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**Determination of isotopic ratio of boron in boric acid solutions by ATR-FTIR spectroscopy**

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## **Abstract**

Due to the low atomic mass of boron, its different isotopes (B-10 and B-11) leads to a measurable impact on vibrational spectra. Indeed, a shift in the asymmetric stretching of the dissolved species has been found using attenuated total reflectance infrared spectroscopy, and those of acid species is higher than those of the borate ion ( $41\text{ cm}^{-1}$  vs.  $20\text{ cm}^{-1}$ , respectively). A calibration from pure B-10 to pure B-11 boric acid has been performed, leading to an accuracy higher than 0.5% on the B-10 percentage of 0.1 M solution of mixtures of the two isotopes.

## **Article Highlights**

- The isotope of boron has an impact on the infrared spectra of solutions
- A difference of  $14\text{ cm}^{-1}$  has been found using attenuated total reflectance infrared spectroscopy
- The isotopic ratio of boron in boric acid can be measured after a calibration step

## **Keywords**

Boron isotopes ; Solution analysis by infrared spectroscopy ; Enriched boric acid

## **Introduction**

Measuring the isotopic ratio of boron, which has two stable isotopes, B-10 and B-11, has an interest in several domains, whose geochemistry and nuclear industry. In geological and environmental sciences, the isotopic composition of minerals and waters is related to the fractionation mechanisms. The isotopic variation in nature is ca. from -30 ‰ to +60 ‰ in  $\delta^{11}\text{B}$  (i.e. a few percent), so very accurate analysis methods are required in this field. Mass spectrometry family methods have been applied for decades. The main advantage is their accuracy, but they remain burdensome with complex protocols [1], [2]. In nuclear industry, boric acid is used to absorb neutron, due to the high cross-section absorption of B-10. Thus, it can be used in radiation shielding [3]. Moreover, the primary circuit of pressurized water reactor (PWR) can contain more than 400 m<sup>3</sup> of a solution up to 4 g/L of boron. This element is added as boric acid, and should be neutralized by the addition of bases, as LiOH or KOH to reduce the corrosion rate of the cooling circuits. The use of enriched boric acid (EBA) (i.e. with a higher fraction of B-10 than in natural boron, 19.9 %) would allow to use lower concentrated solutions, with a benefit for the pH control of the cooling solution. Thus, German Konvoi PWR operated with EBA at 28% B-10 enrichment [4], while in the new generation PWRs as EPR, the enrichment reaches 37% [5]. Due to the absorption of neutrons by B-10 ( $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$  reaction), its concentration decreases and a depletion of natural boron in B-10 could reach 6.83% in a typical cycle [6], what would correspond to a fraction of B-10 decreasing from 19.8% to 18.8%. In this field, the measurement of isotopic composition of boric acid with an accuracy not as high as for the geochemistry studies, but with simpler methods, would be useful.

Analytical methods to determine isotopic ratio are mostly mass spectrometry and nuclear analytical techniques (as Particle Induced Gamma ray Emission spectroscopy [7], Charged Particle Activation Analysis [8] or Neutron Activation Analysis [9]). The use of simplest instruments, as ICP-OES or AAS, could be considered since a significant isotopic shift in atomic emission or absorption lines has been shown. Two chemical reasons can explain an effect of isotopy on emission or absorption energy: either elements are light enough and the mass difference of their isotopes is relatively large (which is the case for boron) or elements are heavy but with a difference in nuclear charge distribution of the isotopes (for example mercury) [10]. Thus, ICP-OES equipped with a high spectral resolution detector can be used to determine the B-10 content with a good accuracy ( $<0.001\%$ ) [10]. More recently, emission spectroscopy with a double laser-induced plasma was tested, leading to an accuracy around one percent [11]. Atomic absorption spectrometry has been also tested, leading to a measurement of B-10 content with an error of about 1% [12].

For the same reason (large mass difference between B-10 and B-11), the energy of vibration modes, at the basis of infrared spectroscopy, is significantly dependent on the isotope. Thus, the asymmetric stretching of gaseous  $\text{BF}_3$  differs by ca.  $100\text{ cm}^{-1}$  with a lower wavenumber for  $^{11}\text{BF}_3$  [13], as expected from the “ball and spring” model. The substitution of B-10 by B-11 in numerous crystalline inorganic borates has been followed by infrared spectroscopy and the impact on the different vibration modes has been detailed. Borate can form either planar triangle or tetrahedral unit but for both geometries, it is expected that symmetric stretching is not shifted by substitution, while for asymmetric stretching  $\nu_3(\text{B-10}) / \nu_3(\text{B-11}) \approx 1.04$ . The interpretation of experimental spectra recorded for crystalline borates remains difficult and depends on the compound, since environment of borate is diverse in these conditions. On the contrary, this calculation should be applicable to the solution species. Spectra of  $\text{H}_3\text{BO}_3$  and  $\text{B}(\text{OH})_4^-$  recorded by attenuated total reflectance (ATR) IR spectroscopy can be found in

several works [14], [15]. Asymmetric stretching is located at  $1410\text{ cm}^{-1}$  for trigonal geometry, and  $945\text{ cm}^{-1}$  for tetrahedral geometry. The application of the factor 1.04 would lead to a shift of around  $40\text{ cm}^{-1}$ , which is enough to have a good separation between the peaks coming from the two isotopes.

In this work, results of ATR-IR spectroscopy on solutions with different isotopic ratios are presented. The possibility to determine B-10 content has been evaluated and ways of optimization are given.

## **Experimental**

Boric-11 acid and boric-10 acid were purchased to Cambridge Isotope Laboratories, Inc. The isotopic enrichment measured by ICP-MS (data from the supplier) was  $>99.95\%$  for B-11, and  $99\%$  for B-10.

The ATR-IR spectra were collected in the range  $4000\text{--}650\text{ cm}^{-1}$  with a dry-air-purged Thermo Scientific Nicolet IS50 FT-IR equipped with an MCT-B detector. Spectral resolution was  $4\text{ cm}^{-1}$  and spectra were averaged from 256 scans. The crystal used was a single reflection diamond/ZnSe crystal with an incidence angle of  $45^\circ\text{C}$  (Smart PIKE). An automatic baseline correction between  $900$  and  $1800\text{ cm}^{-1}$  has been applied. The solutions have been analyzed using a drop of  $25\mu\text{L}$  deposited on the top of the ATR element, following the routine procedure.

The procedure has been repeated 3 times, and the spectrum used for calibration was the average of the three spectra. The ATR-IR spectra of solutions have not been systematically corrected using the advanced ATR correction algorithm [16] developed by Thermo Fisher Scientific in OMNIC software, since in the purpose to develop a calibration method for isotopic measurement, the use of the raw spectra has been considered as more straightforward.

The determination of the peak locations has been performed by smoothing/derivative tools in OMNIC software or OriginLab.

## **Results and discussion**

ATR-IR spectra of boric acid and borate solutions from pure B-10 or B-11 chemicals are presented in Fig. 1. Boric acid (Fig. 1A) is characterized by two bands around  $1420\text{ cm}^{-1}$  and  $1150\text{ cm}^{-1}$ . According to literature where spectra of natural boron solutions have been interpreted [14], the peak at the highest wavenumber corresponds to the asymmetric stretching  $\nu_a(\text{BO})$ . In  $\text{H}_3\text{BO}_3$ , the  $D_{3h}$  symmetry is expected to lead to a doubly degenerated band. However, a careful look at this band in this figure or in published results (Fig. 4 in [14] and Fig. 3 in [17]) shows an asymmetry. From a double derivative analysis, a split of  $25\text{ cm}^{-1}$  or  $29\text{ cm}^{-1}$  was found for B-11 and B-10, respectively. Thus, it appears that the  $\text{H}_3\text{BO}_3$  molecule is slightly deformed. The wide band around  $1150\text{ cm}^{-1}$  is assigned to BOH deformation. This latter band is found also in the spectra of borate anion (Fig. 1B), since this chemical group is common to both species. The other characteristic band of borate anion is located around  $950\text{ cm}^{-1}$  and corresponds to the asymmetric stretching. The addition of a hydroxyl group to  $\text{B}(\text{OH})_3^0$  molecule leads to a red shift of this mode by almost  $200\text{ cm}^{-1}$ . The symmetric stretching expected at  $745\text{ cm}^{-1}$  is not visible in the IR spectra, as expected for a  $T_d$  symmetry, but has been shown in Raman spectra (Table 1). The comparison of the spectra for the two isotopes shows a clear difference for  $\nu_a(\text{BO})$  of the two species. A red shift of  $41\text{ cm}^{-1}$  is obtained for the heavier isotope in  $\text{B}(\text{OH})_3^0$ , in agreement with the value based on ball and spring model. A lower red shift ( $20\text{ cm}^{-1}$ ) is obtained for  $\text{B}(\text{OH})_4^-$ . In purpose to use infrared spectroscopy to determine the isotopic ratio, the analysis of boric acid has been chosen since an important shift of  $\nu_a(\text{BO})$  has been shown.

Table 1. Stretching vibrations of boric acid/borate species.

Species	Vibration mode	Wavenumbers (cm <sup>-1</sup> )		
		<sup>10</sup> B	<sup>11</sup> B	Difference
B(OH) <sub>3</sub> <sup>0</sup>	$\nu_s(\text{BO})$	877 <sup>a</sup>	877 <sup>a</sup>	0
	$\nu_a(\text{BO})$	1446	1405	41
B(OH) <sub>4</sub> <sup>-</sup>	$\nu_s(\text{BO})$	745 <sup>a</sup>	745 <sup>a</sup>	0
	$\nu_a(\text{BO})$	968	948	20

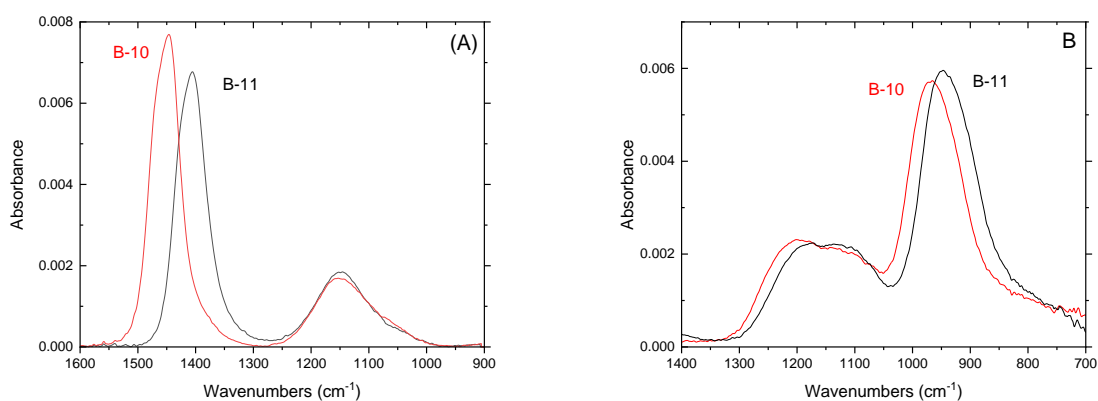
<sup>a</sup> reference [18]

Fig. 1. Spectra of isotopes B-10 and B-11 of 0.1 M boric acid and borate at (A) pH 5.5 and (B) pH 11.5, respectively.

In Figure 2, spectra of B(OH)<sub>3</sub> solutions with different isotopic ratios are presented. An isosbestic point at 1429 cm<sup>-1</sup> is clearly identified, as expected for a spectrum formed by a pair of compounds. From these spectra, a calibration protocol to determine the isotopic ratio of an unknown sample should be established. Since the maximal intensity for  $\nu_a(\text{BO})$  is known for B-10 and B-11 (respectively 1446 cm<sup>-1</sup> and 1405 cm<sup>-1</sup>), measuring the ratio of the intensity at



these two wavenumbers should be a quick and easy way to calculate the isotopic ratio (without needing to know the total concentration). Thus, we should determine the calibration equation between the intensity ratio and the isotopic ratio.

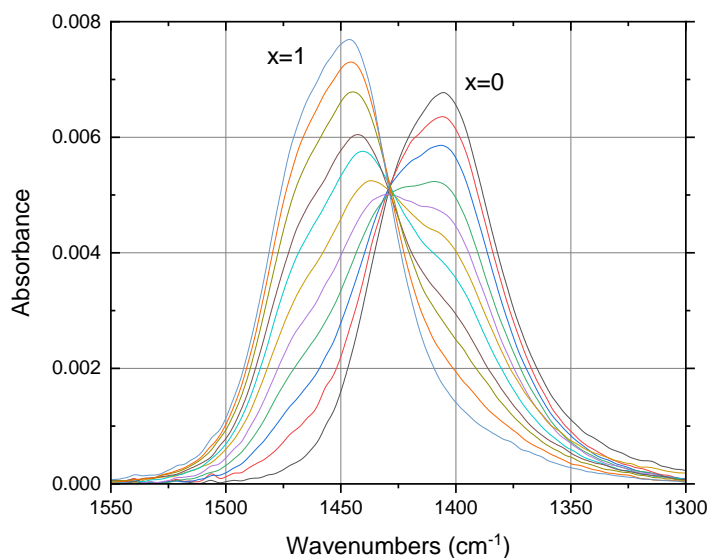


Fig 2. Spectra of boric acid for different B-10 isotopic ratios from 0 to 1 by increment of 0.1.

For a pure solution of B-10 measured using an ATR system, Beer-Lambert law becomes for a given wavenumber  $\nu_1$ :

$$I(\nu_1) = \varepsilon_{B10}(\nu_1)C_{B10}de(\nu_1) \quad (1)$$

With  $I$ , the intensity of the spectrum,  $\varepsilon_{B10}$ , the molar absorption coefficient for B-10,  $C$ , the molar concentration, and  $de$ , the equivalent path length (assumed to not depend on the isotopic ratio of the solution).

For a mixture of both isotopes:

$$I(\nu_1) = \varepsilon_{B10}(\nu_1)C_{B10}de(\nu_1) + \varepsilon_{B11}(\nu_1)C_{B11}de(\nu_1) \quad (2)$$

For a given spectra of the mixture, it is possible to calculate the ratio of the absorbance at two different wavenumbers  $\nu_1$  and  $\nu_2$ :

$$\frac{I(\nu_1)}{I(\nu_2)} = \frac{\varepsilon_{B10}(\nu_1)C_{B10}de(\nu_1) + \varepsilon_{B11}(\nu_1)C_{B11}de(\nu_1)}{\varepsilon_{B10}(\nu_2)C_{B10}de(\nu_2) + \varepsilon_{B11}(\nu_2)C_{B11}de(\nu_2)} \quad (3)$$

We can define  $x$ , the molar fraction of B-10 in the mixture as  $x = \frac{C_{B10}}{C_{B11} + C_{B10}}$

So Eq. (3) becomes:

$$\frac{I(\nu_1)}{I(\nu_2)} = \frac{\varepsilon_{B10}(\nu_1)xde(\nu_1) + \varepsilon_{B11}(\nu_1)(1-x)de(\nu_1)}{\varepsilon_{B10}(\nu_2)xde(\nu_2) + \varepsilon_{B11}(\nu_2)(1-x)de(\nu_2)} \quad (4)$$

To use the spectra to determine the isotopic composition, we need a relation between the ratio of the absorbance at two different wavenumbers and  $x$ . After development, we get the following relation:

$$\frac{I(\nu_1)}{I(\nu_2)} = \frac{r(\nu_2)I_{r,B10}x + I_{r,B11}(1-x)}{r(\nu_2)x + (1-x)} \quad (5)$$

With

$$r(\nu_2) = \frac{\varepsilon_{B10}(\nu_2)}{\varepsilon_{B11}(\nu_2)} \quad (6)$$

And

$$I_{r,B10} = \left( \frac{I(\nu_1)}{I(\nu_2)} \right)_{x=1} \quad (7)$$

$$I_{r,B11} = \left( \frac{I(\nu_1)}{I(\nu_2)} \right)_{x=0} \quad (8)$$

Moreover, from eq. (1), for pure solutions with the same concentrations,  $r(\nu_2)$  can be written as:

$$r(\nu_2) = \frac{(I(\nu_2))_{x=1}}{(I(\nu_2))_{x=0}} \quad (9)$$

Thus, from the spectra of pure B-10 and B-11 solutions with the same concentrations, the parameters for eq. (5) can be calculated (Table 1).

In Figure 3, the two ratios  $I(1446) / I(1405)$  and  $I(1405) / I(1446)$  have been plotted versus the isotopic ratio, with a good consistency between experimental values and equation (5). The isotope purity of boric-10 acid was only 99% ( $x = 0.99$ ), but its spectra has been used as a pure B-10 solution in the formula (7) with a possible impact on the calculated curves.

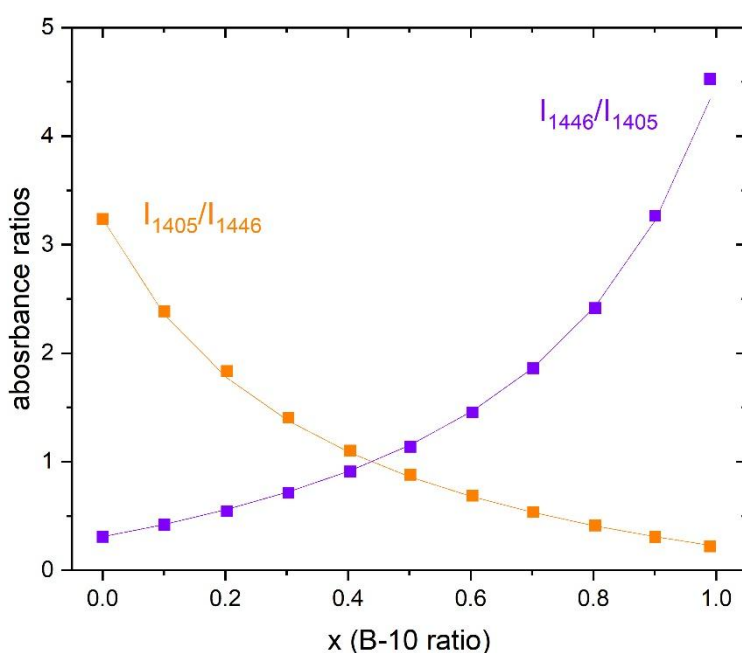


Fig. 3. Ratios of the absorbance spectra intensities at  $1405$  and  $1446\text{ cm}^{-1}$  as a function of B-10 fraction: experimental data (squares) and results (line) from theoretical equation (5) using parameters from spectra of pure isotopes.

To be able to use these data to determine the isotopic ratio of an unknown sample, the equation (5) can be rewritten as follows:

$$x = \frac{I_{r,B11} \frac{I(v_1)}{I(v_2)}}{\frac{I(v_1)}{I(v_2)}(r(v_2)-1) - r(v_2)I_{r,B10} + I_{r,B11}} \quad (10)$$

It can be noted that the spectra of pure isotopic species would be required to apply this approach, what can be a limitation. To extend the use of this method, it is possible to fit the three parameters in the equation (10) using data of the calibration curve, either for a full range from pure isotopes, or for a limited range. In the first case,  $I_{r,B11}$ ,  $r(v_2)$  and  $I_{r,B10}$  have been determined by the fit of the experimental values (Table 2). A slight difference appears, with a positive effect on the accuracy, as this will be shown later. To simulate the calibration on a restricted range of isotopic fraction (but with the same concentrations step), only the data between 10% and 80% have been arbitrary chosen. In this case, using the spectra of pure isotopes to calculate the parameters in equation (5) is no longer possible, so the approach by fit is mandatory. The parameters obtained in this case (Table 2) are close to the previous values, indicating that the values of the calibration curve follow closely the theoretical equation.

Table 2. Calibration parameters obtained from (1) spectra of pure isotopes samples, (2) fit of the whole calibration curve or (3) fit of an arbitrary restricted calibration range.

Parameter	$I_{r,B11}$	$r(v_2)$	$I_{r,B10}$
Method (1)	3.24	3.70	0.222
Method (2)	3.26	3.62	0.215
Restricted range (3)	3.28	3.68	0.220

Once the parameters have been obtained, they have been used to calculate the boron isotopy in a reverse way. In the Table 3 the values calculated using the three methods described above are presented.

Table 3. Experimental and calculated B-10 percentages, based on the use of parameters determined by (1) solutions of pure isotopes, (2) fit of the whole calibration curve and (3) fit of an arbitrary restricted calibration range, where some data have been excluded (excl.).

Exp.	0	10	20	30	40	50	60	70	80	90	99
(1)	0.0	9.6	19.0	29.5	39.6	49.2	59.6	69.8	79.9	90.4	100.1
(2)	0.2	10.0	19.5	30.1	40.2	49.7	60.0	70.0	79.8	90.0	99.3
(3)	excl.	10.0	19.5	30.0	40.1	49.6	60.0	70.1	80.0	excl.	excl.

To illustrate the accuracy, the absolute error is plotted on Figure 4. The first approach is based on only two experimental spectra (corresponding to the pure isotopes), and the uncertainty on these measurements may be responsible to the poor accuracy, with a difference which reaches about -1% between experimental value and calculated one (the average of absolute values of difference for each point is  $\pm 0.48\%$ ). The fit of the whole data set (11 spectra) has a visible impact, with a maximum difference of -0.5% (the average decreases to  $\pm 0.16\%$ ). Using only a part of the experimental data decrease the accuracy, with the same maximum, but an average increasing at  $\pm 0.18\%$ .

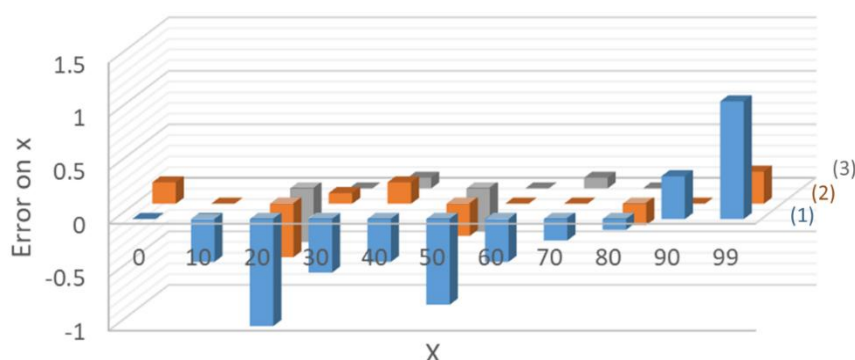


Fig. 4. Difference between the calculated B-10 percentage and the experimental one from the three methods used to determine the calibration parameters (no values are represented for 0, 90 and 100 for the third method).

These results show that plotting a calibration curve is more accurate than using the theoretical curve calibrated on pure isotopic solutions and should be preferred if accuracy is the key element. On the contrary, using the method based on the spectra of the pure isotope is simpler but can lead to an error around one percent on the isotopic composition.

## **Conclusions**

These results confirmed that ATR-IR spectroscopy of solutions is a method able to determine the isotopic ratio of dissolved boron. Two limits of this method have been shown. The first one is the accuracy of the result obtained, to be compared to the accuracy needed depending on the application. This aspect would need some specific works, out of the scope of this study that aims to get a proof-of-concept of the ATR-IR spectroscopic approach. It depends on the calibration step, the statistical treatments, the sampling method (an online measurement is possible and can improve the background treatment) and the instrument. Thus, better performances than those presented in these first experiments could be expected in an operational system, by optimizing the calibration domain around the target isotopic ratio, or by increasing the boric acid concentration (using a first pre-concentration step for example).

The second limit is the minimum concentration of boric acid that is required to be able to determine the isotopic ratio. In a classical ATR configuration, the available analytic range will remain above several millimolar, and the accurate measurement of the ratio of intensities would be difficult below 0.01 M. Recording more scans or using multiple-reflection ATR element would only slightly improve the signal/noise ratio. To reduce this limit, a possibility would be to modify the ATR element surface to concentrate boric species inside the volume probed by the evanescent wave. Thus, the analyte can be concentrated in a layer deposited on the ATR element surface if the material presents a high affinity toward it. This approach has

been successful in the analysis of organic molecules by IR chemical sensors based on ATR elements coated with a hydrophobic polymer. ATR elements as LDPE-coated silver halide [19] or fluorocarbon-coated ZnSe [20] were used to quantify chlorinated hydrocarbons in gas phase or in aqueous solution, respectively. A coating consisting in a solid with a high affinity towards boric acid or borate could be tested, with the possible difficulty of the interference with other adsorbed species, especially anionic ones (for example carbonate which are ubiquitous in water and have a high affinity for several solids).

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