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ADVANCES IN 14 MeV NEUTRON ACTIVATION ANALYSIS BY MEANS OF A NEW INTENSE NEUTRON SOURCE

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A new intense 14 MeV neutron generator with cylindrical acceleration structure has been put in operation at the GKSS Research Center Geesthacht. The sealed neutron tube is combined with a fast pneumatic rabbit system with particular capabilities for neutron activation analysis involving shortlived reaction products. The sample transfer time is less than 140 ms. The maximum neutron flux available for activation is $5.2 \cdot 10^{10}$ n/cm^{2}s. Theoretical sensitivity predictions made in a previous study have been verified for some important trace elements. As a first application, samples of freeze-dried suspended matter and fishes of the Elbe river were analyzed.

Introduction

Although the 14 MeV neutron activation analysis is a well established technique for the determination of various elements, hitherto the detection of trace elements suffered on the lack of neutron intensity. With the advent of neutron generators with yields of $5 \cdot 10^{12}$ n/s the analytical capabilities have been extended considerably. In a recent paper[1] the authors have described the activation analysis prospects by using a concentric $5 \cdot 10^{12}$ n/s sealed neutron tube combined with an ultra-fast pneumatic rabbit system. Meanwhile the facility KORONA (Kombinierte Rohrpost-Neutronengenerator-Anlage) which underlies that feasibility study has been put in operation at the GKSS Research Center Geesthacht. KORONA is intended to be used primarily for rapid analyses in environmental research and geochemistry. Ac-

cording to the sensitivity predictions of the previous study about half the ensemble of 78 elements considered can be detected in quantities of the order of 1 μg or below. The present paper describes the recent experience made in the operation with this facility and reports on the first experimental data concerning elemental detection limits and analytical results for suspended matter and biological samples.

Operational data and experience

KORONA is a high-intense neutron tube in a compact arrangement of an annular ion source, a cylindrical ScTD target and the irradiation terminal of an ultra-fast sample transport device. The neutron source itself results from a modification of a neutron tube originally designed for radiotherapy purposes[2]. It is manufactured under licence by Emile Haefely & Co. Ltd., Basel (Switzerland).

With a total current of 420 mA at 195 kV acceleration voltage, the 14 MeV neutron flux averaged over the sample volume was determined using activation analysis via the reactions $^{27}Al(n,\alpha)^{24}Na$ and $^{93}Nb(n,2n)^{92}Nb$ resulting in the values (4.75 ± 0.17) and $(4.85 \pm 0.11) \cdot 10^{10}$ n/cm^{2}s, respectively. In addition, the knowledge of the mean neutron energy is required for accurate analyses because of the strong energy dependence of some activation cross sections in the 14 MeV region. Following a procedure proposed by Lewis[3] a simultaneous activation by the (n,2n)-reactions of niobium and ^{90}Zr has been performed. The result of this measurement is 14.45 ± 0.15 MeV.

It is a characteristic feature of the cylindrical target structure that the neutron flux distribution within the interior is quite homogeneous. System-

atic errors due to flux gradients are thus minimized. The geometric flux distribution for different sample sizes have been measured with aluminium wires and foils. The experimental results are consistent with previously calculated data[4], which revealed that the maximum relative deviation from the mean flux value is ± 2% or ± 6% for capsules with 0.55 cm^3 or 2.2 cm^3 sample volume, respectively.

During operation of the neutron tube problems arised at higher source strengths from incidental electrical breakdowns within the very compact electrode structure. These effects evidently depend on the age of the tube as they decreased slightly with increasing accumulated operation time. In a first step towards improvement of irradiation conditions a fast automatic cut-off and switch-on device was installed in the high-voltage circuit, in order to prevent possible damage of the source and to limit interruption of the irradiation to a maximum time interval of 5 s. Additional means under study is the amelioration of the surface conductivity of relevant components by appropriate metallurgic treatment. During activation the neutron source strength is monitored by means of a long counter and a multi-channel scaler. Possible breakdowns or fluctuations of the neutron flux are registered and appropriate corrections are made by means of a computer program taking into account the half-life of the reaction product to be studied.

In order to meet the requirements for neutron activation analysis with short-lived nuclides, the interior space of the neutron tube had been made accessible for a fast sample transport system. Samples are pneumatically transferred into the neutron tube and reach the irradiation position within less than 5 s. After activation the sample is transferred to a 16 m distant detector station within less than 140 ms. Till now, neither the

stopping of the rabbit nor the pressure-pulse compelled acceleration has caused any harmful effects upon the neutron tube structure or the detector arrangement. A special feature of the transport system is the separation of carrier rabbit and sample capsule by the centrifugal force in a curved branch of the pneumatic tube[5] near the detector. This separable small capsule contains a sample volume of 0.55 cm^3 (10 mm diam. x 7 mm). For larger samples the carrier rabbit is used as a sample container with a volume of 2.2 cm^3 (10.5 mm diam. x 25 mm). The capsule material is polyethylene. Traces of elements like Al, Si, Mn and Fe lead to blanks which have carefully to be considered. The carrier rabbit has to resist considerable mechanical shocks in particular during the abrupt stopping. It is therefore manufactured of polyamide. A disadvantage of this material is the high interference activity of the positron emitter ^{13}N which deteriorates measurements with short delay times.

With the sample transfer system, controlled by a CBM 3016 computer, also cyclic activation analysis is feasible, which compensates the loss in the time factor

$$f = (1 - e^{-\lambda t_i}) e^{-\lambda t_d} (1 - e^{-\lambda t_m}) \lambda^{-1}$$

with decreasing half-life by the gain factor[1]

$$g = \frac{N}{1 - e^{-\lambda p}} - \frac{e^{-\lambda p}(1 - e^{-N\lambda p})}{(1 - e^{-\lambda p})^2} .$$

Here, the subscripts i, d and m denote irradiation, delay and measurement, while the period p stands for the total cycle time including the return of the sample and N means the total number of cycles.

For the γ-ray spectroscopy of samples in the capsule and the rabbit two Ge(Li)-detectors have been installed with relative efficiencies of 18% and 10%, respectively. The signals are registered and evaluated by a multi-channel analyzer and data processing system (ND 6620).

Verification of elemental sensitivities

One of the objectives of the first experimental efforts was to verify some of the theoretical sensitivity predictions made in the previous feasibility study[1] on the basis of the nuclear data. In these calculations matrix effects have been neglected and 100 counts of a characteristic γ-ray line recorded by a 15% Ge(Li) diode have been regarded as being sufficient for identification. To this purpose activation analyses of single-element (or chloride) samples each with amounts of 1 to 40 μg have been performed for Si, Cr, As, Cd, Sn, Hg and Pb, including cyclic activation. The experimental results agree quite well with the predictions, if the uncertainties of the nuclear data are accounted for. In fig. 1 a spectrum of $Pb(NO_3)_2$ is given, accumulated during a cyclic activation with N = 29 and p = (3.0 + 0.13 + + 3.0 + 6.4) s. The well known 810 ms isomer ^{207m}Pb emitting two γ-rays with energies at 570 and 1064 keV is an outstanding example for activation analysis with short-lived nuclides.

Thus for the elements quoted it is confirmed that with KORONA the minimum detection limits are considerably lower than with conventional 14 MeV neutron sources. The increase of sensitivity may also be utilized to improve the elemental selectivity. Another important capability is that KORONA sup-

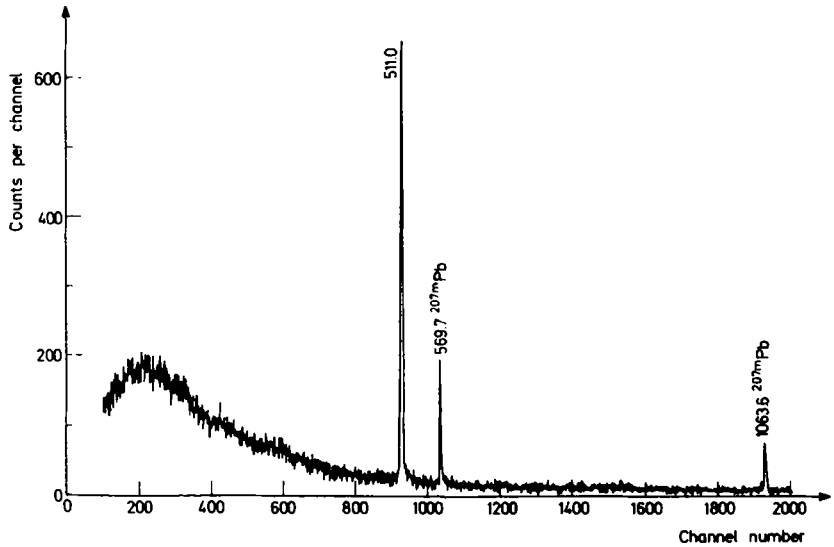

Fig. 1. Cyclic activation analysis of $Pb(NO_3)_2$ using the $^{208}Pb(n, 2)$ and $^{207}Pb(n, n')$ reactions leading to the 810 ms isomer ^{207m}Pb; mass of lead: 20 μg; N = 29, t_i = 3.0 s, t_d = 0.13 s, t_m = 3.0 s, p = 12.5 s; γ-ray energies indicated in KeV

plements very well reactor neutron activation, since several elements are detectable which by thermal neutrons can only be analyzed with poor sensitivity or not at all.

Analysis of suspended matter and fishes

As a first application of KORONA, samples consisting of freeze-dried suspended matter taken in the estuary of the Elbe river were analyzed. Numerous elements were detected: Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Zn, As, Rb, Sr, Zr, J, Ba and Ce (table 1).

Fig. 2 shows a fast-neutron activation γ-ray spectrum of seston after 16 min of irradiation, 30 min delay time and a 30 min measurement. The analytical results obtained by 14 MeV neutron activation (FNAA) for the sus-

Table 1
Analytical Results obtained by FNAA for Suspended Matter from the Elbe River.
Comparison with INAA, TRXRF and the weighted mean from an interlaboratory test.
Numbers of Measurements are quoted in brackets. All values are given in μg/g.

Element	INAA	TRXRF	$\bar{x} \pm 2\sigma$	FNAA
Na	11700 ± 300(7)	-	12183 ± 758(13)	8800 ± 990
Mg	-	-	-	13700 ± 5500
Al	56600 ± 800(3)	-	(56600 ± 800)	52600 ± 5600
Si	-	-	-	181000 ± 2600
Cl	14400 ± 400(3)	-	(14400 ± 400)	16300 ± 2400
K	18200 ± 600(3)	-	18160 ± 557(10)	18500 ± 3600
Ca	43400 ± 4700(7)	37212 ± 1175(9)	39700 ± 4000(19)	39200 ± 9000
Sc	10.8 ± 0.3(7)	-	10.4 ± 0.4(33)	9 ± 2
Ti	3500 ± 700(3)	3547 ± 143(9)	3535 ± 40(15)	3550 ± 350
Cr	163 ± 60(7)	81 ± 9(9)	123 ± 24(34)	230 ± 80
Mn	2525 ± 50(3)	2525 ± 119(9)	2501 ± 69(15)	2900 ± 260
Fe	40300 ± 1100(7)	37908 ± 882(9)	39004 ± 1878(46)	41900 ± 2400
Co	16.6 ± 0.8(7)	< 40 (9)	16.8 ± 1.1(39)	21 ± 8
Zn	330 ± 13(7)	353 ± 10(9)	406 ± 92(32)	450 ± 250
As	25.6 ± 1.2(7)	28 ± 5(9)	27.8 ± 3.4(22)	31 ± 3
Rb	93 ± 3(7)	119 ± 5(9)	104 ± 11(31)	100 ± 7
Sr	168 ± 13(7)	218 ± 9(9)	195 ± 32(19)	190 ± 19
Zr	-	-	-	170 ± 13
J	-	-	-	92 ± 6
Ba	290 ± 20(7)	< 240	298 ± 11(28)	140 ± 70
Ce	62 ± 4(7)	-	67 ± 13(11)	53 ± 7
Pb	-	100 ± 10(9)	91 ± 28(12)	*

*Above detection limit; measurement however still affected by extremely high counting rates (see text).

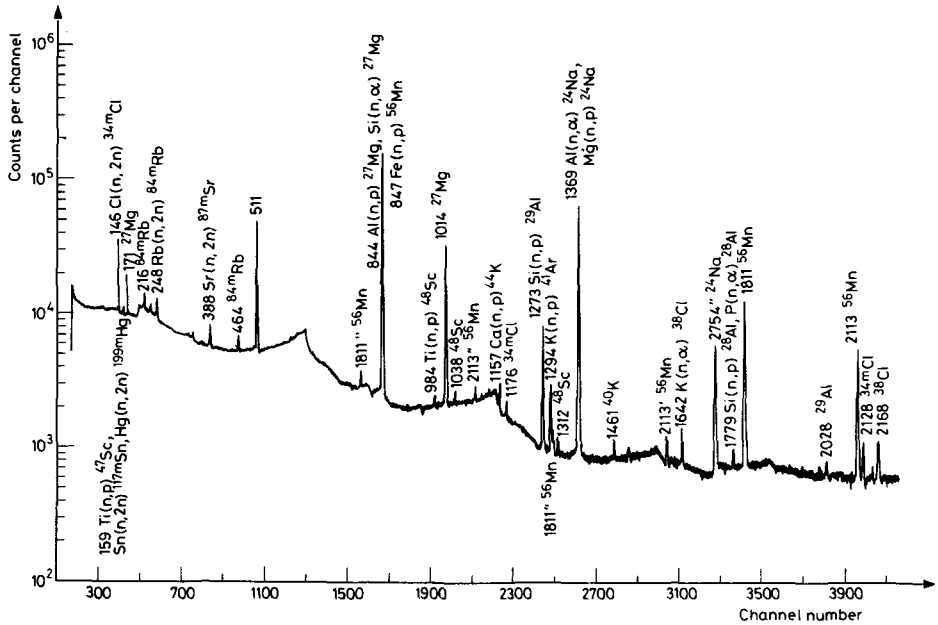

Fig. 2. 14 MeV neutron activation spectrum of suspended matter of the Elbe river; sample mass: 281.4 mg; $t_i = 16$ min, $t_d = 30$ min, $t_m = 33$ min

pended matter sample were compared (table 1) with data derived from instrumental thermal neutron activation analysis (INAA)[6] and from advanced X-ray fluorescence analysis with total reflection (TRXRF) of the exciting beam from the sample support[7]. Moreover, weighted means $\bar{x}$ from an intercomparison laboratory test[8] were available. Evidently some elements were distributed inhomogeneously in the suspended matter, e.g. Cr. By this effect the standard deviation of the weighted mean of Cr, Zn and Pb is increased. The main contribution to the error of the FNAA analysis originates in the cross section uncertainty and the statistical error. The agreement of the results is regarded to be very encouraging.

The analysis of short-lived reaction products, e.g., of Pb via the 810 ms isomer, was somewhat handicapped by competing induced activities of major components in the matrix such as O and Si. The initial activity of the sample irradiated in a fast-neutron flux of $3 \cdot 10^{10}$ n/cm^{2}s for 2 s was too high to start the measurement immediately upon arrival of the capsule, though the utmost sample mass was as small as 280 mg and though the electronic amplification system of the 18% Ge(Li) diode is designed for an upper counting rate limit of 200 000 cps. To overcome this limit the preamplifier will be prepared for switched charge restoration by installing a FET-based optocoupler. The counting losses caused by dead-time and pile-up effects will be corrected by a control unit designed by Westphal[9].

In connection with the pollution of natural waters the heavy metal content of suspended matter as well as of fishes is of considerable interest. Therefore some samples of freeze-dried fish material were analyzed with different irradiation conditions. Long-time activation of inner organs and eatable tissues of Elbe river perch yielded in mercury concentrations of 22 and 13 µg/g dried material, respectively, which corresponds to 4 and 3 µg/g fresh material. For comparison the results of 14 MeV NAA with carp tissue, originating from a natural pool, do not indicate any mercury pollution in the ppm region. Two representative spectra are shown in fig. 3. In contradiction to the suspended matter investigation the induced activity of the fish matrix did not obstruct the short time analysis. Evidently no contamination of arsenic or lead could be detected.

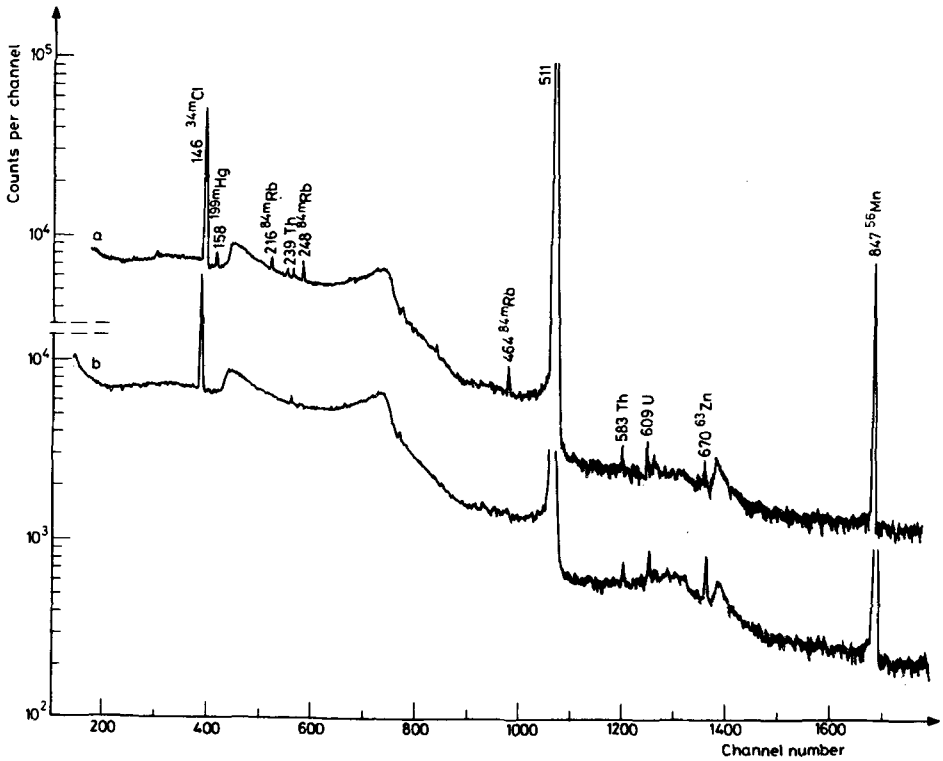

Fig. 3. 14 MeV neutron activation spectrum of fish material; t_i = 30 min, t_d = 27 min. t_m = 117 min; a) Elbe-River perch, sample mass: 162.5 mg; b) Natural-pool carp, sample mass: 108.3 mg

Conclusions

The new intense neutron source with the fast automatic restart device and the fast sample transport system was found to operate satisfactorily in the average without interruptions for more than 15 min. Improvements of the γ-ray spectroscopy system for high counting rates are under investigation. The first activation analyses of natural samples with KORONA have demonstrated the potential for the quantitative determination of numerous elements. The advantages of this method are simplicity in sample preparation and rapidity

of measurements. Although further experience will be necessary to judge the optimum field of application, the verification tests completed so far are promising enough to trust in the previously published theoretical predictions.

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