for the long irradiation program. In addition the reactor has a pneumatic (rabbit) transfer system for irradiating samples for a short duration. The transport period of the system is about 3 to 4 seconds. The system can be automatically controlled up to 3 minutes irradiation time, and if a longer irradiation time is needed the system have to be controlled manually.

The thermal and epithermal flux for both irradiation facilities are about $1 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ and $5 \times 10^{10} \text{ n cm}^{-2} \text{ sec}^{-1}$ respectively, and the cadmium ratio is about 8.

Gamma spectrometer and data acquisition and processing system

A schematic of the system is shown in Figure 1. The system consists of a germanium detector coupled to a high voltage supply, a pre-amplifier, a linear amplifier, an analog - to - digital converted (ADC), a terminal/multichannel (4096 channel) analyser (ND 66) and a computer (ND 6680). The system also equipped with a decrifer and an x-y plotter.

The output signals from the detector are amplified by the pre-amplifier and the amplifier. The signals are then sorted via the ADC in the multichannel analyser. The gamma ray spectrum can be transferred outo a magnetic tape and/or printed by the printer (or plotted by the x-y plotter).

The ND 66 terminal/multichannel analyser can stand either as a computer terminal or a multichannel analyser which capable of acquiring spectrums from 4 individual detectors at one time. The ND 66 terminal/multichannel analyser is provided with 8K bytes memory capacity.

The memory capacity of the ND 6680 computer is 193 Kbytes. The computer also equipped with 25 Megabytes and 5 Megabytes storage capacity of hard disk and magnetic tape respectively. The operating system of the computer is known as MIDAS, the short formed for multiple independent data acquisition, display and processing system. The hardware of the gamma ray spectrometer and data acquisition and processing system are summarise in table 2.

Table 2: Hardware/instrumentation Summary.

Detector: Germanium detectors (model no GEM-20180)

Total active volume : 118.0 cc.

High voltage bias : 3500V

Resolution (FWHM) : 1.90 keV at 1332 keV

Relatif efficiency : 20% relatif to the Na I (3x3)
at 1332 keV

Amplifier : Laben Spectroscopy - MOD 8143

Bias Supply : Ortex Model 459 (0-5 kV)

Data acquisition and processing system (ND 6680)

1. ND 66 terminal/multichannel analyser

channel : 4096

memory : 8 kbytes (expandable to 32 kbytes)

2. ND 6680 Computer

memory capacity : 193 kbytes (expandable to 1 Megabytes)

Hard disk : 2.5 Megabytes Storage Capacity

Magnetic tape : 5 Megabytes Storage capacity.

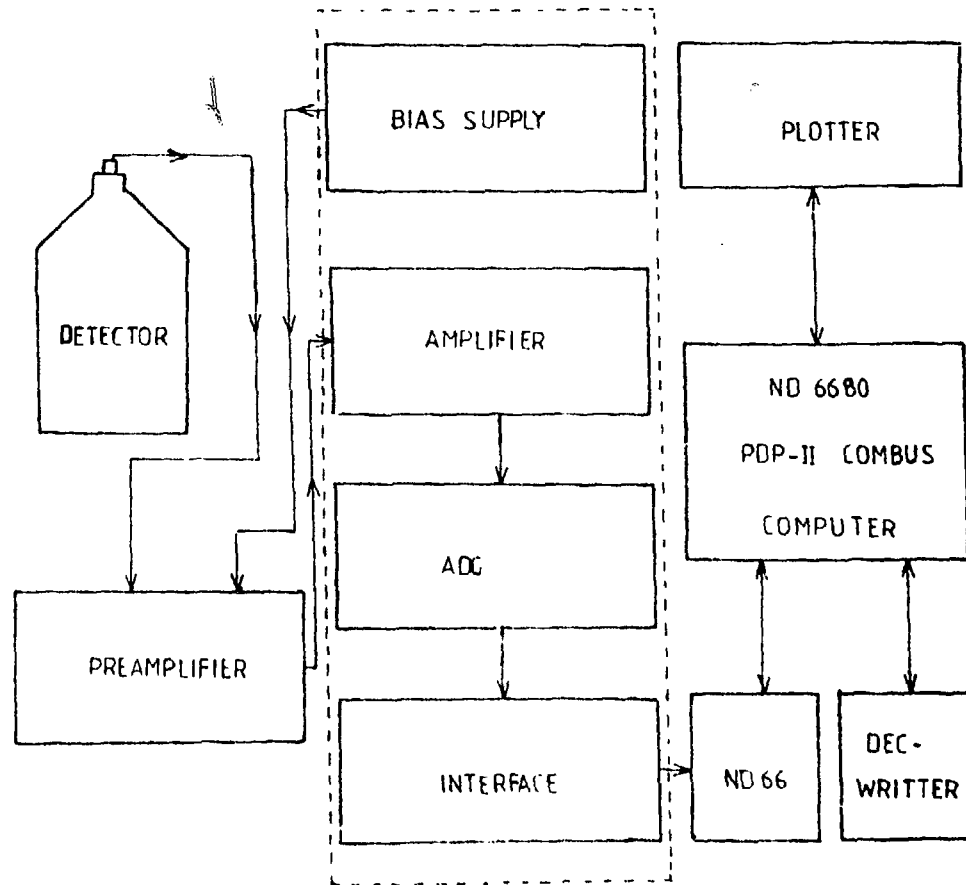


FIG. 1: Schematic Diagram of the Spectrometer and the Data Acquisition System

Software

The software which control and perform the NAA data collection and data processing are available from the Basic Physics and Nuclide Identification and the neutron activation packages. The packages consists of several software modules where a user may use different combinations of the software modules to suit his need. A user who wish to analyse many samples may set up and run complex automatic jobstreams. These may contain any combination of standard ND 6600 software modules. The programs operate under the MIDAS operating system of the ND 6680 computer.

The Basic Physic and Nuclide Identification package contains the set up and analysis programs which are used in setting up the data collection parameters and analysing the spectral data. This includes the resolution (FMHM), energy calibration, efficiency calibration, parameter input program, spectrum header information and automatic peak search program. The peak search program is capable of analysing up to ten overlapping (multiplet) peaks in any spectral region using a gaussian least squares fitting technique.

The neutron activation analysis package provides a means of translating research data, standard specimen information and gamma ray spectra into description of the elemental concentration of analytical samples. The package consists of thirteen programs modules for six different task areas (Figure 2).

- 1, parameter entry and printout;
- 2, job-stream and flick control;
- 3, peak detection and integration;
- 4, reactor constant (flux) analysis;
- 5, standard specimen analysis; and
- 6, enknown specimen analysis.

EVALUATION OF THE SYSTEM

In order to evaluate the NAA system two standard reference materials IAEA SL-1 (Lake Sediment) and NBS-1632a (Coal Ash) have been analysed. The standards were prepared by dropping the standard solutions of elements on specpure silica in polyethylene vials and was then dried in a dessicator. The results were obtained from analysis carried out under normal routine conditions and they are intended to display the reliability of routine analysis. In this work no attention has been paid to the requirements with respect to detection limit.

Table 3 shows the values of elemental concentrations in the standard reference materials obtained in this work along with the certified and non-certified values from the IAEA (1), and NBS (2) certificate and those reported by Germani et. al (3). The elemental concentrations are the average of at least four determinations together the standard deviations which represent the experimental errors. For both standard reference materials analysed, the comparison of the concentration values obtained in this work with those reported by IAEA, NBS, and Germani et.al shows that there is a general agreement within experimental errors. However there are disagreements outside of quoted errors for As (IAEA - certified) and Eu (IAEA - non-certified) in IAEA SL-1, and Sb (NBS - non-certified) and Mg (Germani et.al) in NBS-1632a. The disagreement in some of the materials might be due to the lack of homogeneity for the cited elements and also to the dissimilarity between sample and standard.

The precision of the procedure is below 10% for most of the elements, except for Sb (16.9%), Cr (10.5%), and Ba (10.9%) in IAEA SL-1, and for Sb (13%), ^{Mn (13%)} and Cl (10.3%) in NBS-1632a. Statistical, geometrical, and the technical factors are the main source of errors. The sources of errors in INAA in general have been discussed by Rosenberg et.al (4).

In general the present system meets our requirement as it has proved to be a reliable analysis system. The accuracy and precision of the results is satisfactory for most elements and will further be improved through proper setting the parameters such as the irradiation and counting time. The quality of the results not only depends on the procedure as such but as well as on the professional skill of the personnel.

The present system limits the maximum counting time for routine analysis to two hours per sample. Thus our maximum capacity is about 200 - 300 samples per month. There are areas which are certainly to be developed and established in order to increase the capacity of the system. They are:-

- i) Radiochemical separation NAA (RNAA).
 - For determination of these elements present in a very low concentration and to avoid interference.

- ii) Automatic sample changer.
 - Unit to be attached to the counting system to permit unattended counting especially during night time for routine analysis.

- iii) Fast Pneumatic Transfer System.
 - For determination of very short-lived isotopes which half-lives are in order of seconds such as Se-77m, Sc-46m, Ag-110, and Au-197m.

References

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National Bureau of standards, U.S. Dept. of Commerce
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3. M S. Germani et. al.
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422 (1976) p. 1241.

EXPERIMENTAL NEUTRON ACTIVATION ANALYSIS

Element	Nuclide measured	Energy keV	Half-life	Decay interval
<u>Irradiation I = 2 min.</u>				
Mg	²⁴ Mg	1014	0.46 m	
Al	²⁷ Al	1077	2.32 m	
Cl	³⁸ Cl	1169	37.31 m	
Ca	⁴³ Ca	1384	8.60 m	
Si	⁴⁴ Si	1100	5.79 m	
V	⁵⁰ V	1434	3.75 m	
Fe	⁵⁰ Fe	847	2.58 h	
Br	⁸⁰ Br	517	17.60 m	
Sr	⁸⁷ Sr	368	1.83 h	
Zr	¹²⁸ Zr	140	25.0 m	
Se	¹³⁹ Se	160	12.90 m	
Dy	¹⁶⁵ Dy	94	1.37 h	
La	²⁴ La	1364	15 m	
K	⁴² K	1525	12.1 h	
Ba	⁷⁵ Ba	104	14.1 m	
Bu	^{152m} Bu	122	9.2 h	
<u>Irradiation II = 6h.</u>				
As	⁷⁶ As	559	26.4 h	
Br	⁸² Br	613	35.4 h	
Se	¹²² Se	564	2.7 d	
La	¹⁴⁰ La	1596	40.2 h	
Sm	¹⁵³ Sm	103	46.8 h	
Yb	¹⁷⁵ Yb	396	46.3 d	
Lu	¹⁷⁷ Lu	208	6.7 d	
W	¹⁸⁷ W	686	24 h	
Au	¹⁹⁸ Au	412	2.7 d	
Hg	²³⁹ Hg	223, 177	56.3 h	
Sc	⁴⁶ Sc	1120	84 d	
Cr	⁵¹ Cr	320	27.2 d	
Fe	⁵⁹ Fe	1099, 1292	45.6 d	
Co	⁶⁰ Co	1173, 1332	5.26 y	

TABLE 1


Element	Nuclide Measured	Energy keV	Half-life	Decay Interval
<u>Irradiation Time = 6 h</u>				
	⁶⁵ Zn	1116	245 d	30-40 d 
	⁸⁶ Rb	1079	18.7 d	
	⁸⁵ Sr	814	64 d	
	⁹⁵ Zr	757	65.5 d	
	¹³¹ Ba	496	12.1 d	
	¹³⁴ Cs	736	2.05 d	
	¹⁴¹ Ce	145	32.5 d	
	¹⁴⁷ Nd	531	11.1 d	
	¹⁵² Eu	122, 1408	12.7 d	
	¹⁶⁰ Tb	879	72.1 d	
	¹⁶⁹ Yb	177	30 d	
	¹⁸¹ Hf	462	42.5 d	
	¹⁸² Ta	1221	115 d	
	²³⁰ Pa	312	27.4 d	

Table 3 : Concentration of elements in IAEA-SL 1 and NBS 1632a

<u>Element</u>	<u>IAEA-SL 1</u>		<u>NBS 1632a</u>		
	<u>this work</u>	<u>IAEA values</u>	<u>this work</u>	<u>NBS values</u>	<u>Germini et. al</u>
Na (%)	0.175 \pm 0.010	0.172 \pm 0.012	0.088 \pm 0.007	-	0.085 \pm 0.004
Mg (%)	2.40 \pm 0.20	2.90	0.20 \pm 0.03	-	0.13 \pm 0.03
Al (%)	9.40 \pm 0.70	8.90	2.96 \pm 0.20	3.07	2.90 \pm 0.30
Ca (%)	0.24 \pm 0.02	0.25	0.25 \pm 0.03	-	0.24 \pm 0.02
Ti (%)	0.531 \pm 0.035	0.517 \pm 0.037	0.170 \pm 0.009	0.175	0.163 \pm 0.007
Ba (ppm)	640 \pm 70	639 \pm 70	110 \pm 7	-	122 \pm 11
Cl (ppm)	ND	10	870 \pm 90	-	800 \pm 70
V (ppm)	185 \pm 12	170 \pm 15	48 \pm 4.0	44 \pm 3.0	44 \pm 3.0
Mn (ppm)	3540 \pm 290	3460 \pm 160	30.5 \pm 4.0	28 \pm 2.0	32 \pm 3.0
K (%)	1.45 \pm 0.10	1.5	0.41 \pm 0.03	-	0.42 \pm 0.02
Sr (ppm)	1.82 \pm 0.12	1.6	0.60 \pm 0.3	0.54	0.55 \pm 0.03
Sm (ppm)	9.43 \pm 0.40	9.25 \pm 0.51	2.3 \pm 0.3	-	2.80 \pm 0.3
As (ppm)	34.00 \pm 3.0	27.5 \pm 2.90	12 \pm 2	9.3 \pm 1.0	10 \pm 2
Fe (%)	6.44 \pm 0.32	6.74 \pm 0.17	1.14 \pm 0.01	1.11 \pm 0.02	1.16 \pm 0.03
Cr (ppm)	114 \pm 12	104 \pm 9	31 \pm 3	34.4 \pm 1.5	34 \pm 2
Co (ppm)	19.0 \pm 1.8	19.8 \pm 1.5	6.6 \pm 0.3	6.8	6.5 \pm 0.2
Th (ppm)	13.3 \pm 0.5	14 \pm 1	4.2 \pm 0.4	4.5 \pm 0.1	4.8 \pm 0.2
U (ppm)	4.05 \pm 0.40	4.02 \pm 0.32	1.24 \pm 0.06	1.28 \pm 0.02	1.21 \pm 0.10
Sb (ppm)	1.42 \pm 0.24	1.31 \pm 0.12	0.80 \pm 0.10	0.58	0.60 \pm 0.09
La (ppm)	48.2 \pm 4.5	52.6 \pm 3.1	18.2 \pm 1.3	-	18 \pm 2
Sc (ppm)	18.5 \pm 1.3	17.3 \pm 1.1	7.0 \pm 0.7	6.3	6.8 \pm 0.6