



# On the purity assessment of solid sodium borohydride

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## ABSTRACT

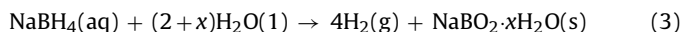
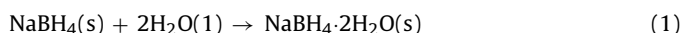
Since sodium borohydride has become extensively used as chemical hydrogen storage material in fuel cells, many techniques have been proposed to assess the purity of this substance. However, all of them are developed in aqueous media, where the reagent is unstable. In addition, its hygroscopic nature was difficult in any attempt to make precise quantifications. The present work compares three different methods, namely, voltammetric, titrimetric, and Fourier transformed infrared spectroscopy (FTIR) in order to assess the purity of sodium borohydride, using an expired and a new sodium borohydride samples as references. Our results show that only the FTIR measurements provide a simple and semi-quantitative means to assess the purity of sodium borohydride due to the fact that it is the only one that measures the sample in the solid state. A comparison between the experimental data and theoretical calculation reveals the identification of the absorption bands at  $1437\text{ cm}^{-1}$  of sodium metaborate and  $2291\text{ cm}^{-1}$  of sodium borohydride which represent a good fingerprint for the qualitative assessment of the sample quality.

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## 1. Introduction

Sodium borohydride is being extensively studied for chemical hydrogen storage and as a fuel in direct borohydride fuel cells (DBFC) [1,2]. Due to the high requirements of water in these cells, the use of solid sodium borohydride is a suitable option [3], and ideally, future DBFC might be stored and handled in a dry form. However, the instability of sodium borohydride in humid ambient constitutes a problem, and the formation of  $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$  as a by-product retards water accessibility to  $\text{NaBH}_4$  particles, and lowers the efficiency in  $\text{H}_2$  production. In this context, the quality control of the purity state of sodium borohydride is on demand.

Sodium borohydride powder is highly hygroscopic both at ambient and steam temperatures [4]. Anhydrous  $\text{NaBH}_4$  progressively reacts with water to yield sodium metaborate,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , according to the following reactions [4–7]:



being the total reaction the sum of Eqs. (1)–(3):



where the number of water molecules,  $x$ , can vary depending on the temperature and the quantity of water present in the reacting system.

Water adsorption begins at 20% relative humidity at ambient temperature [8]. Under these conditions, isothermic microcalorimetric measurements display an exothermic peak, corresponding to the phase transformation from the anhydrous to the di-hydrate form (Eq. (1)). Above this level of water adsorption, the deliquescence process takes place (Eq. (2)), in which solid sodium borohydride dissolves in sorbed water [9]. The process ends with the full hydration of  $\text{NaBH}_4$ , yielding sodium metaborate and gaseous hydrogen (Eq. (3)). *Ab initio* molecular dynamics near ambient temperature indicates that sorbed water penetrates into the (001) surface of  $\text{NaBH}_4$  on a picoseconds time-scale [4]. This indicates that the deliquescence process constitutes the intermediate step towards the formation of sodium metaborate as the final product. In this regard, the chemical transformations produced due to the sorption of ambient humidity are irreversible, and therefore  $\text{NaBH}_4$  is highly unstable towards hydrolysis, even under appropriate storage conditions. Depending on the humidity conditions, the whole process is observed in Eq. (4) or some intermediate degree of deterioration of the reagent can be seen in Eqs. (1)–(3).

Several analytical methods provide simple ways to monitor borohydride concentration in solution, including titrimetry with iodate or hypochlorite [10,11], open circuit potential measurements [12,13] and cyclic voltammetry [14]. All of these methods

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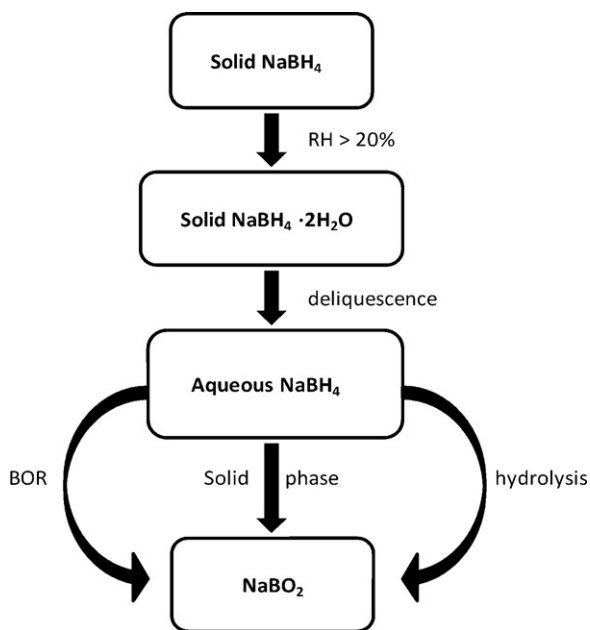
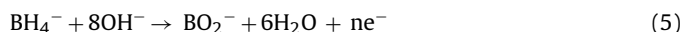


Fig. 1. Processes involving hydration of solid sodium borohydride.

follow the borohydride oxidation reaction (BOR), which under strong alkaline conditions ( $\text{pH} > 12$ ) is:



Such alkaline condition slows down the competitive reactions of hydrolysis, which is strongly dependant on the electrode material [12]. Nevertheless the total number of exchanged electrons ( $n$ ) reported for the BOR at high pH are generally lower than the expected value of 8 [13,15,16], indicating that the hydrolysis reaction cannot be completely disregarded. Moreover, it has been claimed that the presence of metaborate in the solution affects the voltammetric profile of the BOR [17].

As all the reported analytical methods described herein are carried out in aqueous media, the real state of solid sodium borohydride remains obscure, and none of them would be adequate for quality control purposes (Fig. 1). In this context, the need of a rapid tool to control the purity and storage conditions of sodium borohydride in view of its eventual future industrial use is desirable. In this work, we will show that Fourier transformed infrared (FTIR) measurements provide a simple semi-quantitative means to assess  $\text{NaBH}_4$  purity. A comparison between well-established techniques provides the necessary background for a full discussion on the real possibility of assessing the purity of sodium borohydride.

## 2. Materials and methods

Solid sodium borohydride,  $\text{NaBH}_4$ , CAS Number: 16940-66-2, was acquired from Aldrich (Product Code 45,288-2). According to the Lot analysis (LOT STBB1392), it is 98.8% pure, contained 0.52%  $\text{MgCO}_3$  added as anti-caking agent, and the expiration date is March 2012. Other chemicals were, at minimum, reagent quality: sodium metaborate,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O} > 99\%$ , from Aldrich; spectroscopic grade potassium bromide, KBr, from Pike Technologies; NaOH, 97%, from Anedra; sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , 99.5%, from Biopack; potassium iodide, KI  $> 99.5\%$ , from R. Benzo; potassium iodate,  $\text{KIO}_3$ , 98%, from Aldrich. Water-sensitive reagents were stored at ambient temperature in a closed chamber at 20% RH maintained with concentrated sulfuric acid. Borohydride samples were dried in a conventional oven at  $80^\circ\text{C}$  during 24 h. All solutions were prepared

in MilliQ water. An expired sample of sodium borohydride (from Aldrich) was used for comparison.

Cyclic voltammetric experiments were performed using a conventional three-electrode arrangement composed of a BAS gold disc working electrode (0.3 cm diameter,  $0.071\text{ cm}^2$  geometric area), a graphite carbon lead as counter electrode, and a Schott saturated calomel reference electrode (SCE,  $E = 0.244\text{ V-SHE}$  at  $20^\circ\text{C}$ ). The gold electrode was polished with  $0.05\ \mu\text{m}$  alumina slurry, followed by ultrasonication in ultrapure water, and finally rinsing with copious amounts of ultrapure water. The supporting electrolyte was  $2\text{ mol L}^{-1}$  NaOH, and the borohydride solutions in the supporting electrolyte were prepared immediately before the measurements at concentrations between  $0.5 \times 10^{-3}$  and  $10 \times 10^{-3}\text{ mol L}^{-1}$ . All solutions were purged from oxygen by bubbling ultrapure nitrogen, and a nitrogen atmosphere was maintained over the solution during measurements. A Voltalab PGZ 301 computer-controlled potentiostat (Radiometer, Switzerland) was employed for total control of the experiments and data acquisition. Voltammograms were obtained by sweeping the working electrode potential from  $-0.90\text{ V}$  to  $0\text{ V}$  at a scan rate of  $0.1\text{ V s}^{-1}$  in quiescent solutions.

Iodate titrimetry was conducted based on a reported technique [11] on 25–35 mg sample of dried sodium borohydride, which was added to a previously mixed solution containing 25 mL of  $0.5\text{ mol L}^{-1}$  NaOH and a standardized  $\text{KIO}_3$  solution ca.  $0.04\text{ mol L}^{-1}$ , and swirled for 30 s. This order in the reagent addition ensures minimal time exposure of sodium borohydride to the aqueous solution, minimizing hydrolysis reaction.

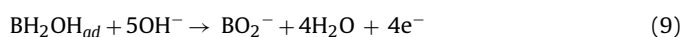
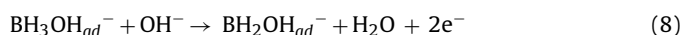
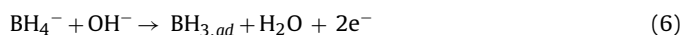
FTIR spectra in the range  $400\text{--}4000\text{ cm}^{-1}$  were obtained at room temperature employing a Shimadzu infrared spectrometer model IR-Prestige 21, averaging 10 scans at a nominal resolution of  $4\text{ cm}^{-1}$  and Happ–Genzel apodization. Dried samples were thoroughly mixed with KBr in an agate mortar, and 13 mm-discs were prepared in a Pike CrushIR at a pressure of 10 ton. For the design of the calibration curve, dried samples of  $\text{NaBH}_4$  and  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  were accurately weighed and mixed with ca. 0.50 g KBr. The absorbance of the vibrational bands related to each compound was measured for the analytical studies.

Geometry optimization calculations were performed *in vacuo* using density functional theory (DFT)/B3LYP with the basis set 6-311++G (2df,2p) and Møller–Plesset perturbation theory at second order (MP2) with a basis set 6-311++G\*\*. In both cases the starting point for the calculations was the molecule taken from the experimental synchrotron data obtained from Fachinformationszentrum Karlsruhe (76344 Eggenstein–Leopoldshafen, Germany, depository number CSD-419045) [18]. All calculations were performed with SPARTAN 08 software, and the unscaled calculated IR spectra were compared with the experimental results.

## 3. Results and discussion

### 3.1. Voltammetric determination of sodium borohydride

The BOR is a complex process involving, theoretically, a total exchange of 8 electrons. Recent *in situ* FTIR study of the BOR [19] agrees with the following mechanism:



According to the theory for an irreversible process [20], the current density ( $j_p$ ) for the BOR varies linearly with the bulk concentration of sodium borohydride,  $C_{BH_4}^*$ :

$$j_p = 2.99 \times 10^5 \left[ (1 - \alpha) n_a D_{BH_4^-} \nu \right]^{1/2} n C_{BH_4}^* \quad (10)$$

In order to calculate the theoretical value for the slope of Eq. (10), we employed data from Santos and Sequeira [21] closest to our experimental conditions: charge transfer coefficient for the oxidation step,  $\alpha = 0.84$ ; total number of exchanged electrons,  $n = 7.6$ , and diffusion coefficient of borohydride anion  $D_{BH_4^-} = 2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

In addition, the number of electrons involved in the rate determining step,  $n_a = 2$ , can be deduced from the mechanism depicted in Eqs. (6)–(9) [19]. At a potential scan rate  $\nu = 0.10 \text{ V s}^{-1}$ , the value for the slope is  $1.99 \text{ A L mol}^{-1}$ . While the theoretical equation fits quite well with our experimental data (Fig. 4, dashed line), the polynomial equation of second order  $j_p = 2.3479 C_{BH_4}^* - 0.03416 (C_{BH_4}^*)^2$  represents a better fit ( $r^2 = 0.9994$ ) (Fig. 4, full line). Hence, the complexity of the BOR process affects the experimental determination of confident values for the current density, and the linearity predicted by Eq. (10) is not accomplished [21]. The determination carried out at concentration levels between  $5 \times 10^{-4}$  and  $15 \times 10^{-3} \text{ M}$  employing the quadratic equation yielded a mean value for the purity of expired sodium borohydride of 86.3 mole% (range: 76.4–92.9%,  $n = 5$ ).

One of the main flows in the electrochemical methods is the competition between the BOR and the hydrolysis, and the possible catalytic effect of the anode material [12,21]. In addition, the heterogeneous processes taking place on the electrode surface by the reaction intermediates give rise mutually superimposed faradic currents, which affect the reliability of the main current peak [22]. Therefore, the main current peak related to the BOR cannot be taken as an additive property, and fails as analytical signal. The high dispersion of the voltammetric determination is a confirmation of such lack of reliability.

### 3.2. Titrimetric determination of sodium borohydride

The iodate method is the analytical methodology considered as the reference, and despite being more than 50 years old and with several pitfalls, has not been substituted with other method with more efficient. In the original work [11] the authors show that even at the highest pH assayed, borohydride hydrolysis is not completely avoided. This becomes a problem in connection with iodate titrimetry, a volumetric technique quite length. The determination carried out on expired sodium borohydride samples yield a mean value for the purity of 82.8%  $\text{w w}^{-1}$  (range: 75.0–89.1%,  $n = 6$ ). On the other hand, the same analytical procedure carried out on the recently opened sodium borohydride yields a value for the purity of 93.2%  $\text{w w}^{-1}$  (range: 91.4–94.8%,  $n = 5$ ).

One of the advantages of this method is that the purity is expressed over the total mass weighted so no calibration curve is needed. However, face the problems of the well-known difficulties related to iodine-based methods [11], which requires extensive precautions to render it quantitatively precise. Like in the electrochemical methods the reagent intrinsic instability in aqueous media may produce unreliable analytical results. Though alkaline media retard the hydrolysis process, it is not completely avoided. In addition, hydrogen gas liberated in the decomposition process Eq. (10), may have as a consequence of an overestimate of the purity of the sample. Given that the purity is expressed as the mass of borohydride over the total of mass of weighed sample, the purity assessed does not provide direct information of the decomposition of borohydride into metaborate, and may also include hydration

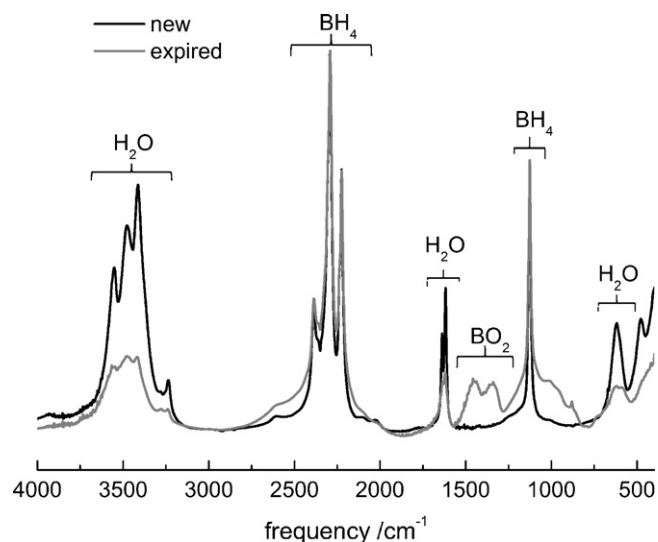


Fig. 2. FTIR spectra of new (recently opened borohydride) (black) and expired (grey)  $\text{NaBH}_4$  normalized by assigning a value of 1.00 to the vibrational band at  $2291 \text{ cm}^{-1}$ .

water as impurity. Notice that for the recently opened reagent, the declared purity by the dealer was 98.8%, and our value obtained by titrimetry was 93.2%. This 5.6% difference may be ascribed to crystallization water, as we will show later.

### 3.3. Experimental FTIR spectra

The FTIR spectra of  $\text{NaBH}_4$  samples (Fig. 2) are composed by well defined bands, in which it is worth to mention their quality in terms sharpness and definition. Such an improvement can be attributed to the absence of liquid water produced by the deliquescence process that is usually reflected in smoothed spectra. Therefore, sample drying improves the quality (see Fig. 2, Appendix C).

Five groups of bands are clearly distinguished in the experimental FTIR spectra of the recently opened borohydride sample (Fig. 2, black line). Two of them correspond to  $\text{NaBH}_4$  signals, and the others to the  $\text{H}_2\text{O}$  crystallization molecules. The appearance of the unexpected  $\text{H}_2\text{O}$  crystallization bands in the recently opened  $\text{NaBH}_4$ , strongly suggest that the  $\text{NaBH}_4$  is either already partially hydrated (before opened) or is rapidly altered during the measuring process. In any case the borohydride sample should be considered as a mixture of  $\text{NaBH}_4$  and  $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$  (global formula  $\text{NaBH}_4 \cdot x\text{H}_2\text{O}$ ), although the actual amount of  $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$  cannot be determined. This compromise all the analytical methods based on the use of a calibration curve.

In order to fill some gaps found in the interpretation of the infrared spectra of sodium borohydride, the experimental data was compared with the calculated FTIR for  $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$  (Table 2). The O–H stretching region reveals three sharp bands at 3414, 3478 and  $3553 \text{ cm}^{-1}$ , and a low intensity sharp band at  $3237 \text{ cm}^{-1}$  that is due to the formation of a di-hydrogen bond between water and  $\text{NaBH}_4$  [18]. Two partially superimposed bands at 1618 and  $1638 \text{ cm}^{-1}$  correspond to H–O–H bending, again suggesting that both water molecules interact differently with  $\text{NaBH}_4$ . Finally, the librational modes of the water molecules are observed at 478 and  $617 \text{ cm}^{-1}$ , while the four scissoring bands together with the wagging band of  $\text{BH}_4$  define one single peak at  $1126 \text{ cm}^{-1}$ . The absence of splitting in this band is indicative of an undistorted tetrahedral symmetry of the borohydride group. The stretching modes of  $\text{BH}_4$  group give rise to three well-distinguished and sharp bands at 2224, 2291 and  $2386 \text{ cm}^{-1}$ , and a small contribution at  $2594 \text{ cm}^{-1}$ . The first three bands correspond to a mixture of stretching modes involving different hydrogen atoms of the  $\text{BH}_4$  moiety, and the latter band

**Table 1**

FTIR vibrational bands (in  $\text{cm}^{-1}$ ) for recently opened and expired solid sodium borohydride. The shaded area corresponds to borohydride vibrational bands.

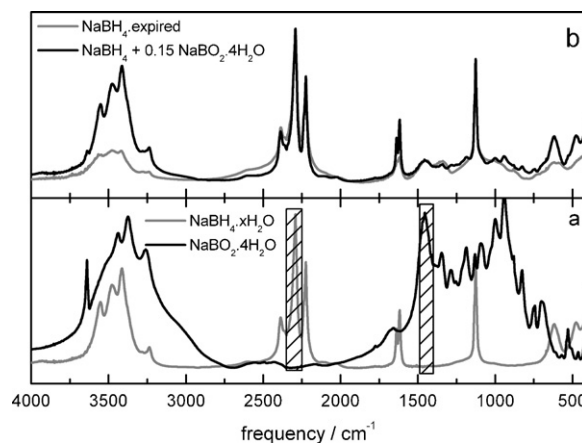
| NaBH <sub>4</sub> (new)        |                       | NaBH <sub>4</sub> (expired)    |                       |
|--------------------------------|-----------------------|--------------------------------|-----------------------|
| Frequency ( $\text{cm}^{-1}$ ) | Normalized absorbance | Frequency ( $\text{cm}^{-1}$ ) | Normalized absorbance |
| 478                            | 0.30                  | 478 <sup>a</sup>               | 0.13                  |
| 617                            | 0.29                  | 617                            | 0.12                  |
|                                |                       | 880 <sup>b</sup>               | 0.09                  |
|                                |                       | 1018 <sup>b</sup>              | 0.14                  |
| 1126                           | 0.72                  | 1126                           | 0.72                  |
|                                |                       | 1339 <sup>b</sup>              | 0.14                  |
|                                |                       | 1437 <sup>b</sup>              | 0.14                  |
| 1618                           | 0.38                  | 1618                           | 0.16                  |
| 1638                           | 0.26                  | 1638 <sup>a</sup>              | 0.13                  |
| 2224                           | 0.69                  | 2224                           | 0.69                  |
| 2291                           | 1.00                  | 2291                           | 1.00                  |
| 2386                           | 0.33                  | 2386                           | 0.35                  |
| 2594                           | 0.04                  | 2594                           | 0.07                  |
| 3237                           | 0.13                  | 3240                           | 0.07                  |
|                                |                       | 3279                           | 0.08                  |
| 3414                           | 0.64                  | 3420                           | 0.21                  |
| 3478                           | 0.54                  | 3474                           | 0.21                  |
| 3553                           | 0.43                  | 3564                           | 0.18                  |

<sup>a</sup> Shoulder.

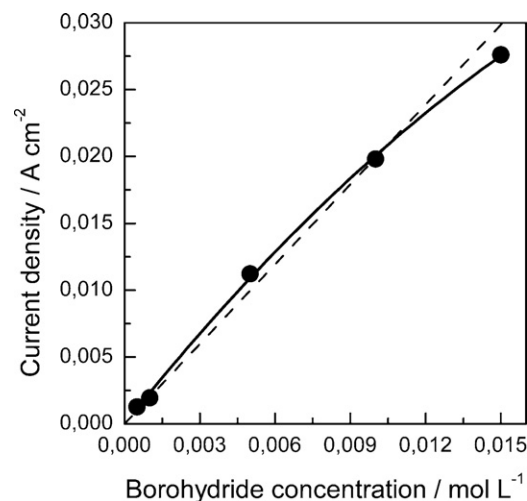
<sup>b</sup> Sodium metaborate bands.

at  $2594\text{ cm}^{-1}$  corresponds to the single stretching mode of B–H<sub>3</sub> (Table 2). Nevertheless, it was also noticed that the normalized absorbance at  $2594\text{ cm}^{-1}$  (Table 1), differs between the new and the expired NaBH<sub>4</sub>, while the others bands assigned to the borohydride molecule do not. The difference was attributed to the small contribution of metaborate absorption (Fig. 3a).

The FTIR spectra of expired sodium borohydride (Fig. 2, grey line) essentially display the same features of the recently opened reactive (Table 1). Comparison between the vibrational spectra (Fig. 3a) of pure NaBO<sub>2</sub>·4H<sub>2</sub>O (black) and expired NaBH<sub>4</sub> (grey) clearly demonstrates that the new vibrational bands at  $880\text{ cm}^{-1}$ ,  $1018\text{ cm}^{-1}$ ,  $1339\text{ cm}^{-1}$  and  $1437\text{ cm}^{-1}$  appear due to NaBO<sub>2</sub>·4H<sub>2</sub>O, formed through Eq. (3) (vide supra). The first two bands can be assigned to the stretching mode while the last two are assigned to the B–O–H bending mode [23]. This confirms why they do only appear in the expired sodium borohydride sample, where NaBO<sub>2</sub> is present. Both the linear combination of pure borohydride and metaborate spectra (Fig. 3b) and the similarities in the



**Fig. 3.** (a) FTIR spectra of NaBH<sub>4</sub> (grey) and NaBO<sub>2</sub>·4H<sub>2</sub>O (black). The shaded areas represent the vibrational bands for NaBH<sub>4</sub> ( $2291\text{ cm}^{-1}$ ) and NaBO<sub>2</sub>·4H<sub>2</sub>O ( $1437\text{ cm}^{-1}$ ) for which there is no mutual interference between both spectra. (b) Experimental FTIR spectra of expired NaBH<sub>4</sub> (grey) and simulation obtained by linear combination of NaBH<sub>4</sub> and NaBO<sub>2</sub>·4H<sub>2</sub>O spectra in 1:0.15 proportion, respectively (black).



**Fig. 4.** Calibration curve for the voltammetric determination of sodium borohydride.

**Table 2**

Unscaled vibrational bands position (in  $\text{cm}^{-1}$ ) for sodium borohydride di-hydrate calculated at different levels of theory, and compared to the experimental spectra.

| Experimental spectra NaBH <sub>4</sub> ·xH <sub>2</sub> O | Theoretical calculations |                               | Assignments <sup>b</sup>   |
|---|--------------------------|-------------------------------|--|
|   | B3LYP 6-311++G(2df,2p)   | Møller Plesset MP2 6-311++G** |  |
| 478   | 487                      | 438                           | BH <sub>4</sub> rocking + OH libration from H <sub>2</sub> O(1) and (2)                    |
| 617   | 645                      | 633                           | OH libration OH from H <sub>2</sub> O(2)   |
|   | 756                      | 679                           | Assym. twisting H <sub>2</sub> O(2)  |
|   | 1083                     | 1142                          | BH <sub>4</sub> wagging  |
|   | 1130                     | 1168                          | BH <sub>4</sub> scissoring   |
| 1126  | 1180                     | 1217                          | BH <sub>4</sub> scissoring   |
|   | 1232                     | 1295                          | BH <sub>4</sub> scissoring   |
|   | 1302                     | 1325                          | BH <sub>4</sub> scissoring   |
| 1618  | 1621                     | 1618                          | Bending H <sub>2</sub> O(1)  |
| 1638  | 1665                     | 1673                          | Bending H <sub>2</sub> O(2)  |
| 2224  | 2239                     | 2303                          | Stretching B–H <sub>1</sub> + B–H <sub>4</sub>   |
| 2291  | 2257                     | 2317                          | Asymmetric stretching B–H <sub>2</sub> (B–H <sub>1</sub> + B–H <sub>4</sub> ) <sup>a</sup> |
| 2386  | 2274                     | 2327                          | Symmetric stretching B–H <sub>4</sub> (B–H <sub>1</sub> + B–H <sub>2</sub> ) <sup>a</sup>  |
| 2594  | 2505                     | 2568                          | Stretching B–H <sub>3</sub>  |
| 3237  | 3294                     | 3593                          | Stretching O(2)–H <sub>w3</sub>  |
| 3414  | 3692                     | 3795                          | Stretching O(1)–H <sub>w1</sub>  |
| 3478  | 3877                     | 3941                          | Stretching O(2)–H <sub>w4</sub>  |
| 3553  | 3903                     | 3971                          | Stretching O(1)–H <sub>w2</sub>  |

<sup>a</sup> In parenthesis the additional contributions of other stretching modes predicted only by B3LYP/6-311++G(2df,2p).

<sup>b</sup> See Fig. B1 in Appendix B of supplementary data for borohydride di-hydrate atom numbering.

**Table 3**  
Summary table of the results and the advantages and disadvantages of each method.

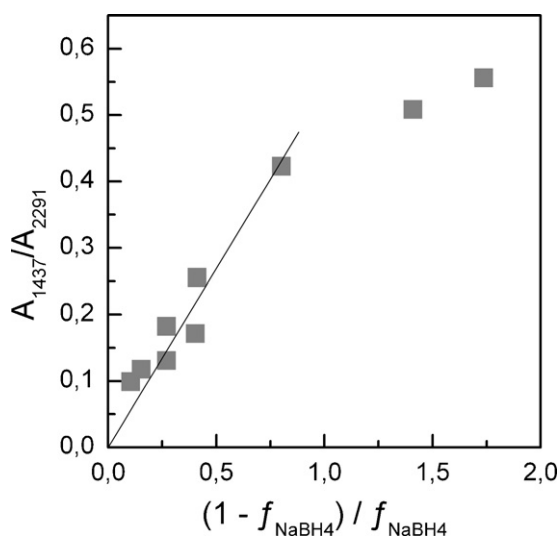
| Technique   | Assessment of the purity                              | Advantages  | Disadvantages   |
|-------------|---|---|---|
| Voltammetry | 86.3 mole% (range: 76.4–92.9%, $n = 5$ ).             | <ul style="list-style-type: none"> <li>• High sensitivity</li> <li>• Although the purity is expressed as the ratio between the <math>\text{NaBH}_4</math> and <math>\text{NaBO}_2</math>, the presence of electro active impurities can be detected</li> </ul>  | <ul style="list-style-type: none"> <li>• Competition between the BOR and the hydrolysis</li> <li>• Possible catalytic effect of the anode material</li> <li>• Requires a calibration curve</li> <li>• Slow technique</li> <li>• The purity is expressed as the ratio between the <math>\text{NaBH}_4</math> and <math>\text{NaBO}_2</math></li> </ul> |
| Iodometry   | 82.8% $\text{w w}^{-1}$ (range: 75.0–89.1%, $n = 6$ ) | <ul style="list-style-type: none"> <li>• Calibration curve is not required</li> <li>• The purity is expressed over the mass weighted thus it takes into account others impurities apart from <math>\text{NaBO}_2</math></li> </ul>  | <ul style="list-style-type: none"> <li>• Slow technique</li> <li>• The instability of <math>\text{NaBH}_4</math> in aqueous solutions</li> </ul>  |
| FTIR        | 81 mole% (range: 78–83%, $n = 5$ ).                   | <ul style="list-style-type: none"> <li>• Fast technique</li> <li>• Measurements are carried out directly on the solid sample</li> <li>• Although the purity is expressed as the ratio between the <math>\text{NaBH}_4</math> and <math>\text{NaBO}_2</math>, the presence of infrared visible impurities can be detected</li> </ul> | <ul style="list-style-type: none"> <li>• Requires a calibration curve</li> <li>• The purity is expressed only as the ratio between the <math>\text{NaBH}_4</math> and <math>\text{NaBO}_2</math></li> </ul>   |

spectra of the expired sodium borohydride and of the recently opened sample left under severe humidity condition for some hours, confirms that the new vibrational bands in the expired sample are due to the hydrolysis of  $\text{NaBH}_4$  to form  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  (see Fig. C.1, Appendix C).

Given that the bands at  $1437 \text{ cm}^{-1}$  of sodium metaborate and  $2291 \text{ cm}^{-1}$  of sodium borohydride (Fig. 3a) do not overlap, both signals represent a good fingerprint for the qualitative assessment of the quality of sodium borohydride. The attempt to use these bands for quantitative purposes should consider the ratio between the measured absorbance of both peaks and the assumption of the accomplishment of the Lambert–Beer law (see Appendix A):

$$\frac{A_{1437}}{A_{2291}} = \frac{\varepsilon_{1437}}{\varepsilon_{2291}} \left( \frac{1 - f_{\text{NaBH}_4}}{f_{\text{NaBH}_4}} \right) \quad (11)$$

where  $f_{\text{NaBH}_4}$  is the molar fraction of sodium borohydride in the sample. Experimental data in the lower concentration range adjusted to Eq. (11) fits with a slope  $\varepsilon_{1437}/\varepsilon_{2291} = 0.54 \pm 0.03$  (Fig. 5), yielding a purity of the expired sample of sodium borohydride of 81 mole% (range: 78–83%,  $n = 5$ ). The non linearity observed in Fig. 5 for values above 0.8 molar fraction ratio could be attributed to deviations from Lambert–Beer law at high concentrations.



**Fig. 5.** Calibration curve for the quantification of  $\text{NaBH}_4$  in the samples by FTIR, according to Eq. (11).

As discussed above this procedure is based on a calibration curve, therefore the calculated results can slightly differ from the real value. Despite of that, unlike other methods, FTIR methodology is the only one which assesses the purity of sodium borohydride in the solid state, so problems related to the BOR and hydrolysis process are avoided. Moreover, FTIR spectra can be effectively used as a positive–negative assay for the presence of metaborate.

Table 3 summarizes all the results together with the advantages and disadvantages of each method. The analysis of the combined results give rise to a more complete picture of the actual state of solid sodium borohydride, and all data should be taken as complementary. For example, from iodate titrimetry we know that sodium borohydride represent 93.2% of the total mass of the newly open reagent, and in combination with FTIR, we know that the rest is mainly water. This water uptake of ca. 6% is in accordance [8] with the rate of water uptake during the time usually spent in the laboratory ( $\text{RH} < 40\%$ ) in the confection of the KBr disks. From FTIR spectrum, we notice that this amount of adsorbed water did not yield detectable amounts of sodium metaborate, suggesting that the reagent is in the first step of the deterioration process (Eq. (1)). In the case of the expired sample, the purity obtained by titrimetry was 82.8%, indicating that the level of impurities has dramatically increased. FTIR measurements indicate that  $\text{H}_2\text{O}$  and  $\text{NaBO}_2$  are present, and the level of deterioration of the reagent achieved the level represented by Eqs. (3) and (4). The presence of sodium metaborate seems not to affect the lack of linearity in the voltammetric determination of borohydride anion; are the ad-species formed during the BOR the responsible for the incomplete number of electrons exchanged.

#### 4. Conclusions

We propose FTIR as a simple method for the assessment of the purity of sodium borohydride. Contrary to voltammetry and titrimetry, the present one is carried out directly on the solid sample, avoiding the interference of the hydrolysis and oxidation processes that take place in aqueous solutions. A precautionary note is that  $\text{NaBH}_4$  is highly hygroscopic, and so whatever technique is employed one should keep the samples dry, and/or account for adsorbed moisture. Theoretical calculations help to confirm that the two most useful vibrational frequencies are  $1437$  and  $2291 \text{ cm}^{-1}$  for  $\text{BO}_2$  and  $\text{BH}_4$  respectively which are used for the semi-quantitative analysis of the sample. The simplicity and rapidness of the method constitutes an additional and welcomed advantage for quality control purposes.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jpowsour.2011.09.055](https://doi.org/10.1016/j.jpowsour.2011.09.055).

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