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INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS TECHNIQUE USING SUBSECOND RADIONUCLIDES

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The fast irradiation facility Mach-1 installed at the Danish DR 3 reactor has been used in boron determinations by means of Instrumental Neutron Activation Analysis using ^{12}B with 20-ms half-life. The performance characteristics of the system are presented and boron determinations of NBS standard reference materials as well as fertilizer materials are compared by literature value and spectrophotometric measurements, respectively. In both cases good agreement is obtained.

Introduction

The application of sub-second radionuclides at Risø National Laboratory began in the early 1970s with the determination of Li in a large number of geological reference materials, as well as in Orchard Leaves (SRM-1571) by Heydorn et al (1977) /1/. This was done by using thermal reactor neutrons at the Danish DR 2 reactor, now decommissioned, and based on Cerenkov counting of the 13 MeV β-particle of ^{8}Li. The result was successful, leading to the change of the indicative value from NBS of Li in Orchard Leaves from 14 mg/kg to 0.7 mg/kg.

In order to determine boron using a similar technique, a sample transfer time out of the reactor comparable to the halflife of ^{12}B was needed. These considerations led to the construction of a new irradiation facility, Mach-1, with the timing properties reported by Heydorn and Westermann (1981) /2/. Mach-1 was installed in 1981 at the Danish DR 3 reactor, which is a heavy water moderated and cooled research reactor operated at 1o MW in a steady-state condition.

Experimental

The fast capsule transfer system Mach-1 is driven by bursts of commercially available nitrogen with an input and output gas pressure of 0.7 MPa and 1.0 MPa, respectively. Further, the system includes a second nitrogen supply in which the gas pressure can be increased to 2.5 MPa to expel a capsule stuck in the irradiation position. The whole system is controlled by an Intel 8080 microprocessor system in automatic mode, and switches on a panel in manual mode, including a number of photodiodes to monitor the position of the capsule.

The detector is a perspex Cerenkov irradiator coupled to a XP2040 photomultiplier tube supplied with an active dynode chain based on the design by Kerns (1977) /3/. The dynode chain is operated with a negative high tension for the purpose of keeping the electronics dc-coupled.

The samples are contained in standard half-dram vials made of polyethylene, which are placed into a bigger transport capsule of the same material. The transport capsule is formed as a cylinder with a diameter of 10 mm and a length of 55 mm. The cylinders are sealed by heating the lid to the melting point.

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The capsule transport times involved are measured indirectly by means of pressure transducer- and photosensor signals with three timers, one for input time (measured as a velocity), one for irradiation time and one for output time. The indirect way is obtained by the detection of the nitrogen pressure wave outside the core. Details are available in the paper by Heydorn and Westermann (1981) /2/.

Performance

In order to determine the correlation between the measured and the actual irradiation times, an experiment with boron was performed. For a number of increased preselected irradiation times, the measured irradiation time and the corresponding boron response are shown in Figure 1. The measured points are fitted with the theoretical activation function

$$A(t) = A_0 * (1 - \exp(-\lambda * (t - t_0)))$$

A least squares fit gave $A_0 = 3.7 * 10^9$ counts/kg and $t_0 = 0.196$ s. The value of t_0 is a consequence of the indirect measuring method and the reactor flux profile; this value has to be subtracted from the measured irradiation time in order to get the true irradiation time. A_0 is a constant depending on the actual discrimination level.

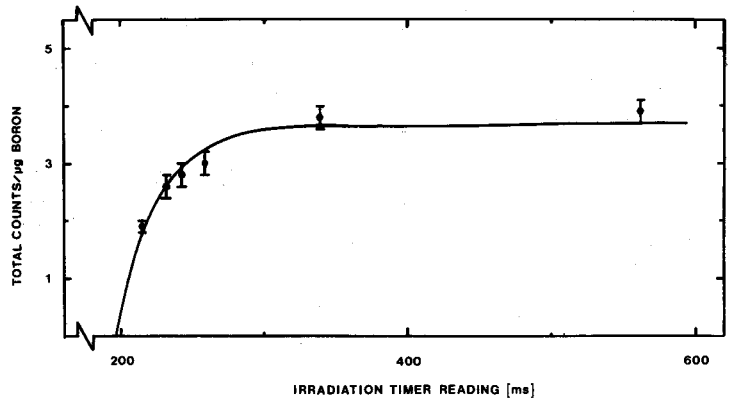

Fig. 1. Boron response as a function of the irradiation timer reading. The bars shown represent uncertainty due to counting statistics

The measured response is corrected for transport-time differences out of the reactor, and though the instrumentation reads approximately the same input velocity for all the irradiations, some reservations must be made for true irradiation times below 200 ms. This is due to the disturbance from the input gas pulse, which might be left at the instant when the output gas pulse acts to blow out the capsule. Bearing in mind those experimental conditions, the activation function explains the behaviour quite well.

It should be pointed out that a sufficient irradiation time with respect to boron is approximately 150 ms or less. Longer irradiation times result in a larger background, which reduces the signal-to-noise ratio.

Besides being sensitive to β-particles, the Cerenkov counter is also sensitive to γ-irradiation due to Compton interactions in the perspex irradiator. This sensitivity makes it difficult to determine mg/kg amounts of boron if sodium is present at the percent level due to the similar halflives of ^{12}B and $^{24}Na^m$. Figure 2 illustrates the boron and sodium responses as functions of discrimination level. It is

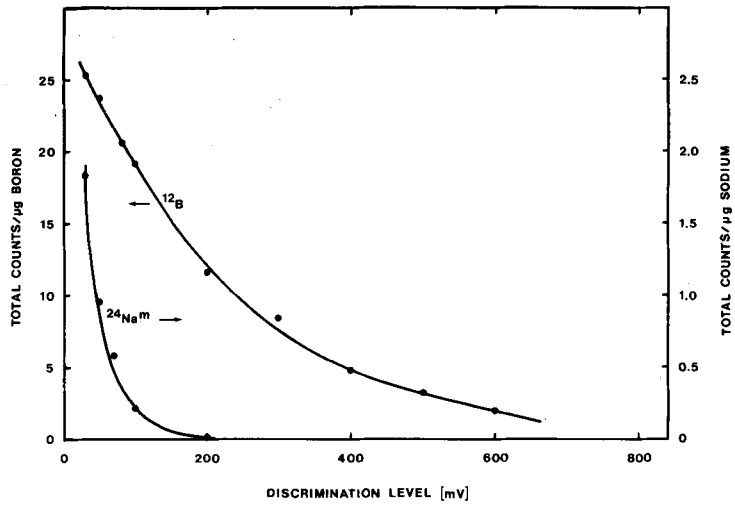

Fig. 2. Total counts of boron and sodium as functions of the discrimination level. Note the different scales. Illustrative only

seen that the different sensitivity of the 13 MeV ^{12}B β-particle and the 472 keV $^{24}Na^m$ γ-line makes it possible to discriminate the sodium response but at a cost of a decreased boron response. The correlation between the discrimination level and the boron response is strongly depending on the high tension of the photomultiplier and the gain of the amplifier stage.

Results and discussion

The fast transfer system has been used to determine boron in several standard reference materials. In Table 1, the results shown are obtained at a discrimination level corresponding to a boron response of about $5*10^9$ counts/ kg. At this discrimination level, the sodium response from the Cerenkov detector is negligible at concentrations of 5-10%. This discrimination level has no absolute correlation to the discrimination level used in figures 1 and 2 due to changes in high tension on the photomulitplier tube base. The data are collected over a period of several months, which gives different experimental conditions differ for the measurements because of changes in the reactor flux profile. In spite of this, a X^2-test shows no significant difference between the measured and the litterature value for the 10-20 % standard deviation obtained.

Boron has also been determined in fertilizer materials for the Danish company, Superfos. Table 2 shows the results and those obtained by spectrophotometric method performed by Superfos according to the Association of Official Analyti-

Table 1
Measured boron concentration compared with the value from
(a) BCR Information (1983) /4/, and
(b) NBS Special Publication (1984) /5/.
The number of observations are shown in brackets

Material	Boron concentration		
	This work (mg/kg)	Literature value (mg/kg)	
Phosphate rock	21.2±1.4 (4)	22.6±2.2	(a)
Spinach	26.9±5.2 (2)	24	(b)
Orchard leaves	32.4±3.9 (2)	33 ±4	(b)
Tomato leaves	30.9±2.7 (4)	32 ±4	(b)
Pine needles	14.8±2.1 (2)	17 ±3	(b)
Coal 1635	99.0±5.1 (3)	115 ±17	(b)

Table 2
Measured boron concentration for a number of fertilizer materials and the results obtained according to method 2-135 of the Association of Official Analytical Chemists (1984) /6/. For 1426 and 1435, the concentration is expressed in percent.
The number of observations are shown in brackets.

Sample identification and major constituent	This work (mg/kg)	Spectophotometric method (mg/kg)
1422 Potash	19.6 ±1.7 (6)	13
1423 Raw Kieserite	85.2 ±3.4 (3)	88
1425 H_3PO_4	43.7 ±2.6 (3)	54
1426 Colemanite	11.1 ±0.9 (2) %	10.8 %
1427 End product	200.4±4.2 (4)	188
1431 Potash	9.7 ±4.1 (1)	3
1434 H_3PO_4	44.4 ±2.7 (3)	41
1435 Colemanite	12.5 ±1.0 (2) %	10.2 %
1730 Raw Kieserite	61.0 ±5.9 (2)	100
1436 End product	188.0 ±4.8 (4)	185

cal Chemists (1984) /6/. As seen from the table, there is a good correlation between the two methods except for sample 1730. Samples 1427 and 1436 are end products and consist partly of all the other products mentioned. It should be noted that the detection limit for boron using our present equipment is in practical application approximately 5 mg/kg, increasing for increasing content of sodium and background level.

Conclusion

The fast irradiation facility Mach-1, installed at the Danish DR 3 reactor, has been used to determine boron using instrumental neutron activation analysis with Cerenkov counting on ^{12}B. The optimum irradiation time with respect to boron has been determined and the discrimination capability of the system against $^{24}Na^{m}$ has been shown. Further, its practical application has been applied on standard reference materials with good results. When comparing the above with boron determinations using a spectrophotometric method on fertilizer materials we find good correlation between the two methods.

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