Separation of Boron from Borated Paraffin Wax by Pyrohydrolysis and Alkali Extraction Methods and Its Determination Using Ion Chromatography

Vaibhavi Vishwajeet Raut,* Subbiah Jeyakumar,** Dipti Jayesh Shah,* Uday Kumar Thakur,* Bhupendra Singh Tomar,* and Karanam Lakshminarayana Ramakumar**

*Radioanalytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India
**Radiochemistry and Isotope Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

A method based on the pyrohydrolysis extraction of boron and its quantification with ion chromatography was proposed for paraffin waxes borated with H3BO3 and B4C. The optimum pyrohydrolysis conditions were identified. Wax samples were mixed with U3O8, which prevents the sample from flare up, and also accelerates the extraction of boron. Pyrohydrolysis was carried out with moist O2 at 950°C for 60 and 90 min for wax with H3BO3 and wax with B4C, respectively. Two simple methods of separation based on alkali extraction and melting wax in alkali were also developed exclusively for wax with H3BO3. In all the separations, the recovery of B was above 98%. During IC separation, B was separated as boron-mannitol anion complex. Linear calibration was obtained it between 0.1 and 50 ppm of B, and LOD was calculated as 5 ppb (S/N = 3). The reproducibility was better than 5% (RSD).

Keywords Boron, paraffin wax, pyrohydrolysis, alkali extraction, ion chromatography, boron-mannitol complex

(Received September 22, 2014; Accepted January 15, 2015; Published March 10, 2015)

Introduction

Boron has two stable isotopes, 10B and 11B, with natural isotopic abundances of 20 and 80%, respectively.¹ ¹¹B has a high-neutron absorption cross section (3837 b), and hence boron compounds are extensively used in nuclear technology.²,³ For example, natural and enriched boron carbides are used as control rods in the nuclear reactors.⁴ Boron compounds are also found to be useful in shielding against high-energy neutrons. Water, hydrocarbons and borated waxes are used for neutron shielding.⁵ In radiotherapy treatments, in order to protect occupational workers and patients from the undesirable neutron and gamma doses, paraffin wax containing B,C is used.⁶ Low-level borate wastes generated from the nuclear power plants have been immobilized with paraffin wax using a concentrate waste drying system (CWDS).⁷ Borated paraffin waxes are prepared by mixing calculated amounts of either boric acid or boron carbide with the molten wax. This necessitates the determination of boron at different locations in order to check the homogeneous distribution of B over the borated wax. The determination of boron in nuclear materials is inevitable due to its high neutron absorption cross section.⁸ Both non-destructive analysis (NDA) and destructive analysis (DA) methods were reported for boron analysis.⁹⁻¹¹ For boron analysis at trace-level concentrations, DA methods based on wet chemistry is preferred over the ND methods due to their high sensitivity, whereas the ND techniques are used in determining boron at the percentile level. The separation of boron from the matrix prior to the instrumental analysis is a prerequisite in DA methods, whereas NDA methods offer direct analysis of the sample.¹² NDA methods require facilities like accelerator and high-flux neutron sources and reference materials to accomplish the analysis. Hence, destructive analyses are more in practice due to better precision, high sensitivity and simplicity.

For the determination of boron in borated waxes, not many methods have been reported. The difficulty associated with the destructive analysis of boron in paraffin wax is its separation from the matrix because boric acid or boron carbide is aqueous soluble, whereas the paraffin wax is insoluble. This demands a separation method that does not require dissolution of the matrix, but at the same time it should selectively separate boron. Pyrohydrolysis (PH) is one of such methods that can directly extract boron at trace concentrations from solid samples of diverse nature.¹³ During PH, the sample is pulverized at high temperature (above 900°C), and is allowed to react with water by passing steam over the sample with the help of a carrier gas. Subsequently, the steam is condensed as a distillate, which contains boron as H3BO3.¹¹ There is no direct evidence available in the literature regarding the use of pyrohydrolysis for extracting a large amount (percentage) of boron. During PH, boron in any form in the sample is converted into B2O3(s), which dissolves in water (steam) and forms H3BO3. Significant boron loss was observed when samples with a high content of boron are subjected to PH. To explain this loss, it is necessary to consider three important conversions that are expected to occur with B2O3(s) during PH. The conversions include (i) the oxidation of boron compounds to B2O5, which occurs at about 250 – 300°C, (ii) B2O5 starts melting at 550°C, which completely becomes

---

¹ To whom correspondence should be addressed.
E-mail: sjdkumar@barc.gov.in
B₂O₃(g) beyond 600°C, and (iii) the volatilization of B₄Cₐ to B,O₅, which occurs at 900°C.¹⁴,¹⁵ Hence, during pyrohydrolysis, only at 900°C B₄Cₐ is being carried over by the steam, which leads to the formation of H₂BO₃. Therefore, when the PH temperature reaches to around 900°C a sudden release of huge amounts of B₄Cₐ occurs, which leads to an incomplete conversion of H₂BO₃ either due to a limited volume of steam in the reaction tube or to a quick escape at the trapping solution. Hence, the present study made an attempt to control the loss of boron by increasing the steam flow and the volume of the trapping solution. Because large-volume distillate collection dilutes the boron concentration, and a sensitive and precise method of boron analysis needed to be employed. In this study it was proposed to employ ion chromatography with conductivity detection.

The present study is an attempt to extract a percentile level boron by pyrohydrolysis extraction with a view to develop a pyrohydrolysis extraction cum ion chromatography method for the determination of boron in paraffin wax borated either with B₄C or H₂BO₃. The study also proposes two more simple methods of separating H₂BO₃ from wax borated with H₂BO₃. The results of the present study were compared with the values obtained from PIGE method. They are in good agreement.

**Experimental**

**Instrumentation**

A quartz pyrohydrolysis apparatus housed in a fume hood was used. The commercial IC system, a Model Dionex DX 500 (Sunnyvale, CA), consisted of a gradient pump (GP 50), a conductivity detector (ED 50A) and an Anion Self Regenerate Suppressor (ASRS-II). A Waters IC Pak-Anion column (4.6 × 50 mm) was used for separation. The injection loop was 50 μL. All separations were carried out with a flow rate of 1 mL/min.

**Reagents**

A standard stock solution of boron was prepared by dissolving boric acid. Working standards were prepared by appropriate dilution of the stock solution. A solution of 0.56 M d-mannitol in 5 mM NaHCO₃ was used as a mobile phase. All of the chemicals used were of 99.99% purity (Merck, Germany), except for D-mannitol (99%). All solutions were prepared in high-purity water obtained from a Milli-Q system (Millipore, Bedford, MA). Nuclear-grade U₃O₈ (DAE, India) was used for mixing with samples.

**Ion chromatography (IC) analysis of boron**

An IC determination of boron in the pyrohydrolysis distillate or alkali extracts was carried out by following a reported method,¹¹ in which an anion-exchange column with a mobile phase of 0.56 M d-mannitol in 5 mM NaHCO₃ (1 mL/min) was used. Suppressed conductivity was used for detection and quantification. Since H₂BO₃ is a weak acid (pKᵥ 9.1),¹⁶ it will be difficult to separate H₂BO₃ as borate ion on an anion-exchange column, and therefore H₂BO₃ is converted into a strong boron-mannitol anion complex.¹⁷⁻¹⁹ A linear calibration plot was constructed for boron over a concentration range of 0.1 to 50 ppm, and the regression coefficient (r²) obtained was 0.9999. The limit of detection (LOD) of the method was 5 ppb of boron (S/N = 3). Samples are appropriately diluted to the linear concentration range, wherever necessary, prior to IC analysis.

**Results and Discussion**

**Pyrohydrolysis of borated wax**

The pyrohydrolysis apparatus employed was an all-quartz system; its details were published elsewhere.²⁰⁻²¹ Previously reported PH procedures could not be followed in the case of borated wax due to the matrix complexity. This includes a sudden flare-up of wax, even at low temperatures, leading to the deposition of soot and oily materials on the reaction tube. This leads to chock-up and difficulty in opening the B₄C matrix, due to its highly refractive nature.²² After the melting of wax, a black residue of B₄C was obtained, which could not be pulverized even after heating at 950°C (the maximum working temperature of this PH system) for more than 2 h. Hence, pyrohydrolysis needed to be carried out with a view to realize (i) a controlled burning of wax so as to eliminate soot deposition and (ii) a complete pulverization of wax containing B₄C in a reasonable time at 950°C. A study that explores the feasibility of pyrolysed liquid samples reports that a controlled evaporation of liquid is possible by mixing it with U₃O₈ powder.²³ Another study reveals that U₃O₈ can be used as an accelerator in pulverizing B₄C for extracting trace chlorine.²⁴ Therefore, in this investigation it was proposed to use U₃O₈ as a covering material so as to reduce the flare up of wax, and also to accelerate the pulverization of B₄C. The efficiency of PH extraction is depends upon the nature of the material, temperature, rate of release of the analyte, carrier gas flow rate, volume of steam or distillate collection rate etc. During PH after the combustion of wax, either B₄C or H₂BO₃ is left for PH, and because of their differences in material property, it is necessary to optimize the pyrohydrolysis conditions separately for paraffin wax borated with B₄C or H₂BO₃.

**Pyrohydrolysis of paraffin wax borated with boric acid**

To realize the controlled combustion of wax for releasing B₄C or H₂BO₃, it is necessary to know the minimum amount of U₃O₈ required. For this purpose, 300 mg of U₃O₈ was mixed with varying amounts of the sample (20 – 200 mg), and subjected to pyrohydrolysis initially at 100 – 150°C for 15 min, and then slowly increased to 950°C and maintained at this temperature for 2 h. It was observed that a sample to U₃O₈ ratio of 1:3 was sufficient to control the slow combustion of wax. In order to avoid any direct contact of wax on the hot surface of the sample boat, a bed of U₃O₈ (~100 mg) was made, and a sample mixture was placed over the bed. Though this arrangement controlled the combustion, for each sample, the temperature of the furnace is required to be reduced to 100 – 150°C after pyrohydrolysis of the previous sample. This takes considerable time for PH extraction. With a view to increase the throughput, a gradient heating procedure was incorporated wherein the furnace at 950°C was placed on a rail. The furnace was kept at pre-decided distances away from the reaction tube. The temperature felt at the reaction tube varied on the distance in which furnace was placed. It was observed that a sudden release of huge B₄C leads to choked PH system; its details were published elsewhere.²⁰⁻²¹ It was observed that a sudden release of huge B₄C leads to choked PH system; its details were published elsewhere.²⁰⁻²¹ However, it was observed that a sudden release of huge B₄C leads to choked PH system; its details were published elsewhere.²⁰⁻²¹ It was observed that a sudden release of huge B₄C leads to choked PH system; its details were published elsewhere.²⁰⁻²¹ It was observed that a sudden release of huge B₄C leads to choked PH system; its details were published elsewhere.²⁰⁻²¹
for effective trapping. However, for safety, 50 mL was considered to be as optimum. The time of pyrohydrolysis is an important factor for ensuring the maximum recovery, and hence it was optimized by carrying out PH at different time durations (Fig. 1 plot-A). The maximum recovery was realized in 60 min (excluding the initial wax combustion). In the absence of an appropriate reference material, it is necessary to ensure the extraction of boron by replicate analyses. In view of this, under the optimized conditions, the reproducibility of extraction was ensured by analyzing six aliquots of paraffin wax borated with H3BO3 (containing 1% of boron). The obtained values were in good agreement (Table 1).

Pyrohydrolysis of paraffin wax borated with boron carbide
Paraffin wax borated with B4C has a different PH behavior due to its refractive nature. A poor recovery of boron was observed while pyrohydrolyzing wax borated with B4C by following the PH procedure that was optimized for wax borated with H3BO3. Moreover, at about 800°C the molten B4C attacks the silica boat and forms silicon carbide, which leads to a breach of the boat. To prevent this damage and with a view to improving the rate of pulverization, the amount of U3O8 was varied. Sample aliquots having 1.2 mg of B4C (0.939 mg of B) in 50 mg of wax were mixed with varying amounts of U3O8 (100 to 1000 mg) and pyrohydrolyzed for 120 min. Figure 2 shows a plot of the mass of U3O8 vs. amount of boron extracted (obtained by multiplying the concentration of boron and the volume of the distillate). It shows that a sample to U3O8 ratio of 1:6 was required to accomplish the maximum extraction of boron. However, it was proposed to take a 1:10 ratio so as to realize trouble-free extraction. An attack on the boat by the molten B4C was prevented by placing the sample on the center of a 100 mg U3O8 bed, and subsequently another 100 mg of U3O8 was placed on the sides of the sample to prevent the flow of molten B4C towards the surface of the boat. The pyrohydrolysis time was optimized, and it was found that unlike wax with boric acid, 90 min pyrohydrolysis is necessary for obtaining the maximum recovery (Fig. 1 plot-B). Six aliquots of a paraffin wax samples with a known amount of B4C were pyrohydrolyzed, and the observed reproducibility of extraction was good (Table 1). Table 2 provides a summary of the pyrohydrolysis conditions optimized separately for wax borated with B4C and B3O3.

Alternate methods for separating boric acid from wax borated with H3BO3
Both B4C and H3BO3 do not form any compound with wax, but are only dispersed in the wax matrix. Unlike B4C, boric acid is a crystalline substance soluble in water, and hence it can be directly dissolved in water or alkaline solutions after its release from the wax. Two simple methods based on the solubility of H3BO3 have been developed exclusively for the wax with H3BO3. They are not applicable to wax borated with

---

**Table 1 Analytical reproducibility of the PH-IC method for wax borated with boric acid and boron carbide**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Boron, % obtaineda</th>
<th>Sample No.</th>
<th>Boron, % obtaineda</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAX-6/1</td>
<td>0.95 ± 0.05</td>
<td>Wax-B4C/1</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>WAX-6/2</td>
<td>0.92 ± 0.05</td>
<td>Wax-B4C/2</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>WAX-6/3</td>
<td>0.95 ± 0.05</td>
<td>Wax-B4C/3</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>WAX-6/4</td>
<td>0.92 ± 0.05</td>
<td>Wax-B4C/4</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>WAX-6/5</td>
<td>0.90 ± 0.05</td>
<td>Wax-B4C/5</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>WAX-6/6</td>
<td>0.93 ± 0.05</td>
<td>Wax-B4C/6</td>
<td>1.9 ± 0.1</td>
</tr>
</tbody>
</table>

Mean: 0.92 ± 0.05 (5.4%)  
Expected: 1.0%  
Mean: 1.82 ± 0.08 (4 %)  
Expected : 1.8%

a. mean of three IC analysis.

**Table 2 Optimized pyrohydrolysis conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wax with B4C</th>
<th>Wax with H3BO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>950 ± 25°C</td>
<td>950 ± 25°C</td>
</tr>
<tr>
<td>Sample Mass</td>
<td>~300 mg&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~120 mg&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Covering material U3O8</td>
<td>200 mg</td>
<td>100 mg</td>
</tr>
<tr>
<td>Time of PH</td>
<td>90 min</td>
<td>60 min</td>
</tr>
<tr>
<td>Distillate collection rate</td>
<td>0.5 mL/min</td>
<td>0.5 mL/min</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>moist O2</td>
<td>moist O2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Total mass of the sample where wax to U3O8 ratio is 1:10, <sup>b</sup> Total mass of the sample where wax to U3O8 ratio is 1:3.

---

Fig. 1 Plots of pyrohydrolysis time vs. Boron, % extraction. Plot-A obtained for paraffin wax containing 5.7% boric acid (boron, 1%) and Plot-B obtained for paraffin wax with 2.2 % B4C (boron, 1.8 %).

Fig. 2 Effect of the U3O8 mass on the pyrohydrolysis extraction of boron from paraffin wax containing B4C.

---

**Fig. 1** Plots of pyrohydrolysis time vs. Boron, % extraction. Plot-A obtained for paraffin wax containing 5.7% boric acid (boron, 1%) and Plot-B obtained for paraffin wax with 2.2 % B4C (boron, 1.8 %).

**Fig. 2** Effect of the U3O8 mass on the pyrohydrolysis extraction of boron from paraffin wax containing B4C.
Table 3 Results of alkali-extraction methods

<table>
<thead>
<tr>
<th>NaOH/ mM</th>
<th>Alkali extraction (Boron, %)</th>
<th>Melting method (Boron, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaOH</td>
<td>NaOH + 0.6 M</td>
</tr>
<tr>
<td>0</td>
<td>0.5 ± 0.1</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>1.8 ± 0.2</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>1.9 ± 0.2</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>15</td>
<td>2.0 ± 0.2</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>20</td>
<td>2.1 ± 0.2</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>30</td>
<td>2.1 ± 0.2</td>
<td>2.6 ± 0.3</td>
</tr>
</tbody>
</table>

All values are mean of 3 replicate analysis.

Table 4 Typical results obtained for samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Boron, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PH&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Wax-1</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>Wax-2</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>Wax-3</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>Wax-4</td>
<td>0.1 ± 0.05</td>
</tr>
<tr>
<td>Wax-5</td>
<td>1.1 ± 0.05</td>
</tr>
<tr>
<td>Wax-6</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Wax-7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>Wax-8&lt;sup&gt;e&lt;/sup&gt;</td>
<td>3.1 ± 0.2</td>
</tr>
</tbody>
</table>

a. PH: Pyrohydrolysis extraction, b. AE: Alkali extraction, c. MM: Melting wax of method, d. PIGE: Proton induced gamma ray emission method, e. Both samples are wax with B<sub>4</sub>C; analyzed by PH and PIGE methods.

B.C.

Alkali extraction of H<sub>3</sub>BO<sub>3</sub>

Paraffin wax borated with H<sub>3</sub>BO<sub>3</sub> was grated into tiny pieces (~30 mg of sample) and taken into a leak-proof equilibration tube containing 50 mL of 10 mM NaOH. The mixture was filtered after shaking for 2 h, and the filtrate was analyzed for B content by IC. The effect of the concentration of NaOH was studied by varying its concentration between 5 and 50 mM. Though the concentration of NaOH above 20 mM showed around 95% extraction of H<sub>3</sub>BO<sub>3</sub>, the procedure showed poor reproducibility, which did not improve by increasing the volume of NaOH. Hence, with a view to improving the reproducibility in the extraction, 0.6 M d-mannitol was added along with 20 mM NaOH. Table 3 gives the % of extraction of boron with varying concentrations of NaOH and d-mannitol. It also reveals that with 20 mM NaOH and 0.6 M d-mannitol provided the maximum extraction with an hour of shaking.

Melting wax in NaOH solution

Extraction of H<sub>3</sub>BO<sub>3</sub> in the above method is based on mincing wax pieces in a NaOH solution. Though this method showed good extraction and reproducibility, it is time consuming. In this method the paraffin wax was melted (Bp 56°C) in a hot alkali solution. For this, the weighed wax sample was taken in a quartz beaker having 50 mL of 20 mM NaOH and heated to 80°C. At this temperature the wax melted and released the H<sub>3</sub>BO<sub>3</sub> into the solution, which was filtered through 0.45 μm filter paper after stirring for 10 min. This method showed a complete recovery of H<sub>3</sub>BO<sub>3</sub> and did not require any addition of d-mannitol because the melting of wax released all of the boric acid into the medium, unlike in the previous case. Table 3 lists out the results obtained by this method.

Real sample analysis

Paraffin wax samples borated with H<sub>3</sub>BO<sub>3</sub> were analyzed by all of the three proposed methods, whereas wax with B<sub>4</sub>C was analyzed by a pyrohydrolysis method alone. Typical results are listed in Table 4. A chromatogram overlay of a standard and sample is shown in Fig. 3.

Conclusions

Pyrohydrolysis extraction of boron as boric acid from paraffin wax borated either with H<sub>3</sub>BO<sub>3</sub> or B<sub>4</sub>C was established for the determination of boron. For the first time pyrohydrolysis was successfully applied in extracting boron at the percentile level. In addition, two simple extraction procedures based on the alkali extraction of boric acid were developed for wax borated with H<sub>3</sub>BO<sub>3</sub>, and between the two methods the wax melting method is simple, rapid and highly reliable. The pyrohydrolysis and wax melting methods are routinely adopted for the determination of boron in wax borated with B<sub>4</sub>C and wax with H<sub>3</sub>BO<sub>3</sub>, respectively.

Acknowledgements

The authors thank Mr. M. K. Das, Mr. Ashwani kumar and Mr. D. B. Paranjape for their kind support.

References

1. S. Barth, Geol. Rundsch., 1993, 82, 640.
8. A. Farhat, F. Ahmad, and H. Arafat, Desalination, 2013, 310, 9.
25. Private communication, Ashwani Kumar (Bhabha Atomic Research Centre, Mumbai, India), Nov., 2014.