Mass spectrometric Determination of Boron Stable Isotopes And Its Application on Some Geological Materials.

قياس نظائر البورون المستقرة بواسطة جهاز مطياف الكتلة وتطبيقاتها على بعض المعادن الجيولوجية .

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Abstract :

Boron isotopic composition measurements were carried out by using a thermal ionization mass spectrometer. The evaporation and ionization currents were employed in the range of 1.5 – 1.7 ampere. Masses 88 and 89 which were detected are corresponded to the ions $Na_2B^{10}O_2^+$ and $Na_2B^{11}O_2^+$ respectively. The isotopic ratio measurements of boron isotopes (B^{10}, B^{11}) are determined for numbers of compound standard deviation of measurements are in the range of (1- 7 x 10^{-5}). A pyrohydrolysis technique is being used for recovery of boron from some materials like B_4C , B_2O_3 and boron amorphous.

الخلاصة :

جرى قياس نظائر البورون المستقرة (B^{11},B^{10}) باستخدام مطياف الكتلة ذو التآين الحراري, حيث استخدم تياري التبخير والتآين (1.7-1.5) امبير عند كتلتي (89,88) والتي تنطبق على قياس الايونات $Na_2B^{10}O_2^+$ و $Na_2B^{11}O_2^+$ على التوالي. ان قياس النسبة النظائرية للبورون (B^{11},B^{10}) تم تعيينها لمجموعة من المركبات عند انحراف قياسي بمعدل (1- 7 × 10^{-5}). ان طريقة الـ pyrohydrolysis استخدمت لاستخلاص البورون لمجموعة من المركبات مثل كاربيد البورون , اوكسيد البورون والبورون العشوائي (غير المحدد).

Introduction :

There are two naturally occurring isotopes of boron, B^{10} (19.8%) and B^{11}(80.2%).(1)

The B^{10} isotope is of considerable significance in nuclear chemistry because of its large cross section, 3840 borns, for thermal neutron capture(1). Recently, the determination of the isotopic abundance of boron can be carried out with a high degree of accuracy only by the use of the thermionic mass spectrometer, which is characterized by the extremely small amounts of substance required(1). The technique can be employed not only to define isotopic compositions, but also to assay the quantities and concentrations of elements by means of isotopic dilution analysis(2).

Usually for isotopic ratio measurement of boron, the recovery of this element is obtained by employing the pyrohydrolysis method which is an effective technique for converting elemental boron and boron carbide to boric acid(1,3,4). It is also useful in separating boron from a wide variety of compounds, alloys, such as boron- stainless steel, boron- uranium, zircaloy, boron carbide-uranium dioxide and refractory borides. However, from most materials, the boron is separated completely, and substantially a pure boric acid solution is obtained.

In this work pyrohydrolysis is chosen as an excellent method for boron separation, since it gives nearly 100% recovery of the boron to avoid any appreciable fractionation and it is free of contamination possibilities that would affect the isotopic ratio(1).

In the pyrohydrolysis, humid oxygen is passed over the sample at 1000-1050°C. The pyrohydrolysis reactions for boron carbide are belived to be as follow(5):

$$B_4C + 3O_2 \xrightarrow[\sim 1000^{\circ}C]{H_2O} 2B_2O_3 + C$$

$$B_2O_3 + 3H_2O \xrightarrow{\sim 1000^{\circ}C} 2H_3BO_3$$

$$C + H_2O \xrightarrow{\sim 1000^{\circ}C} H_2 + CO$$

$$C + 2H_2O \xrightarrow{\sim 1000^{\circ}C} 2H_2 + CO_2$$

Hydrogen, carbon monoxide, carbon dioxide are found in the gaseous products, also trace amounts ($F^{\tilde{}}$ and $Cl^{\tilde{}}$) which are volatile under the working conditions selected, Fe_2O_3 and SiO_2 remain in the boat used for analysis(6). The pyrohydrolysis reactions for elemental boron is:

$$4B + 3O_2 \xrightarrow[\sim 1000^{\circ}C]{H_2O} 2B_2O_3$$

Experimental

Apparatus:

1. Thermal ionization mass spectrometer (MAT 261), Finnegan Mat Co. (W.Germany). This instrument is used for a precision measurements of isotopic compositions of boron.

The characteristics of this instrument as follow:

- Single foeussing.
- A multiple filament assembly.
- Varying magnetic field.
- The ion current is measured by either a Faraday cup in conjuction with a vibrating reed electrometer or a SEM secondary electron multiplier coupled to a d.c. amplifier.
- Ion accelerating voltage ~ 10 KV.
- Source slit width 0.2 mm.
- Collector slit width 0.6 mm.
- Angle of deflection 90°.
- Radius of curvature 23 cm.

Also the MAT 261 is coupled with a computer and is flexible enough to be operated completely automatically without any operator intervention, i.e. manually or semi- automatically.

2. Inductively coupled plasma optical emission spectroscopy,(polyvac E 970), HILGER analytical Co., England.
3. Tubular furnace, (LM 8106) Stanton Redcroft Co.
4. Quartz tubes , polyethylene vessels, Al_2O_3 – boats.

Procedure :

Boron sample was first crushed in a mortar to a powder and sieved to size less than 80 mesh. An aliquot of the sample was weight (about 500 mg.) in a Al_2O_3 – boat. The boat was inserted into a quartz tube which was placed in a tubular furnace(3,4,6,7).

The tubular furnace was heated to 1050°C in an oxygen atmospher, which serves as the carrier gas, and passed with a flowrate (20 L/h) via a rubber tube with a capillary connected to a 1-liter 3-neck round- bottom flask containing water. The water was heated and the gas stream saturated with steam and was allowed to pass over the sample in the Al_2O_3 – boat which was placed in quartz tube. The end of the quartz tube was bent to form a right angle and was immersed in a vessel containing 0.05 M NaOH. Fig.(1) shows the apparatus for the pyrohydrolysis of boron.

In the first hour of preparation the collected portion of the boric acid was titrated with 5ml of NaOH, then 2, 0.5ml for the second, third hour respectively. Under these conditions the required pH was maintained to about (8-8.5). All the collected portions (Borax) were concentrated by reducing their total volume from 400 to 30 ml via gentle heating using a quartz plate over a porcelain dish. Because of the low concentration of boron in the second and third portions a further preconcentration was needed. A find volume of 10 ml was suitable for analysis.

The Borax solution pH must be adjusted after the preconcentration step between (8-8.5).

During pyrohydrolysis the reaction to form the boric oxide appears to be faster than the distillation of the volatile boric acid, Borax was extracted by the pyrohydrolysis method from some compounds. The procedure consists of converting boron oxide to boric acid by passing steam and its reaction with sodium hydroxide.

The Inductively Coupled Plasma / Optical Emission Spectroscopy (ICP/OES) is also used to determine the boron quantitatively.

Sample Loading :

The filament used for loading is consisting of a single filament made of Rhenium. The sodium tetraborate obtained is placed on the Rhenium filament by a pipette of Eppendorf type, using disposable tips . The quantity of boron loaded on each filament was in the range of 1.5 – 35 μg boron. The filament which is in the loading position is connected automatically via spring contacts to the preparation heating unit this unit provides facilities for reproducible, temperature programmed heating up of the loaded filaments, making possible to concentrate the sample on a small area in the mid of the filament.

Computer Parameters for Boron Experiment :

In this work a computer type HP (9845 B) is used, which it work as a controller and data collector. This computer was set according to the following parameters:

- Single collector .
- Type of collection (COL.2).
- FAR 2 for measurement .
- Sequential peak jumping.
- Background determination after each scan.
- Peak centring for each peak at each scan.
- Dynamic calibration (DYNCAL).
- Std. DEV and Rel. Dev [%].

Masses (No. 23, K^{o} 39) are calibrated to measure the intensities of boron isotopes (88 and 89).

Results and discussion :

In the preparation of sodium tetraborate by pyrohydrolysis method for mass spectrometric measurements, the boric acid distilling over NaOH must be adjusted to pH 8-8.5 . A large excess of NaOH should be therefore avoided because it may affect adversely the emissivity of the $Na_2BO_2^+$ ions.

Table 1 shows the recovery of boron from the compounds chosen for the pyrohydrolysis method, using ICP / OES. The portions (first , second, third) represent the amounts of boron obtained during the first second and third hour of the pyrohydrolysis respectively. The major quantity of the boron is usually recoverd in the first hour of the pyrohydrolysis as shown in Fig (2,3). The minerals represented in table 2 show a low boron concentration (~ 10 µg/mL) which make it impossible to measure the isotopic ratios of B^{10} and B^{11} in these minerals.

The chemical form for sample loading of boron on the filament is sodium tetraborate, which gives almost exclusively $Na_2BO_2^+$ ions by thermionic conversion having the masses 88(B^{10}) and 89(B^{11}) (8).

The boron isotopes are not measured as (B^+) because the boron has high ionization energy, it needs high heating to produce B^+ and at high temperature boron is easily evaporated, therefore it is measured as $Na_2BO_2^+$ rather than B^+ to avoid isotope fractionation.(8) The heating current for ionizing and evaporating filaments is slowly increased (about 0.2 A every 3 minutes) until the boron signal is detectable on the grid. The best intensity of the $Na_2B^{11}O_2^+$ and $Na_2B^{10}O_2^+$ signal were obtained at a heating current of (1.5 ~ 1.7 A)for each of the ionizing and evaporting filaments. Boron signal is normally decaying during most of the analytical time, therefore, all filaments are pre-baked at 4A for 1.5 hour in a vaccum and under a potential field. Baked filaments are free of background signals at the mass 88 and 89.

Occasionally a sample of sodium tatraborate gives poor emissivity because of either the presence of foreign ions or some other unknown reason. Mass discrimination effects can be determined by measurement of boron isoptopes standard of comparable boron isotopes compositions (e.g., for natural boron samples the N.B.S. boron isotopes standard No. 951 is used, this is shown in table 3. Also this table shows that the ratio of B^{10}/B^{11} determined and the theoretical value are in good agreement (Rdet. / R the = 1.0008). For calculation of the percent of B^{10} and B^{11}, the correction for the O^{17} in the portion of mass 89 which correspond to $Na_2B^{11}O_2^+$ is necessary and as follow(9) :

$$\frac{\text{Mean ratio } (B^{10}/B^{11})}{1-0.00079\text{xMean ratio}(B^{10}/B^{11})} = \text{correction mean ratio}$$

Table 4 shows a significant variation in the B^{11}/B^{10} abundance ratio in different compounds. Further more, it can be seen from the table that the mean value of B^{11} / B^{10} ratio for the Boron amorphous of Riedelde. Haën AG company (4.028) is approximately in agreement with the mean value of the ratio for the Boron amorphous of Fluk AG company (4.027). Also this table shows, that the mean value of B^{11}/B^{10} ratio in the Borax of BDH company (4.045) is the higher compared with the others ratios.

Conclusions :

The measurement of isotopic ratios of B^{11} / B^{10} for various boron compounds (B_4C, B_2O_3 , boron amorphous, colemanite) were accomplished. The variation in the isotopic ratio measurement of boron isotopes (B^{11} / B^{10}) were determined and compared with the data published elsewhere (9). Precision and reproducibility of the isotopic measurements were calculated for boron standards (N.B.S. 951). For good boron recovery, a pyrohydrolysis method proved to be an excellent technique to obtain a highly pure products.

References :

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Table (1) : Concentrations of Boron in (µg/mL) for Some Compounds Determined by ICP/OES.

Compound	First	Second	Third
Boron carbide B4C	1581	1709	517
Boric oxide B_2O_3	2647	1280	733
Boron amorgous $B^{*}1$	7416	1594	280
Boron amorphous B^{*} 2	1726	1726	647.6
Colemanite	2810	2105	680

First: The first hour of preparation .
Second : The second hour of preparation.
Third : The third hour of preparation.

*1 : Riedel- de Haën AG company.
*2 : Fluka AG, Buchs SG company .

Table (2) : Concentrations of Boron in (µg/mL) for Some minerals determined by ICP/OES.

Mineral	Source	First	Second
Clay Limestone	Iraq	1.70	0.4
Shale	Iraq	5.00	2.0
Pure NaCl	BDH	1.95	1.2
Oolitic Kaolinite	Iraq	7.00	3.0
Phosphate Rocks	Iraq	10.00	-

First : The first hour of Preparation .
Second : The Second hour of Preparation .

Table (3) Mass spectrometric analysis of boron isotopes standard.

Sample	Measurement	B^{10}/B^{11} Theoretical	B^{10}/B^{11} * Determined	Ratio of dete.rvalue to theo.value	Mean standard deviation
N.B.S(951)	1	0.2473	0.2475	1.0008	$7.5x10^{-5}$
N.B.S(951)	2	0.2473	0.2475	1.0008	$4.5x10^{-5}$
N.B.S(951)	3	0.2473	0.2476	1.0012	$4.0x10^{-5}$
N.B.S(951)	4	0.2473	0.2475	1.0008	$1.4x10^{-5}$
N.B.S(951)	5	0.2473	0.2475	1.0008	$2.8x10^{-5}$
N.B.S(951)	6	0.2473	0.2473	1.0000	$6.4x10^{-5}$
N.B.S(951)	7	0.2473	0.2474	1.0004	$4.8x10^{-5}$
N.B.S(951)	8	0.2473	0.2476	1.0012	$1.5x10^{-5}$
N.B.S(951)	9	0.2473	0.2475	1.0008	$6.5x10^{-5}$
N.B.S(951)	10	0.2473	0.2474	1.0004	$2x10^{-5}$
N.B.S(951)	11	0.2473	0.2475	1.0008	$3.9x10^{-5}$
N.B.S(951)	12	0.2473	0.2476	1.0012	$1.1x10^{-5}$
N.B.S(951)	13	0.2473	0.2475	1.0008	$6.3x10^{-5}$

*** each value of B^{10}/B^{11} determined is a mean of 50 reading.**

Table 4: Mass spectrometric determination of boron isotopic ratio (B^{10}/B^{11}) of some boron compounds.

Compound	Source	B^{10}/B^{11}	Mean B^{10}/B^{11}	Mean standard devation
Boron carbide B_4C	Riedel-de Haën AG.	4.010 4.001 3.997 3.999	4.002	$2.21x10^{-4}$
Boric oxide B_2O_3	BDH	3.984 3.988 3.986 3.987	3.986	$3.54x10^{-4}$
Boron Amorphous B	Riedel-de Haën AG.	4.027 4.028 4.027 4.029	4.208	$1.00x10^{-4}$
Boron Amorphous B	Fluka AG. Buchs SG.	4.028 4.028 4.025 4.028	4.027	$9.22x10^{-5}$
Borax $Na_2B_4O_7$. $10H_2O$	BDH	4.044 4.044 4.044 4.046	4.045	$7.50x10^{-5}$
Colemanite $Ca(OH)_3(B_3O_4).H_2O$	Turkya	3.994 3.996 3.995 3.998	3.996	$6.05x10^{-5}$

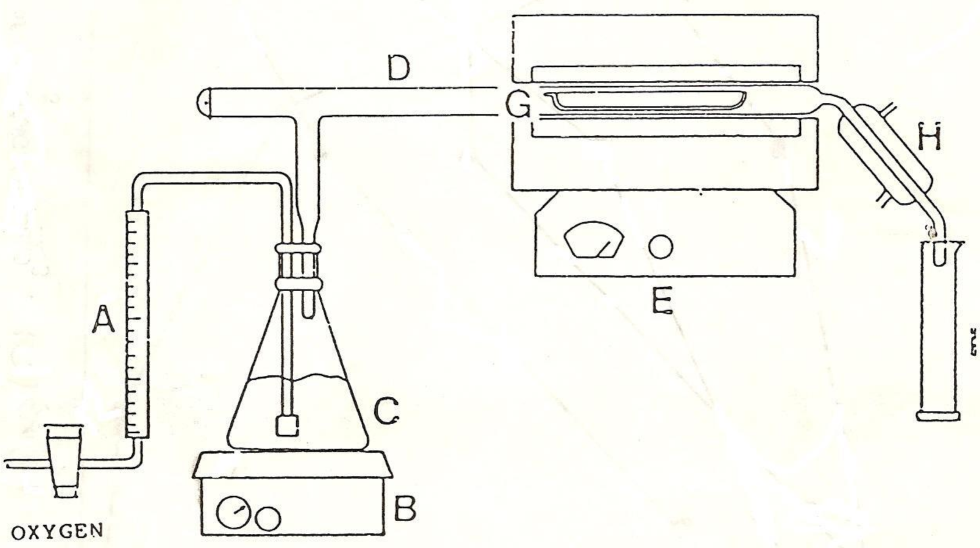
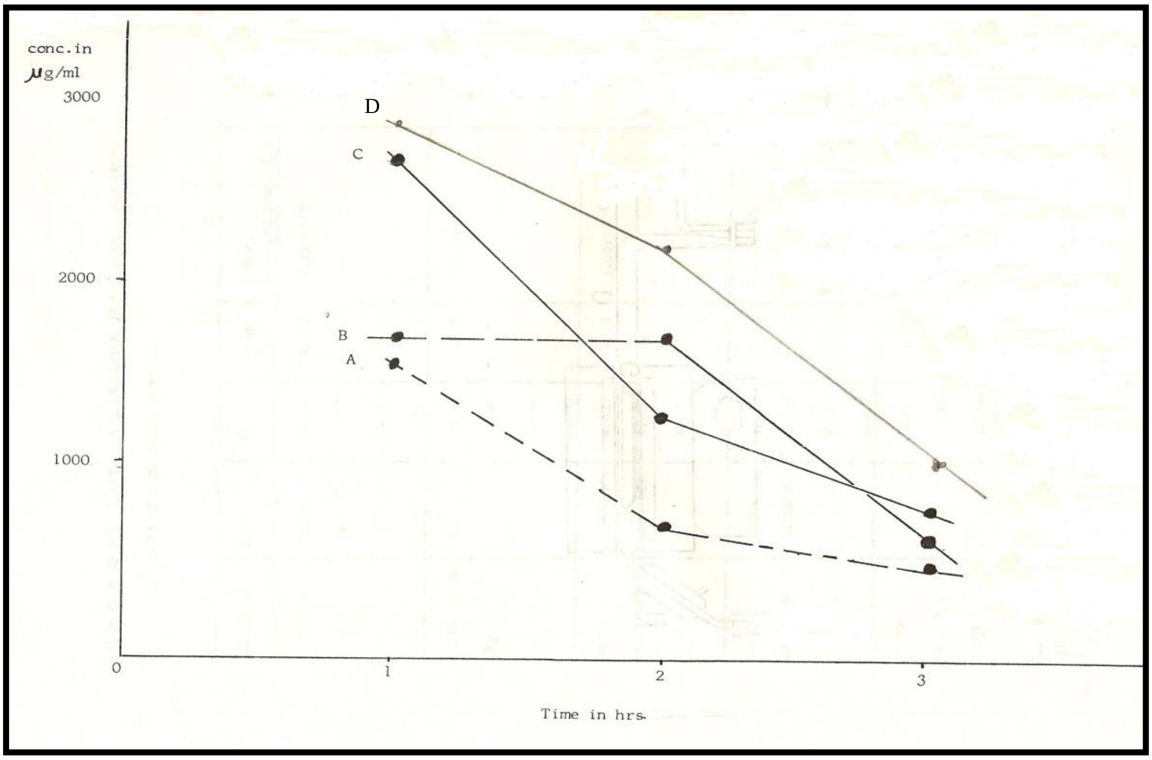


Fig. 1 : Layout of the pyrohydrolysis equipment.

A = rotameter
B = heating plate
C = water tank
D = sample feed connection
E = tubular furnace
G = sample boat
H = water cooler
I = sample collector



Fig(2) : Concentration of Boron in µg/ml per each hr. in :
(A) B4C ; (B) Boron amor phous of fluka AG: (C) B_2O_3 , (D) Colemanite.

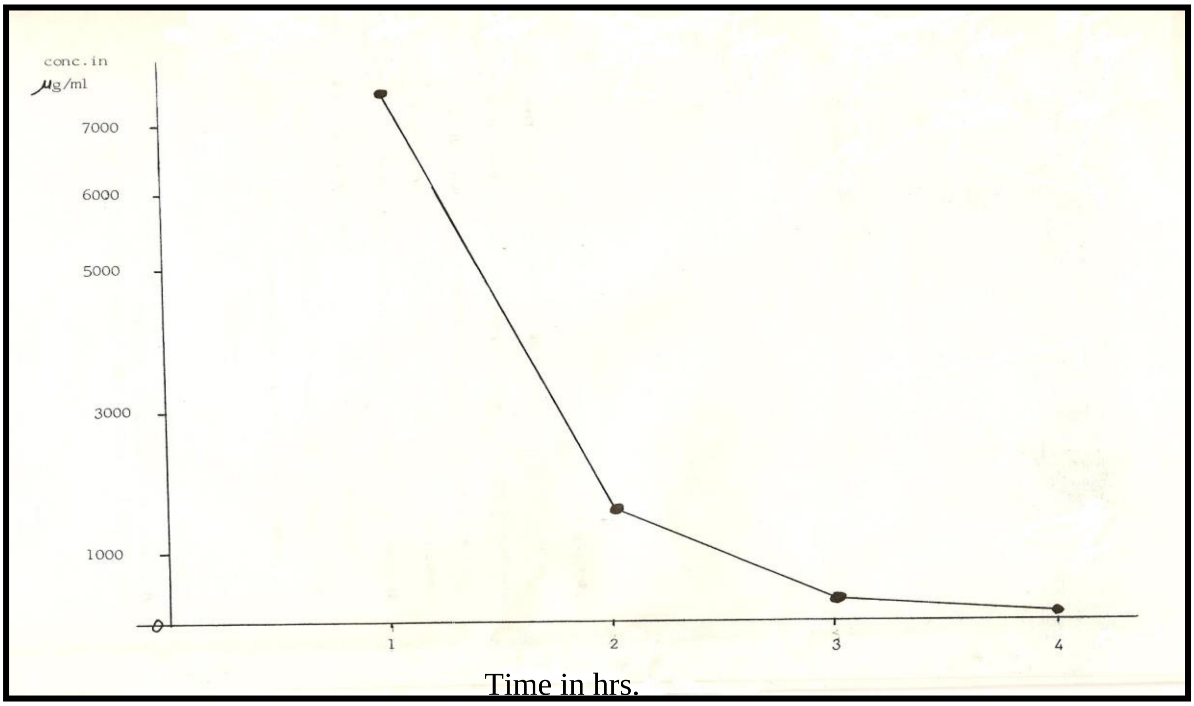


Fig.(3) : Concentration of boron in µg/ml pereach hr-in Boron amorphous of Riedel de Haen AG.