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ANALYTICAL TECHNIQUE FOR DETERMINING THE BORON CONTENT
IN IRRADIATED URANIUM DIOXIDE FUEL

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Abstract

Post-irradiation examination of some prototype nuclear fuels, which have been doped with boron as a consumable neutron poison, includes assay and isotopic analysis of the residual boron in the fuel. A method has been developed for the quantitative recovery of the boron from the fuel and its assay by mass spectrometric techniques. The boron is recovered from the fuel sample by pyrohydrolysis and distillation at 1250°C in an induction-heated nickel furnace. Fission products are removed from the solution by cation exchange. Enriched boron-10 is added as a spike for the concentration assay by isotopic dilution. The spike solution has been calibrated against boron reference samples by mass spectrometric isotopic dilution.

The use of silica throughout the procedure results in acceptable blank values even in shielded cell conditions. Since the isotopic composition of the irradiated boron differs from natural boron, the measured isotopic ratios in successive fractions collected from the pyrohydrolysis allow to calculate and correct for the actual blank value in the sample.

The procedure has been tested with uranium oxide doped with zirconium boride at about 100 ppm and shows boron recovery yields in excess of 95 %.

1. Introduction

The post-irradiation examination of some prototype nuclear fuels, which have been doped with boron as a consumable neutron poison, includes the assay and isotopic analysis of the residual boron in the fuel. The boron can be separated from the fuel by pyrohydrolysis with steam at 1250 °C. The volatilized boron oxide is collected and the boron concentration in the solution measured. The implementation of this method to highly active samples in a shielded cell requires particular developments to achieve quantitative recovery of the boron, to obtain low blank values for the apparatus and reagents used and to eliminate radioactive elements interfering with the final boron analysis in the solution. Those developments are described in the following paragraphs.

2. Procedure

2.1. Pyrohydrolysis of the sample

To ensure that the fuel surface is well exposed during the pyrohydrolysis, the sample is extruded from the cladding and placed in a nickel boat. The pyrohydrolysis apparatus is shown in figure 1. The nickel boat is centered in a hollow nickel tube which serves as the furnace and is heated by induction. A long nickel rod extending from the tube is fixed into a slot of the quartz reaction chamber and serves as support for the tube and the thermocouple. Steam is entering the reaction chamber from a quartz boiling flask together with a continuous flow of argon used to obtain a steady flow rate. The reaction gases are condensed on a quartz cooler and collected into a plastic flask. The use of quartz is mandatory to obtain low blank

values. A thermocouple is necessary because the furnace should be maintained at 1250 °C without exceeding the nickel melting temperature at 1453 °C. Nickel is slowly attacked and oxidized but the design of the apparatus allows easy replacement of the furnace tube. Platinum is an alternative. The presence of uranium oxides catalyses the pyrohydrolysis of boron from the boron compounds. The uranium pellets however kept their general aspect after pyrohydrolysis. Trial runs with boric acid showed quantitative recovery at moderate heating speed by the induction furnace. Fast heating of the sample resulted in boron loss up to 70% by incomplete condensation. This effect has not been observed on more refractory boron compounds such as ZrB_2 . The time for complete pyrohydrolysis depends on several factors. Usually several runs lasting about 2 hours are made on the same sample and the boron concentration in different runs is measured. The analysis is terminated when nominal blank values are reached.

2.2. Chemical purification

Volatilization of fission products during pyrohydrolysis results in contamination of the boron solution with ^{137}Cs , ^{134}Cs , ^{95}Nb , ^{125}Sb and other activities as shown in table I. By passing the borate solution over a cation exchanger in hydrogen-form an overall decontamination factor of about 100 is obtained. The column is about 50 mm high with a diameter of 8 mm. For boron quantities of the order of hundred micrograms, this decontamination is sufficient to allow mass spectrometric measurements. The assay of smaller quantities approaching the blank value necessitates a better decontamination particularly from ^{125}Sb which is not removed by the cation exchange procedure. A coprecipitation method on Sb_2S_3 is presently under investigation. The eluate from the

cation exchanger is evaporated in a quartz beaker to a volume of approximately 4 ml. Our experience shows that a loss boron from neutral solution is not to be expected at low concentrations if the volume is at least 3 to 4 ml. At this stage sodium hydroxide is added to obtain a Na/B ratio of 5 to 1 and also one drop of a 10 % glycerol solution is added to prevent boron loss during further evaporation to dryness. The sodium borate is then redissolved in water and about one microgram is loaded onto a single filament for mass spectrometric analysis.

2.3. Boron analysis

The accurate analyses of isotopic composition and concentration by isotopic dilution are carried out by thermal ionization mass spectrometry measuring the $\text{Na}_2^{10}\text{B O}_2^+$ and $\text{Na}_2^{11}\text{B O}_2^+$ ions at masses 88 and 89. The calibration of the mass spectrometer is based on a natural boron reference material with a ^{10}B to ^{11}B ratio of 0.2473 ± 0.0002 . An isotopically enriched tracer with a ^{10}B to ^{11}B ratio of 1.53149 is added before the chemical separation procedure for isotopic dilution measurements. To obtain optimal sample loadings and isotopic dilution data the approximate concentration of boron in the sample should be known before mass spectrometric analysis. This is achieved by the colorimetric method using the colour changes induced by boron in a sulphuric acid solution of carminic acid.

3. Results

3.1. Blank values and reference samples

Low blank values are of primordial importance in the analysis of small

quantities of boron and are sometimes difficult to achieve by virtue of its common occurrence in laboratory glassware, reagents and airborne dust. The analysis of ZrB_2 reference samples led to results within the specified accuracy of $\pm 10\%$ for the boron content, but left some ambiguity concerning the proper blank correction. A blank taken after a reference sample could contain a small quantity of the sample left due to the non-quantitative nature of the pyrohydrolysis. In this case, part of the blank must be subtracted as a real blank and part must be added to the sample. The difficulty lies on the correct evaluation of both parts. The situation is depicted in figure 2. According to the interpretation, the result can vary between 92 % and 103 % of the value of the reference material. Another difficulty limiting the accuracy of the analysis is the variation of the blank value as a function of time. Initial values of 60 to 90 μg per hydrolysis have now dropped to a level between 15 and 25 μg as can be seen in figure 3. Since boron in irradiated samples is expected to differ in isotopic composition from natural boron it was anticipated that the isotopic analysis could provide a better evaluation of the blank value.

3.2. Irradiated samples

The results obtained on the irradiated samples are presented in table II. The initial isotopic composition is depleted in ^{10}B as expected. Subsequent "blank" assays with the sample remnants in the furnace show decreasing quantities of boron with an isotopic composition approaching the natural boron composition at the limit. From the different isotopic compositions the relative contribution of the sample and the blank can be calculated. It has to be assumed however that the isotopic composition of boron in the sample is homogeneous

i.e. the boron collected during several pyrohydrolysis runs and possibly originating from different parts in the sample has one single isotopic composition. Before the corrections can be applied, the real isotopic composition of the sample has to be derived from the apparent composition as measured and this is of course dependent on the blank correction made. The best approximation for this blank value seems the blank value obtained for the second pyrohydrolysis. The latter value is rather insensitive to variations in the real sample isotopic composition. The result of this procedure is depicted in figure 4. The blank value chosen for the initial pyrohydrolysis influences the total quantity of boron in the sample and its isotopic composition ; both quantities however are linked and must lie on the curve shown in the figure. The blank value for the second pyrohydrolysis was 50 μg and the corresponding results can be read from the graph. An uncertainty of $\pm 15 \mu\text{g}$ associated with the blank value induces a corresponding uncertainty of $\pm 2 \%$ on the quantity of boron but $\pm 6.4 \%$ on the ratio $^{10}\text{B}/^{11}\text{B}$, which is about 20 to 30 times larger than the intrinsic quality of the measurements.

4. Conclusions

The method developed for boron analysis in irradiated samples ensures quantitative recovery if 3 to 4 pyrohydrolysis runs are carried out. At the first pyrohydrolysis 94 to 98 % of the boron is recovered. The isotopic composition of the boron can be used as a monitor for indentifying reagent and apparatus blanks. The blank value however strongly influences the accuracy obtained for the isotopic analysis of the samples and forms the major part in the overall uncertainty of the measurements. In shielded

cell conditions and for a procedure accomodating samples of 5 to 10 g, blank values of 15 to 25 μg have been obtained. The corresponding uncertainty propagated on the boron concentration is of the order of 2 to 3 % but may reach up to 6 % on the $^{10}\text{B}/^{11}\text{B}$ ratio. The uncertainties introduced by the mass spectrometric measurement itself, by the spike calibration and by a possible non-quantitative recovery of the boron from the sample are negligible with respect to the effect of the blank value.

5. Acknowledgement

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TABLE 1

Radioactivity of borate solutions
 obtained by pyrohydrolysis
 Sample size ~ 5 g UO_2

Run Activity in Bq	1	2	3
^{137}Cs	$6.81 \cdot 10^7$	$6.75 \cdot 10^7$	$3.39 \cdot 10^7$
^{134}Cs	$1.37 \cdot 10^7$	$1.35 \cdot 10^7$	$6.77 \cdot 10^6$
^{95}Nb	$4.14 \cdot 10^6$	$6.25 \cdot 10^6$	$4.40 \cdot 10^6$
^{125}Sb	$1.22 \cdot 10^6$	$2.52 \cdot 10^6$	$1.99 \cdot 10^6$
Dose rate at 5 cm	0.3 R	0.3 R	0.2 R

TABLE 2

Analysis results of two irradiated samples

Pyrohydrolysis	Relative quantity	Sample I Blank to sample ratio	$^{10}\text{B}/^{11}\text{B}$ measured	Relative quantity	Sample II Blank to sample ratio	$^{10}\text{B}/^{11}\text{B}$ measured
No. 1	94.2	0.0692	0.07173	98.7	0.0436	0.07816
No. 2	4.3	1.497	0.1724	0.7	6.031	0.2203
No. 3	1.2	2.768	0.1973	0.2	16.14	0.2359
No. 4	0.3	6.72	0.2222	0.4	6.76	0.2222
	<u>100.0</u>			<u>100.0</u>		

Captions for the figures

Fig. 1. Pyrohydrolysis apparatus seen through the lead glass shielding

Fig. 2. Dependence of boron assay in a reference sample on the uncertainty of the blank value

Fig. 3. Time dependent variation of blank values observed in the shielded cell apparatus

Fig. 4. Dependence of boron assay and isotopic composition of an irradiated sample on the uncertainty of the blank value.

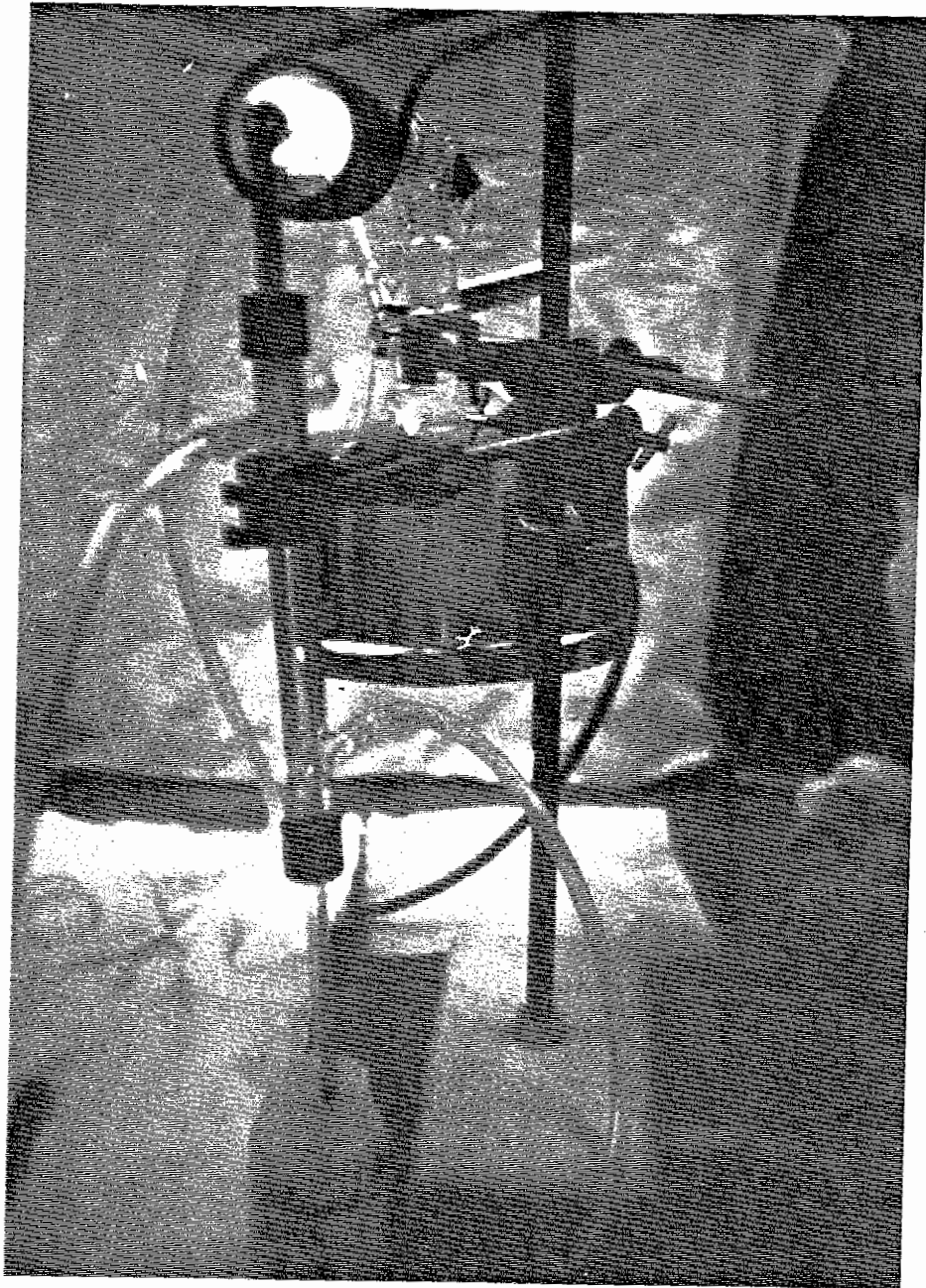


FIGURE 1 : PYROHYDROLYSIS APPARATUS

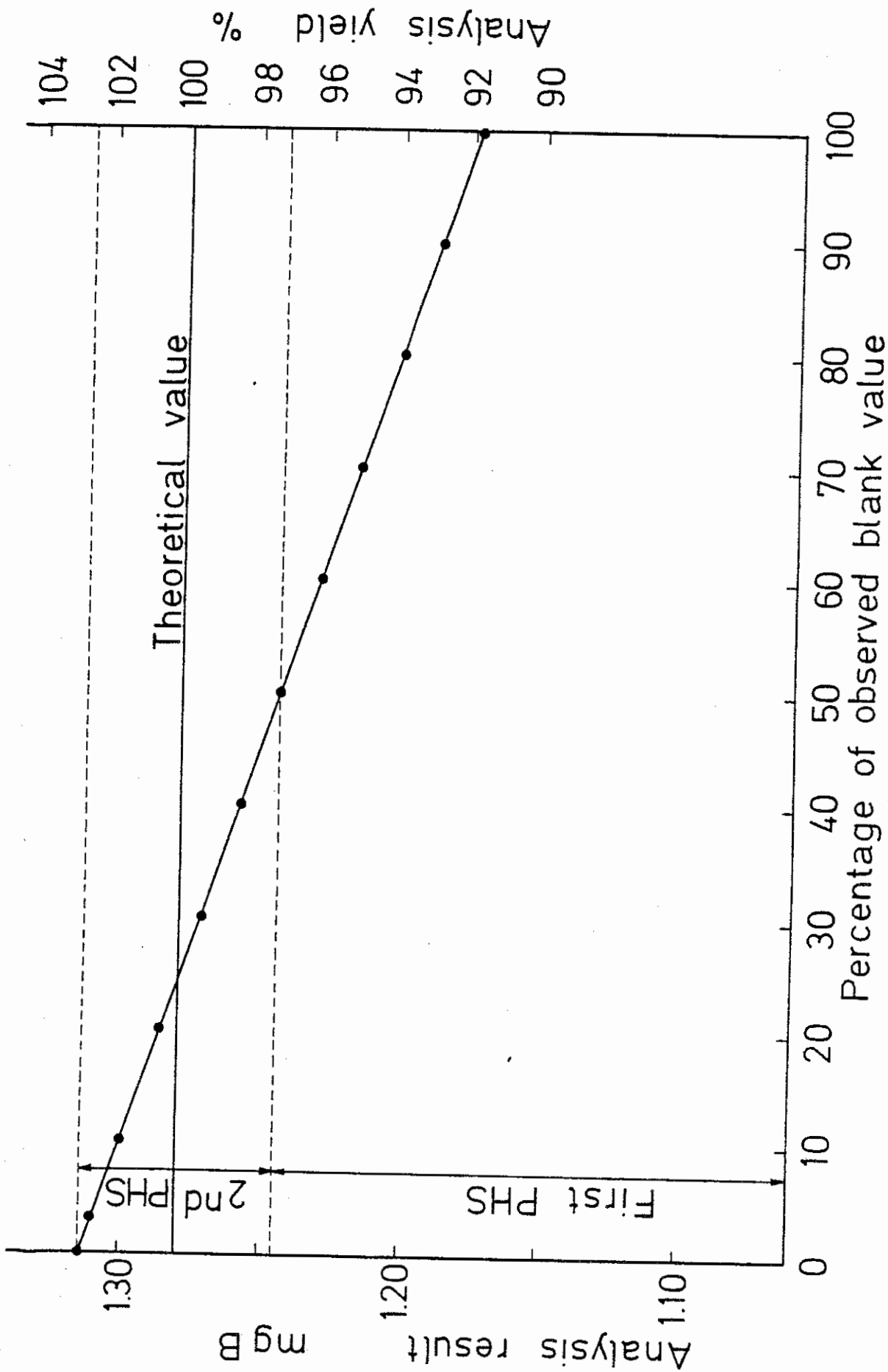


Figure 2 : Effect of blank value on boron recovery

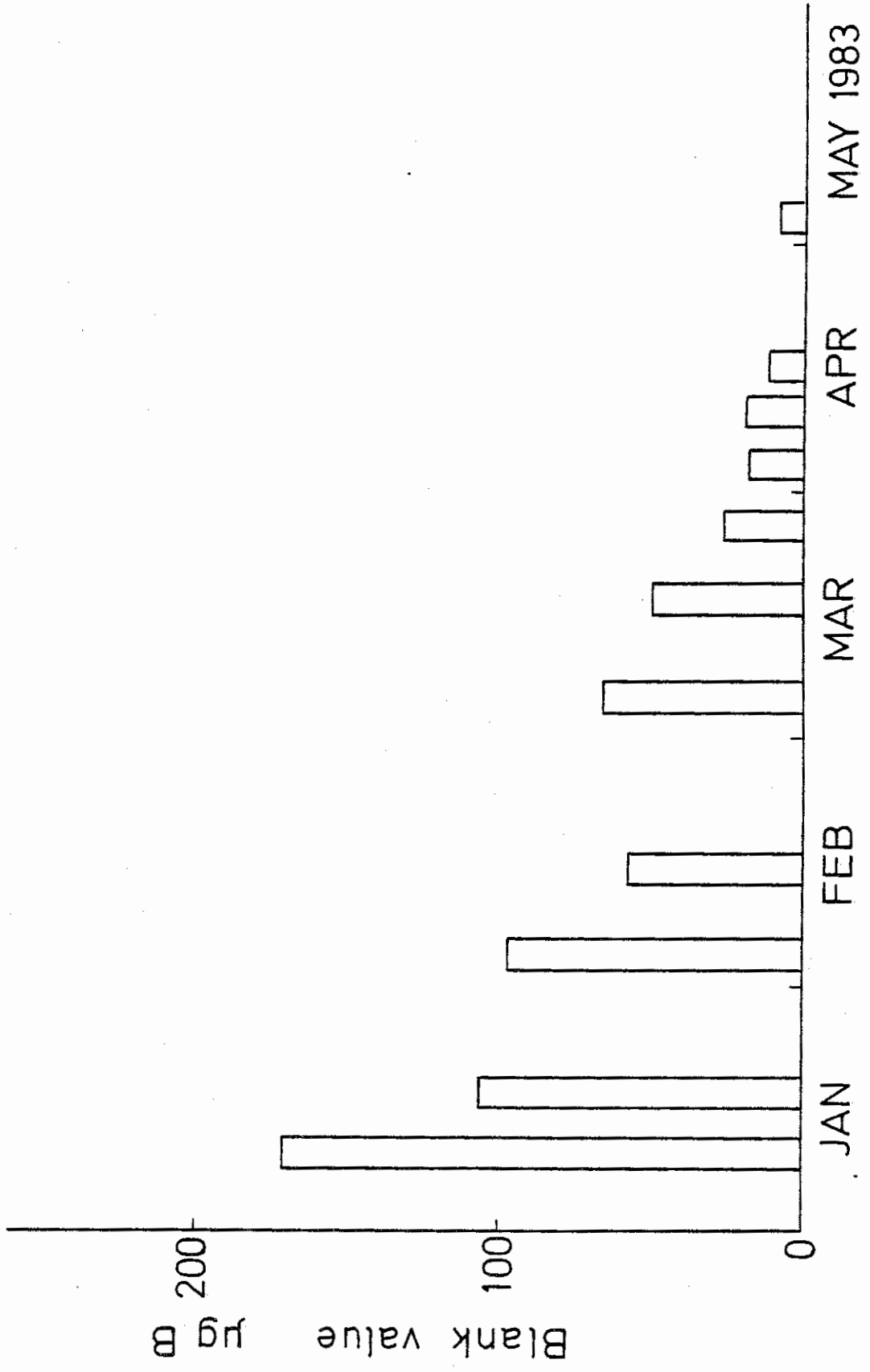


Figure 3 : Evolution of blank values

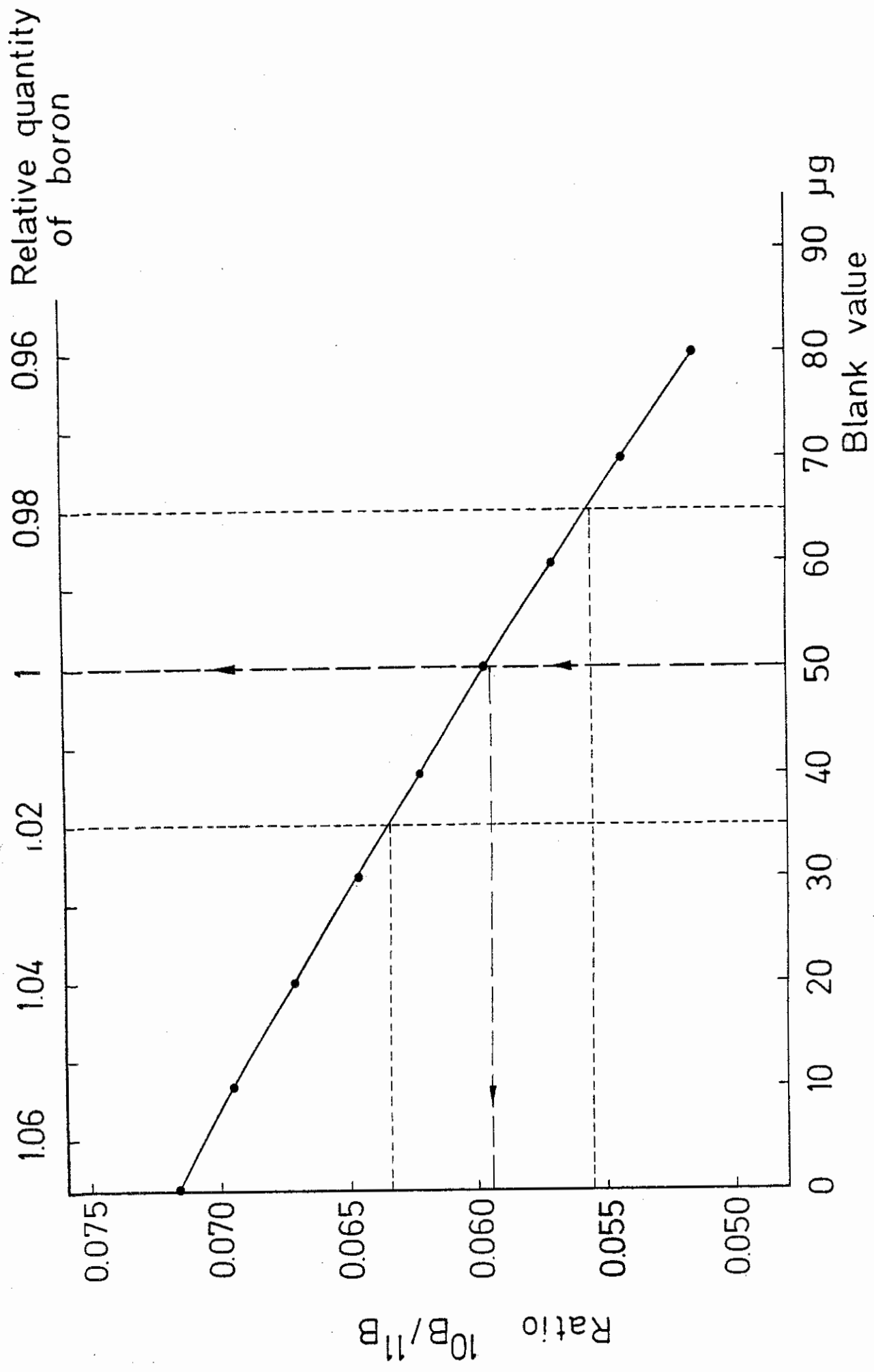


Figure 4 : Effect of blank value on boron analysis