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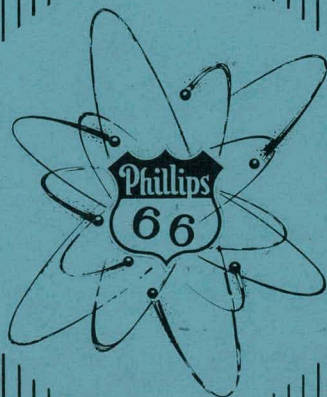
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ISOTOPIC ANALYSIS OF BORON AS
TRIMETHYL BORATE

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A B S T R A C T

Boron-impregnated polyethylene tape has been irradiated in the Engineering Test Reactor Critical Facility to study the effect of boron as a burnable poison in reactor fuel. Isotopic analysis of the boron was performed with a conventional CEC Model 21-103 mass spectrometer. The tape was distilled off and the residual boron was converted to trimethyl borate. The reaction mixture was analyzed without separation. Good precision was obtained with samples containing less than 0.5 mg. boron. Features of the mass spectrum of trimethyl borate are discussed. Other applications of the method are suggested.

Presented orally at the ASTM Committee E-14 Meeting on Mass Spectrometry at Los Angeles, May, 1959.

Work done under Contract AT(10-1)-205 to the U. S. Atomic Energy Commission.

ISOTOPIC ANALYSIS OF BORON AS

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INTRODUCTION

Boron¹⁰ has been extensively studied as a "burnable poison" in reactor fuel. In pursuing this study, polyethylene tape which had been impregnated with amorphous boron was irradiated in the Engineering Test Reactor Critical Facility. In evaluating the results, it was necessary to know the quantities of boron¹⁰ used in the experiment. Total boron was determined by a colorimetric method.⁽¹⁾ The isotopic composition of the boron was to be determined by mass spectrometry. A method was sought by which isotopic analyses of sub-milligram amounts of boron could be done in a length of time suitable for routine use. Thermal ionization mass spectrometry was considered first and, with available equipment⁽²⁾, was found to require material of higher purity than was obtainable from the polyethylene and in the small quantities available. Conversion to boron trifluoride was considered and was abandoned because of the involved preparation and purification required and because of lack of sufficient sample for pre-conditioning of the equipment. Conversion to trimethyl borate was investigated and a procedure was developed that is quite simple and satisfactorily precise.

EXPERIMENTAL

Sufficient tape to contain about 0.5 milligram of boron was heated in a small quartz test tube to depolymerize and distill off the polyethylene. The residual boron was then oxidized with warm nitric acid and dried under vacuum. A drop of methanol was added to the boric acid residue, and the entire reaction mixture vaporized into the inlet manifold of a CEC 21-103 mass spectrometer. A suitable aliquot was taken and the mass spectrum recorded in the usual manner with one exception. The m/e 10 and 11 peaks were recorded at increased ionizing current and with automatic electrostatic scanning, but with manual adjustment of the magnet current between peaks so that both beams were recorded at 3400 accelerating volts. This was done to eliminate voltage discrimination against the heavier mass. With electrostatic scanning, the higher voltage required to focus m/e 10 gives significantly higher ion drawout efficiency. In the m/e 72-73 and 103-104 region, the discrimination between adjacent masses is smaller than peak measuring error and can be neglected.

Background errors were found to be greatly reduced by a methanol rinse between samples of different composition. The high pressure section of the inlet system was saturated with methanol vapor, allowed to stand a few minutes, and the methanol pumped out. Then a blank run was made using methanol without boric acid and was recorded to be used as a background correction. After the second introduction, the intensity of the background peaks became reasonably constant at a few tenths of a percent of normal sample intensity.

Preparation of a single sample from tape required about an hour. Additional samples can be prepared as a series in about 15 minutes per additional sample.

CALCULATION

Table I is a tabulation of the most important peaks in the mass spectrum of commercially available trimethyl borate. It is evident that boron isotope ratios might be calculated from at least three regions of the spectrum: the parent peaks (m/e 103-104), the parent - minus - methoxy fragment peaks (m/e 72-73), and the boron peaks. The m/e 42-43 peaks were not considered because of the greater complexity of the spectrum in this region. The major peaks in this region are assumed to be due to rearrangement, probably by means of a cyclic intermediate⁽³⁾, rather than to BO_2^+ . It will be noted that the m/e 26 and 27 peaks are not in the proper ratio for BO^+ ions from natural boron. These may indicate C_2^+ rearrangement ions, BOH^+ rearrangement ions, or BOH^+ ions from impurities in the borate.

Inghram recommends using the B^+ ion for isotope ratio measurement because, while it is of low intensity, there is usually no instrument background and no corrections for carbon, oxygen and hydrogen isotopes are required.⁽⁴⁾ However, in the presence of excess methanol, as in this procedure, the B^+ peaks were found to give a $\text{B}^{11}/\text{B}^{10}$ ratio that in some cases was known to be too high. In samples of known high B^{11} enrichment, the m/e 11 peak was found to be too high by an amount equal to about 20% of the m/e 10 peak, while the heavier ion groups gave the correct ratio. This error appeared to be independent of reservoir pressure and methanol/methyl borate ratio.

The mass difference between B^{11} and B^{10}H is not great enough to permit resolution of these possible components of the m/e 11 beam. However, examination of beam widths indicated that the m/e 11 beam was slightly wider than the m/e 10 beam. It was therefore assumed that BH^+ ions were formed in this system. The m/e 10 and 11 peaks were not used for calculation except in the case of material with a very high $\text{B}^{11}/\text{B}^{10}$ ratio, where the B^{10}H error is small and can be corrected satisfactorily, and where cracking pattern uncertainty in the higher masses becomes more troublesome.

Table II(A) gives portions of a spectrum of trimethyl borate which is monoisotopic in boron. These can be derived from the spectra of two samples of different enrichment. One or both of these reference spectra were used to calculate the isotope ratios in the manner illustrated in Table II(B). The mixture spectrum is resolved into two components, one component due to the ions containing B^{10} , the other to ions containing B^{11} . The ratio of the parent (or base) peaks is then the atom ratio of the boron isotopes.

At the natural $\text{B}^{11}/\text{B}^{10}$ ratio of about 4, the standard deviation by this method is 0.024; at a 1:1 ratio, the standard deviation is 0.008. It is believed that this could be improved by the use of a metastable suppressor and by closer control of instrument operating conditions. The metastable suppressor should improve accuracy by improving resolution and removing base line irregularity. This should also provide more accurate monisotope pattern information.

OTHER APPLICATIONS

This general procedure can be modified to handle several forms of samples. Isotopic analysis of the boron in a borax bead thermocouple coating has been performed by simply dissolving the borax in a minimum amount of hot sulfuric acid, adding methanol, and performing the analysis as with the tape.

In the case of highly radioactive solutions, such as result from dissolution of spent reactor fuel elements, it is sometimes possible to get adequate decontamination and complete boron recovery by ion exchange in remote apparatus. A good spectrum is obtained from as little as 20 micrograms of boron and the precision is still good at this level. Because of the small amount of time required for direct handling in preparing the trimethyl borate, and because of the small quantity of boron required, it is possible to make isotopic analyses of reasonably radioactive solutions without decontamination.

CONCLUSION

Isotopic analysis of boron can be performed with a conventional analytical mass spectrometer by a simple conversion to trimethyl borate. Only a few micrograms of boron are required, and boric acid, borates or elemental boron are satisfactory.

TABLE I

Commerical Methyl Borate
Partial Spectrum

<u>m/e</u>	<u>relative abundance</u>	<u>m/e</u>	<u>relative abundance</u>
10	0.34	41	1.2
11	1.37	42	7.3
15	43.9	43	21.3
26		72	40.9
27	0.93	73	100.
28	4.0	103	11.5
29	20.2	104	32.4

TABLE II (A)

Reference Spectra
Monoisotopic in Boron

B(OCH₃)₃⁺ Group

P*-2	0.4
P -1	10.6
P	100.
P +1	3.50

B(OCH₃)₂⁺ Group

B*-2	0.2
B -1	16.1
B	100.
B +1	2.35

*P = Parent, B = Base

TABLE II (B)

Calculation

<u>m/e</u>	<u>mixture</u>	<u>B¹⁰</u>	<u>B¹¹</u>
102	59	50.	8.
103	676	474.	202.
104	1923	16.6	1906.

$$\frac{B^{11}}{B^{10}} = \frac{1906}{474} = 4.02$$

$$B^{10} \text{ P.P.} + 0.106 B^{11} \text{ P.P.} = 676$$

$$0.035 B^{10} \text{ P.P.} + B^{11} \text{ P.P.} = 1923$$

$$B^{10} \text{ Parent Peak} = 474$$

$$B^{11} \text{ Parent Peak} = 1906$$

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