

Analytical monitoring of sodium borohydride

Cite this: *Anal. Methods*, 2013, **5**, 829Biljana Šljukić,^a Diogo M. F. Santos,^a César A. C. Sequeira^a and Craig E. Banks^b

Received 21st September 2012

Accepted 12th December 2012

DOI: 10.1039/c2ay26077h

www.rsc.org/methods

Sodium borohydride (NaBH_4) determination, both qualitative and quantitative, is of great significance in a plethora of areas. These include NaBH_4 for energy systems such as direct borohydride fuel cells and in hydrogen production and storage, as well as use as a reducing agent in organic and inorganic synthesis reactions or in electrodeposition processes. Herein the main methods for NaBH_4 monitoring have been summarised and described, including hydrogen evolution, hydride hydrolysis and iodate methods, and different electrochemical and spectroscopic techniques overviewed.

Introduction

Sodium borohydride (NaBH_4) has broad application as a reducing agent in numerous organic and inorganic reactions, including chemical synthesis and electroless plating of metals,¹ as well as in energy systems, such as fuel cells or for hydrogen (H_2) production and storage.² NaBH_4 was first synthesised in the 1940s by Schlesinger and Brown^{3–5} and soon attracted significant attention (Fig. 1).⁶ In 1942, researchers at Chicago University were looking for volatile compounds to be used in rocket engines and signal balloons for military purposes. Their findings, being war-time military secrets, were not published

until 1953. In 1979 Brown was awarded the Nobel Prize in Chemistry “for the development of use of boron-containing compounds into important reagents in organic synthesis.” Following the first work of Schlesinger and Brown, intense research related to NaBH_4 was performed resulting in many papers about it being published in the succeeding twenty years. At this early stage it was shown that NaBH_4 is a potential hydrogen carrier as well as a potential energy carrier. During the following period from the mid-1960s to the late 1990s, mostly fundamental studies were carried out. NaBH_4 received more attention as a reducing agent in the synthesis of organic compounds, while very few studies about NaBH_4 as a hydrogen/energy carrier were done. In the late 1990s, NaBH_4 had once again drawn the attention of scientists. The late 1990s marked the revival of the scientific and technological community's interest in NaBH_4 as a hydrogen/energy carrier due to the emerging energy crisis that is even more pronounced nowadays.

^aICEMS, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: biljana.paunkovic@ist.utl.pt

^bFaculty of Science and Engineering, School of Biology, Chemistry and Health Science, Division of Chemistry and Materials, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, Lancs, UK



Biljana Šljukić has worked as an Assistant Professor at the Faculty of Physical Chemistry, University of Belgrade since 2009. She is currently working as a Postdoctoral Research Fellow at the Instituto Superior Técnico, TU Lisbon, with her present research focusing on direct borohydride fuel cells. She is participating in several projects on energy conversion (lithium-ion batteries and fuel

cells) and redox-active polymers, and acts as a reviewer for several international journals. She has published more than 30 papers and presented her work at 20 conferences.



Diogo M.F. Santos is a post-doctoral research fellow at Instituto Superior Técnico, TU Lisbon. He has authored more than 40 papers in peer-reviewed journals and over 30 conference proceedings. He has presented more than 15 oral communications and 25 posters in international conferences. He is a member of several renowned international societies and serves as a reviewer for many

scientific journals. He is the Assistant Director of Ciência & Tecnologia dos Materiais (SPM, Portugal). His main research interests are related to electrochemical energy storage and conversion, such as direct borohydride fuel cells or new electrocatalysts for hydrogen production by alkaline water electrolysis.

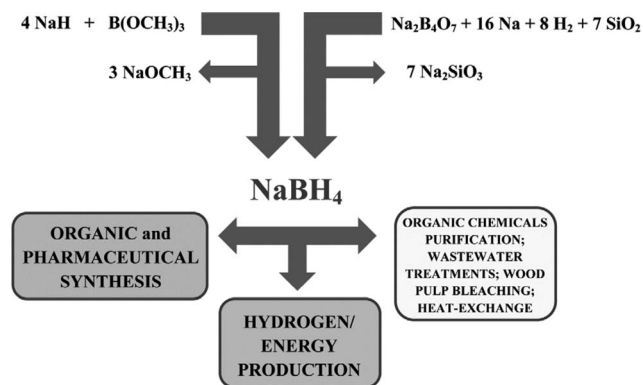


Fig. 1 Schematic representation of the main NaBH_4 synthesis procedure and its applications.

The first investigations were related to NaBH_4 for hydrogen storage and generation by chemical hydrolysis, while NaBH_4 direct electrooxidation with application in fuel cells received more attention somewhat later. Today NaBH_4 is studied as a hydrogen/energy carrier from energy and environment as well as economic points of view.

With applications of NaBH_4 being so numerous and broad, a need for development of new synthesis procedures as well as techniques for its determination has arisen. Monitoring of NaBH_4 is especially significant during its synthesis (for instance in electrosynthesis), assessment of its purity, and for monitoring its leaking in fuel cells. This paper provides an overview of analytical methods for monitoring of NaBH_4 . These are grouped into 4 groups, with each one covering a different set of techniques: gasometric, volumetric, electrochemical and spectroscopic.

NaBH_4 as a reducing agent

NaBH_4 is stable under dry conditions but undergoes chemical hydrolysis in the presence of water. It is hygroscopic, with slow

decomposition starting at temperatures above 400°C and progressing rapidly above 500°C .¹ It is a selective, mild reducing agent which can be used for organic and pharmaceutical synthesis, wastewater treatments and wood pulp bleaching in paper manufacturing. For example, it converts aldehydes and ketones to the corresponding alcohols in the production of pharmaceuticals and other fine chemicals, but on its own it does not react with esters, amides, or carboxylic acids, and it serves as a foaming agent for rubbers, *etc.* The advantage of NaBH_4 in comparison with lithium aluminium hydride (LiAlH_4) for example is that it can be used for reactions in a range of solvents. It can be dissolved or suspended in various solvents due to its high resistance, allowing corresponding reductions to be carried out in these media. The reduction effect can be controlled by the choice of the solvent, by the working temperature and by the NaBH_4 concentration. Furthermore the NaBH_4 reactivity can be influenced by addition of iodine or methanol in borane-tetrahydrofuran ($\text{BH}_3\text{-THF}$) for reduction of esters into the corresponding alcohols.

NaBH_4 has also found commercial use in the purification and stabilisation of numerous organic compounds such as alcohols, epoxides, ethers, amines and hydrocarbons. During the purification process, different impurities are removed, including aldehydes, ketones and peroxides that can cause discoloration even if present just in traces. Moreover, NaBH_4 solutions are customarily employed as heat-exchange media for cooling purposes.

NaBH_4 as a hydrogen/energy carrier

Use of NaBH_4 as an energy material is more recent, but has applications for H_2 production and storage and as a fuel in direct borohydride fuel cells (DBFCs) which are proving to be quite promising.^{2,7,8} NaBH_4 is widely studied for use in electrochemical power generation in portable devices due to its



César A.C. Sequeira is a professor at the Instituto Superior Técnico, TU Lisbon. He has directed international projects on electrochemistry of corrosion, metal extraction, conducting polymers, energy storage and conversion, (co)authored over 200 papers and (co)edited 12 books. He is a Fellow of the Institute of Materials (UK), a Fellow of the Institute of Corrosion (UK), an Active Member of

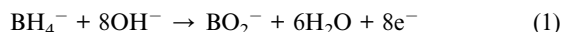
the Electrochemical Society (USA), a Founder Member of the Portuguese Electrochemical Society, the Portuguese Materials Society, and the Moscow International Energy Club. His research interests include electrical and electrochemical properties of nanomaterials, hydrogen production/storage, and low temperature fuel cells.



Craig E. Banks is an Associate Professor of Chemistry at Manchester Metropolitan University and has published over 220 papers with a h-index over 38 (Web of Science, Nov 2012). He has written 4 books, contributed 10 book chapters and is an inventor of 13 patents. Craig has also spun out two companies from his research. Craig was awarded the Harrison-Meldola Memorial Prize in 2011 for his

contributions to the understanding of carbon materials, in particular graphene and its application as an electrode material. His current research is directed towards the pursuit of studying the fundamental understanding and applications of nano-electrochemical systems such as graphene, carbon nanotube and nano-particle derived sensors and developing novel electrochemical sensors via screen printing and related techniques.

high theoretical hydrogen density (10.8 wt%) and ease of H₂ release as well as low cost and safe handling.^{9,10} The DBFC anode is characterised with a high theoretical specific capacity, *i.e.*, 5.7 A h g⁻¹ (based on NaBH₄), provided that borohydride (BH₄⁻) is fully oxidised to the metaborate (BO₂⁻) product. The complete eight-electron oxidation process presented in eqn (1) has a standard electrode potential of -1.24 V vs. SHE.



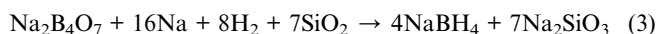
DBFCs were first proposed in the early 1960s^{11,12} but it is noted that in order to utilise NaBH₄ as fuel, its cost must be reduced by at least one order of magnitude from its present value (~40 € kg⁻¹). For a new technology to be widely accepted and employed, it has to meet not only energy and environmental requirements, but economic ones as well. An acceptable cost can be achieved by introducing new NaBH₄ synthesis procedures, its mass production and/or recycling of the sodium metaborate product (NaBO₂) back to NaBH₄.

Synthesis of NaBH₄

The most important NaBH₄ manufacturing technology is the Brown-Schlesinger process that is based on Schlesinger and Brown's original work and has practically remained the same since it was first commercialised in the 1950s. This process involves the reaction of fine sodium hydride (NaH) with trimethyl borate (B(OCH₃)₃) in high boiling hydrocarbon oil between 250 and 280 °C,^{3-5,13} as described by the overall reaction:



This procedure yields high purity NaBH₄, but individual reaction steps are not optimised in terms of energy efficiency leading to only 20% efficiency of the overall reaction (eqn (2)). Consequently, the cost of NaBH₄ produced *via* this process is still too high for certain marketable applications, such as in motor vehicle production. Another process that has been employed on a commercial scale to produce NaBH₄ is the Bayer process first developed by the Bayer Corporation for the company's internal NaBH₄ needs.¹⁴⁻¹⁶ The Bayer process is a one-pot synthesis combining finely grounded borax (Na₂B₄O₇), metallic sodium (Na), and H₂, in the presence of silica (SiO₂), to generate NaBH₄ as described by the following expression:



The NaBH₄ is extracted from the borohydride-silicate mixture with liquid ammonia under pressure. The Bayer reaction carries the risk of explosion, primarily because it proceeds at the temperature of about 700 °C, which is above the NaBH₄ decomposition temperature. Additionally, it is a batchwise method where raw materials are added to the reaction, processed into products and then sent on for separation. Regarding the cost, all materials used in the Bayer process are inexpensive with the exception of Na. Consequently, there are current efforts to modify the Bayer process by employing the less expensive

reducing metal magnesium (Mg) instead of Na,¹⁷⁻¹⁹ yielding a NaBH₄ product of price acceptable for all commercial applications. So far, these modified Bayer processes have not met the requirement of being both fast and giving high yield. Other organic reductions, such as multistep thermal reductions or similar processes, have been attempted for NaBH₄ synthesis, but their complexity prevents lowering of the product cost for it to be considered as a low-cost fuel for commercial applications.

The electrosynthesis of NaBH₄ in aqueous media, particularly molten salts and ionic liquids, has been examined as a potentially simpler process for the production of NaBH₄.²⁰ Sun and Liang²¹ and Guilbault *et al.*²² are among those who have reported the electrochemical conversion of borate to borohydride in aqueous media. During the last six decades, about 100 methods for NaBH₄ synthesis have been suggested with more than 80 patents and numerous scientific papers being published. Along with the development of NaBH₄ synthesis and expansion of its utilisation, development of methods for its monitoring has been explored such as monitoring leaks within DBFCs. Herein, different techniques for the sensing of NaBH₄ have been summarised and the most pertinent are described in greater detail.

Methods for monitoring NaBH₄

Numerous applications of NaBH₄ have urged the need for development of a simple, fast and accurate method for its qualitative and quantitative determination. Still, finding a simple and reliable analytical method for NaBH₄ monitoring represents something of a challenge. The amount of NaBH₄ can be determined gasometrically, by the most commonly used hydrogen evolution method,^{23,24} or volumetrically.^{25,26} Borohydride releases H₂ in the presence of a suitable catalyst under appropriate conditions; since the amount of H₂ produced is proportional to the amount of borohydride, the measurement of the evolved H₂ was the first method used for the determination of the borohydride present in a system.^{23,24} This method is also employed in studies searching for suitable electrocatalysts for H₂ generation from borohydride under different experimental conditions.^{27,28} The hydrogen evolution method has been reported to be the most accurate among the gasometric and volumetric procedures for borohydride analysis.²⁹

The four most cited volumetric methods of assay are the acid-base titration,²³ the iodate method,²⁵ the hypochlorite method²⁶ and a potentiometric titration with potassium permanganate (KMnO₄).³⁰ In the iodate method, excess iodate (IO₃⁻) is added to the medium and the remaining IO₃⁻ after reaction with BH₄⁻ is back titrated with buffered thiosulfate (S₂O₃²⁻).²⁵ The hypochlorite method involves the direct titration of NaBH₄ solution with standard sodium hypochlorite (NaClO) utilising Bordeaux red as an indicator.²⁶ The pH value of the solution during the titration is a critical parameter and should be maintained in the pH range of 9.6 to 10.3. Although not commonly used in the literature, the disappearance of the characteristic pink colour of KMnO₄ solution upon the addition of strongly basic 0.05–0.1 M NaBH₄ solution can be used as a spot test for the presence of BH₄⁻. Other volumetric methods

have also been explored for NaBH_4 sensing such as the chloramine-T³¹ and the argentimetric method.³² The use of chloramine-T as an oxidising agent for NaBH_4 oxidation and subsequent determination was suggested because of its higher stability in comparison with, for example, NaClO .³¹ Furthermore, this method can be employed for NaBH_4 quantification in some non-aqueous solvents. The argentimetric, semi-quantitative silver–ethylenediamine (Ag–EDA) procedure is based on the reduction of Ag(I) by BH_4^- in 50% NaOH , 4% EDA solution.³² The precipitated Ag is removed from the solution by filtration and the excess of Ag^+ ion is determined by a standard volumetric procedure. In the volumetric methods, especially those involving redox reactions in acid media, there are two competing reactions: the oxidation – reduction reaction, involving NaBH_4 and the oxidising species, and also the NaBH_4 hydrolysis reaction. Therefore, for accurate quantitative results using iodometric methods for instance, the BH_4^- has to react with the iodine (I_2) or alternatively with an iodine complex at a much faster rate than the rate of hydrolysis; however this hydrolysis mechanism has been reported to be quite complicated.³³

There are also other techniques that have been reported to be successfully employed for NaBH_4 determination, including a gas chromatographic method based on the reduction of isobutylaldehyde to isobutyl alcohol and an indirect spectrophotometric method based on the reduction of acetone to isopropyl alcohol.²⁹

The spectrophotometric determination of BH_4^- is based upon its reaction with an additive agent yielding a coloured product that gives a signal at a certain wavelength. For instance, NaBH_4 in reaction with trinitrobenzenesulfonate ion in alkaline aqueous solutions gives a red-orange product with an absorption maximum at 460 nm.³⁴ The reduction of phosphotungstate ($\text{PW}_{12}\text{O}_{40}^{3-}$) by BH_4^- can also be conveniently used as a spot test for the determination of the presence of BH_4^- in the medium.³⁵ The neutral solution exhibits the characteristic blue – violet colour of the heteropoly blue species formed by the BH_4^- reduction of $\text{PW}_{12}\text{O}_{40}^{3-}$ that gives an absorbance maximum at 680 nm.

Electrochemical techniques such as polarography^{36–38} and voltammetry,^{39,40} usually with gold (Au) working electrodes, allow sensing with much lower limits of detection (LOD) compared to the above mentioned methods.

For trace analysis, some modifications of the described methods used for regular samples are necessary in order to reach lower detection limits. For instance, in the H_2 evolution method for trace analysis, a confining solution designed to dissolve only small amounts of gas is used instead of water.⁴¹ Other approaches used successfully for sensing trace BH_4^- include: the nicotinamide adenine dinucleotide (NAD^+),⁴² crystal violet,^{43,44} phosphomolybdic acid (PMA)⁴⁵ and the nicotinamide benzyl chloride (NBC^+) methods.⁴⁶ In the NAD^+ method, NaBH_4 reduces NAD^+ to the ultraviolet absorbing species NADH , which is then detected spectrophotometrically at 340 nm. The crystal violet method is particularly suitable in non-aqueous media where a solution of crystal violet in *N,N*-dimethylformamide (DMF) is employed to titrate an organic

solution containing NaBH_4 to a purple endpoint. In the case of the PMA colorimetric method, PMA is reduced with NaBH_4 to a blue colour that can be measured at 665 nm.

Nuclear magnetic resonance (NMR) spectroscopy has also been used for qualitative analysis, but not for quantitative determination of BH_4^- . Both ^1H NMR and ^{11}B NMR have been tested.^{47–50} Another technique that has given noteworthy results is infrared (IR) spectroscopy which allows the observation of the B–H bond characteristic vibration frequencies.^{20,50,51}

Table 1 summarises the main advantages and disadvantages of some of the above mentioned methods for borohydride qualitative and quantitative determination.

Hydrogen evolution method

The most common method used for the quantitative determination of NaBH_4 is the hydrogen evolution method.^{23,24} This technique is based on the measurement of the volume of H_2 gas released upon the complete hydrolysis of a NaBH_4 solution of known volume. BH_4^- hydrolysis yields H_2 gas evolution as described by:



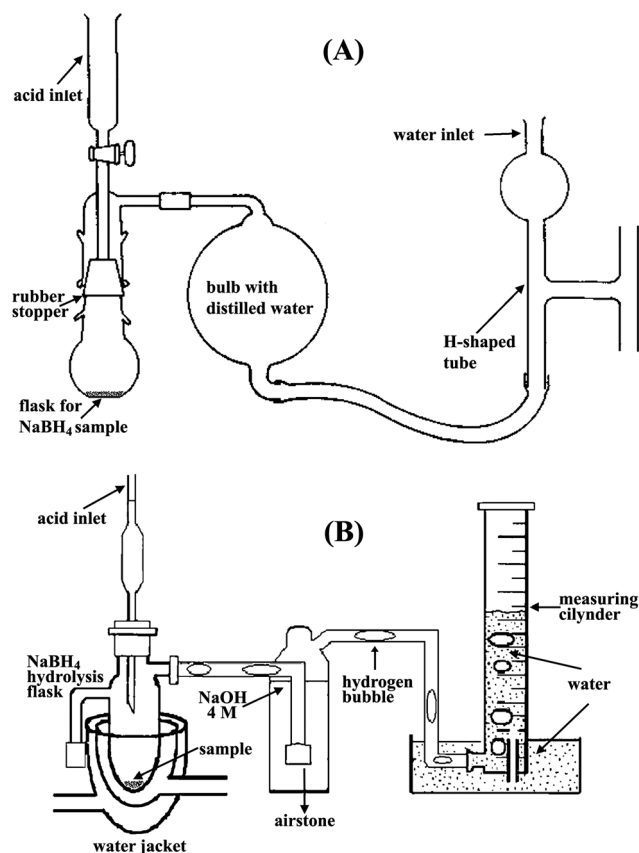
The amount of H_2 gas released upon hydrolysis is proportional to the quantity of BH_4^- present in the solution. In this technique, the released H_2 gas is collected and its volume measured in a water trap that consists of two inverted cylinders immersed in a water tray (Fig. 2A). The pressure head of the water and the water vapour pressure at the temperature of the water need to be taken into account when determining the volume of H_2 produced. The measurement and control of the mentioned parameters makes this technique somewhat complicated. Additionally, efficient temperature control of the process is necessary. Otherwise, inaccurate results could be obtained if changes of water pressure with temperature are considered.

Hydride hydrolysis method

Santos and Sequeira, aiming to overcome some difficulties of the hydrogen evolution method (see above), have developed a new procedure for determination of the approximate NaBH_4 content in a given sample, named the hydride hydrolysis method.²⁰ This newly developed approach is based on the gasometric measurement of the H_2 released during the BH_4^- hydrolysis. However, the apparatus used is less complicated than the one used in the conventional hydrogen evolution method (*viz.* Fig. 2B), and importantly does not require temperature and pressure control during the measurement process. In this method, a regular measuring cylinder is filled with water, closed with a stopper with two exits, inverted and dipped into a water tank. One exit of the measuring cylinder is connected to the reaction vessel, while the other one allows the equivalent volume of water to exit to the tank. The sample is placed inside the reaction vessel and a diluted acidic aqueous solution is added to the closed reaction vessel. Since all the equipment is in a closed circuit, the only mass entrance is from

Table 1 Comparison of several borohydride detection methods

Method	Advantages	Disadvantages	Limit of detection
Hydrogen evolution	High accuracy	Specialised glassware and temperature control required	100 ppm
Hydride hydrolysis	Simplicity; high reproducibility	LOD depends on correct optimisation of the system	500 ppm
Iodate	No calibration curve required	Somewhat erroneous quantitative results due to a possible hydrolysis side reaction; possible interference of other oxidants and reductants; slow	20 ppm
NAD ⁺	Rapidity; simplicity; applicability over a wide pH range	High cost and instability of the reagent; applicability only in aqueous solution	1 ppm
Crystal violet	Rapidity; simplicity; applicability to both aqueous and non-aqueous systems	Non-applicability to caustic solutions or when strong nucleophiles are present	Depends on the solvent used
Voltammetry	High sensitivity	Competition between BH_4^- oxidation and hydrolysis reactions; possible catalytic effect of anode material	3×10^{-5} M (1 ppm, SWV)
FTIR	No effect of competition between BH_4^- oxidation and hydrolysis	Sample preparation can be time-consuming	—

**Fig. 2** Schematic representation of the apparatus for hydrogen evolution (A) and the hydride hydrolysis method (B).^{1,20}

the acid pipette connected to the reaction vessel and the only exit of the system is in the measuring cylinder, which allows the water to come out to the tank. The volume of water that leaves the measuring cylinder is the sum of two volumes: the added acidic solution plus the volume of gas produced in the reaction.

The method appears to be much simpler in comparison with the hydrogen evolution method, as parameters such as the pressure head of the water or water vapour pressure at the temperature of the experiment do not play a role when determining the volume of H_2 produced. Alternatively, to determine the exact gas quantity produced during the BH_4^- hydrolysis, a manometer can be used instead of an inverted measuring cylinder. This method is based on the use of a calibration curve: plots of the volume of water that leaves the measuring cylinder *versus* the mass of pure NaBH_4 show linear trends and thus can be used as an analytical calibration curve. Consequently, when a sample is analysed using the hydride hydrolysis method, the measured volume immediately indicates the NaBH_4 content in the sample. Of course, it is assumed that the calibration curve and the NaBH_4 sample analysis are performed under the same temperature and pressure conditions.

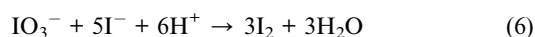
Good reproducibility is observed with the hydride hydrolysis method, but the obtained LOD of 500 ppm is still too high to meet the requirements of some applications, such as NaBH_4 monitoring during its electrochemical synthesis. Further design optimisation is required in order to reduce the LOD and to enable broader application of the method.

Iodate method

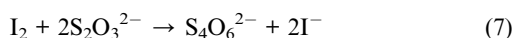
Apart from the measurements of H_2 released, the amount of NaBH_4 in a sample can conveniently be determined by the use of titrimetric methods. Among them, the iodate method is still fairly a popular approach despite being more than 50 years old and exhibiting several drawbacks. The iodate method was developed by Lyttle *et al.* in 1952²⁵ and is based upon the oxidation of BH_4^- with an excess of IO_3^- , which is, after conversion of excess to I_2 , back titrated using $\text{S}_2\text{O}_3^{2-}$. The procedure starts by adding a sample of NaBH_4 , solid or in alkaline solution, to an excess of standard potassium iodate (KIO_3):



If a solid sample of NaBH_4 is used, sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be added to the IO_3^- solution. Subsequently, I^- is added, followed by addition of an acid:



Liberated I_2 is then titrated with standard $\text{S}_2\text{O}_3^{2-}$:



Lyttle and co-workers first reported very good agreement of this method with the standard hydrogen evolution procedure, with slightly higher values obtained by the iodate method (see below). They claimed that the BH_4^- reduction of IO_3^- is an instantaneous reaction as the presence of alkali in amounts greater than that necessary to neutralise all boric acid (H_3BO_3) formed had no effect on the reaction between IO_3^- and BH_4^- . Based on their study, they concluded that commercial NaBH_4 quickly deteriorates in aqueous medium, but is fairly stable in alkaline medium, where a greater stability is observed at the higher pH values.

However, several authors have reported erroneous results obtained with the iodate method.^{20,35,51} This procedure also has the disadvantage of having an overall lengthy analysis time. Gyenge and Oloman³⁵ suggested that erroneously high BH_4^- concentrations obtained with the iodate method could be due to the insufficient acidification of the highly alkaline samples. During I_2 titration with $\text{S}_2\text{O}_3^{2-}$ in samples of insufficiently low pH, hypoiodite (IO^-) is generated as an intermediate and eight times less $\text{S}_2\text{O}_3^{2-}$ is consumed per mole of I_2 , causing the process described in eqn (7) to be replaced by that described by eqn (8).³⁵



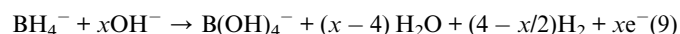
With back-titration, the consumption of a smaller amount of $\text{S}_2\text{O}_3^{2-}$ can be interpreted mistakenly as the presence of a certain amount of BH_4^- in the sample leading to higher total BH_4^- values. Additionally, formation of a black precipitate upon the addition of potassium iodide (KI) has been observed during the BH_4^- analysis of some samples making the results particularly inaccurate.³⁵ Incorrect NaBH_4 content values, in general,

arise from its intrinsic instability in aqueous medium that produces unreliable analytical results. H_2 gas liberated in the BH_4^- decomposition process may also lead to an overestimate of the BH_4^- in a sample. The BH_4^- hydrolysis process is slower in alkaline medium, but still it is not completely avoided even at the highest pH. Thereafter, special, extensive precautions are required for the iodate method to give quantitatively accurate results.

When comparing the iodate method with the hydrogen evolution method, it can be noticed that the first one has a detection limit as low as 20 ppm, while the second one only detects quantities above 100 ppm. Both these methods are normally used for regular assays but these detection limits allow them to also be used for trace analysis. Though these two methods are almost sixty years old and have several drawbacks, they are still the most commonly used ones in the borohydride manufacturing companies. The hydrogen evolution method is used for finished goods where high accuracy and precision are required. The iodate method is used for in-process control, in kinetic studies and by customers who avoid using the hydrogen evolution method since it requires more specialised equipment than that usually available in the laboratory. The above discussion shows that development of new methods for NaBH_4 analysis, both qualitative and quantitative, is necessary.

Electrochemical methods

Electrochemical methods are finding broad application in sensing of both organic and inorganic substances,^{52–54} and potentiometric and voltammetric methods have been studied for the determination of BH_4^- in aqueous solutions as well. These methods include potentiometric titration, linear scan voltammetry (LSV), cyclic voltammetry (CV), and square wave voltammetry (SWV), all based on the borohydride oxidation reaction (BOR) that in highly alkaline solutions ($\text{pH} > 12$) proceeds as:



where x is the coulombic number, *i.e.* the actual number of electrons transferred and it depends on the anode material.⁵⁵ The electrode material to be used in NaBH_4 analysis has to be inactive for BH_4^- hydrolysis and inactive for oxidation–reduction of any other species present in the system in the potential window used. Some authors⁵¹ argue that electrochemical methods have the disadvantage of the competition between the BOR (eqn (9)) and BH_4^- hydrolysis process yielding H_2 gas evolution (*viz.* eqn (4)), and the possible catalytic effect of the anode material.^{56,57} Strong alkaline conditions slow the competitive hydrolysis reaction, which is mainly dependent on the electrode material.⁵⁶ Still, the actual number of electrons transferred in the BOR at high pH is usually lower than the expected value of 8,^{58–60} indicating that the hydrolysis reaction cannot be completely avoided.⁶¹ Also, the heterogeneous processes proceeding on the electrode surface by the reaction intermediates can give rise to mutually superimposed Faradaic currents, which consequently affect the reliability of the main

BOR current peak as an analytical signal and the method selectivity.⁵¹

Potentiometric techniques have been known to allow monitoring of numerous compounds, and therefore the use of potentiometry for determination of BH_4^- in a wide range of concentrations was proposed.^{36–38} Amendola *et al.*³⁸ suggested a non-destructive, *in situ* potentiometric titration technique for detection of relatively low NaBH_4 concentrations in the range from 10^{-3} to 10^{-4} M. The method is based upon a metal open circuit potential (OCP) change with BH_4^- concentration. The study was performed with three different electrode materials: platinum (Pt), rhodium (Rh) and cobalt (Co) and the BH_4^- concentration could be determined by simply measuring the OCPs of these electrodes in BH_4^- solutions. It was shown that for a certain electrode material it is possible to determine a characteristic potential for a given NaBH_4 concentration and, therefore, to obtain curves that can help determine the amount of BH_4^- .

For all three studied metals, it was found that the OCP as a function of NaBH_4 concentration in 20% NaOH undergoes step-function change at a certain BH_4^- concentration value.³⁸ For example, Co OCP was relatively constant at approximately -0.95 V vs. the saturated calomel electrode (SCE) reference, for BH_4^- concentrations below 6×10^{-3} M. At higher concentrations, the Co OCP changed abruptly to *ca.* -1.3 V vs. SCE and remained relatively constant at that potential. Two different operating mechanisms were proposed in order to explain step function changes in the three metal OCPs as a function of BH_4^- concentration;³⁸ one that describes the behaviour of Rh and Pt, and another that explains Co behaviour. All of these transition metals are capable of catalysing BH_4^- hydrolysis even in strongly alkaline solutions⁶² with their catalytic activity towards BH_4^- hydrolysis following the trend: $\text{Rh} > \text{Pt} > \text{Co}$. It was shown that H_2 formed during BH_4^- hydrolysis adsorbs on the Pt and Rh metal surface (which are much stronger BH_4^- hydrolysis catalysts than Co). This adsorbed H_2 is responsible for the more negative OCP observed on these metals at high BH_4^- concentrations. Once the metal surface is covered with adsorbed H_2 , its OCP sharply changes. For Co, at high BH_4^- concentrations, OCP is due to the BOR on bare metal as given by eqn (1), whose reduction potential is -1.48 V vs. SCE.³⁸ Abrupt changes in the Co OCP as a function of BH_4^- concentration are, thus, due to competition between hydroxide removal from Co, and BOR on bare Co.

Santos and Sequeira studied thirteen different materials as indicator electrodes for NaBH_4 monitoring in alkaline medium using the potentiometric method.⁵⁶ These included Pt, Au, palladium (Pd), cadmium (Cd), copper (Cu), nickel (Ni), iron (Fe), AISI 304 stainless steel, zinc (Zn), molybdenum (Mo), niobium (Nb), graphite and silicon (Si). It was shown that materials whose OCP is significantly different in the absence and in the presence of NaBH_4 in 4 M NaOH supporting electrolyte have the potential to be used as indicator electrodes in a novel BH_4^- microelectrode sensor. For example, Pd OCP starts to decrease for NaBH_4 concentrations above 10^{-2} M, with an OCP response range of about 1 V (see Fig. 3A). Analysis of the obtained OCP vs. NaBH_4 concentration plots was performed

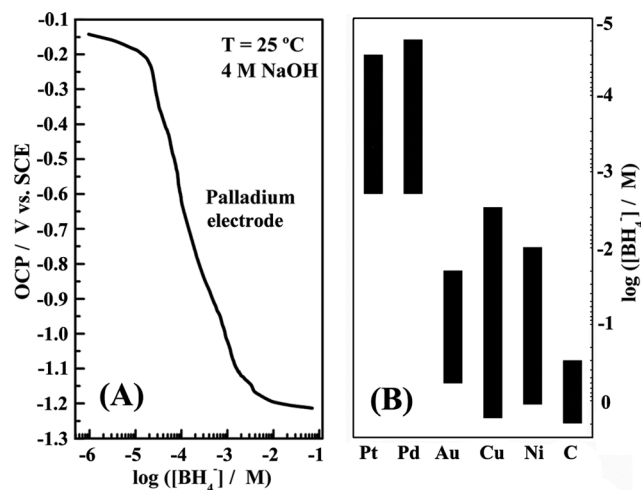


Fig. 3 OCP vs. BH_4^- concentration for a Pd electrode at 25 °C in 4 M NaOH solution (A) with the list of top materials for BH_4^- detection in specific concentration ranges (B).⁵⁶

using thermodynamic data^{63–65} and complemented by additional OCP measurements in H_2 -saturated NaBH_4 -free alkaline solutions. The later kinetic experiments were used for differentiation between the effects of NaBH_4 and H_2 on the OCPs of the indicator electrodes. Among the tested materials, Pt, Pd, Au, Co, Ni and graphite were found to be the top indicator electrode materials, each one for each specific NaBH_4 concentration range where its OCP change takes place (Fig. 3B). This potentiometric titration method based on the OCP response of different indicator electrode materials proved to be fast and relatively precise, suggesting further improvements for application in a microelectrode array for BH_4^- sensing.⁵⁶

Determination of NaBH_4 in a solution by voltammetric methods was first proposed by Mirkin and Bard in 1991³⁹ as these methods fulfil major sensor requirements of being simple, rapid and accurate. Moreover, voltammetric methods

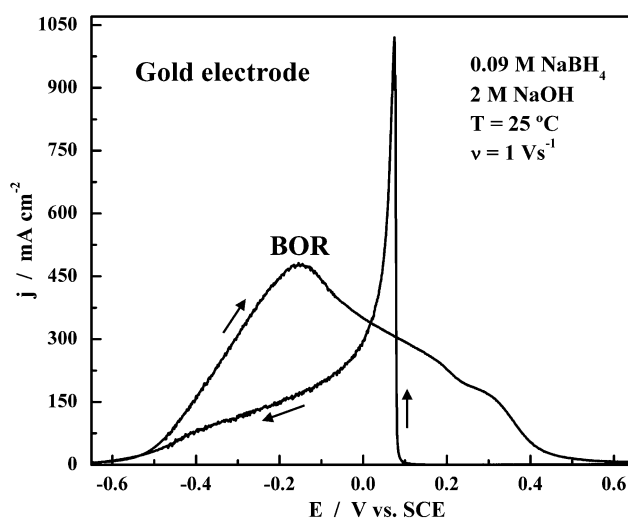
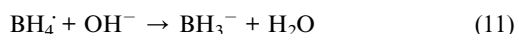


Fig. 4 CV of an Au working electrode recorded in 0.09 M NaBH_4 + 2 M NaOH solution using a scan rate of 0.5 V s^{-1} at the temperature of 25 °C.⁵⁷

have the advantage of allowing continuous monitoring of the NaBH_4 concentration directly in a reaction system, such as an electrochemical cell, by simply inserting the electrodes directly into the cell during the studied process.

Gold electrodes in alkaline NaBH_4 solution gave linear scan voltammograms with a well-defined signal suitable for analytical determinations (see Fig. 4), unlike for example Ni and Pt electrodes.³⁹ A single wave due to the BH_4^- oxidation could be observed between -0.364 and $+0.136$ V vs. SCE at voltammograms recorded with a Au electrode in NaBH_4 solutions of different concentrations in 0.2 and 2 M NaOH supporting electrolyte.^{39,57,66} There were no significant differences between successive voltammograms at the Au electrode indicating that the electrode surface does not undergo any irreversible changes during this process. By performing fast CV studies using a Au microelectrode, Mirkin *et al.* have found at least two reversible electrochemical stages.⁶⁶ The overall (kinetic) irreversibility of the process is caused by very unstable intermediate products that can be reduced only under conditions of a sufficiently fast electrochemical method. Although the process forming this intermediate is a two-electron process, the first intermediate cannot be the rather stable BH_3OH^- , as Mirkin and Bard first suggested.³⁹ Instead, the authors have proposed a borane species, such as monoborane (BH_3) or diborane (B_2H_6). However, the following six-electron transfer could not be elucidated even using very high scan rates up to 3×10^4 V s⁻¹. Therefore it was suggested that the BH_4^- oxidation on Au is an eight-electron process with an ECE reaction mechanism sequence.⁶⁶



It has been proposed that the BH_3 formed in the ECE sequence (eqn (10–12)) is further engaged in fast reactions with OH^- and/or dimerisation, yielding species that are further oxidised to produce the total eight-electron wave.⁶⁶

The very small background current at an Au electrode in alkaline solution in this potential region allows the use of voltammetry for detection of low levels of BH_4^- . The interference could be expected only by substances that can be oxidised or promote the oxidation of Au electrode in alkaline solution in the potential region from 0 to -0.4 V vs. SCE or that can absorb onto an Au surface. The high selectivity of voltammetry is considered as the most important advantage when compared with other methods such as the iodate method. During BH_4^- electrosynthesis attempts, the iodate method suggested erroneously high concentrations of BH_4^- in some solutions due to other reductants produced during the electrolysis process;²⁰ using the voltammetric method, no traces of BH_4^- were found in these solutions following electrolysis.^{20,39}

CV has been further studied as a method for BH_4^- determination.^{67,68} McLafferty and co-workers⁶⁷ tested CV with a Au disc working electrode as an *in situ* probe for NaBH_4

determination. A decrease in peak current was noted on subsequent cycles, though linear dependence of peak current on the NaBH_4 concentration was observed for all ten cycles. Thereafter, the authors suggested that CV, as a relatively inexpensive and easily implemented technique, is still an acceptable quantitative method as long as the same cycle is used for the concentration analysis. Colominas *et al.*⁶⁸ developed a simple CV method with Au microelectrode disc working electrodes for analysis of NaBH_4 in aqueous solutions, for example in catholyte solutions during electrochemical reduction of H_3BO_3 or BO_2^- experiments. Better linearity in peak current with concentration was noted for the lower concentration range of 0.2 to 1 mM NaBH_4 in pH 12 solution. The sensitivity was evaluated to be $0.0163 \text{ mA mM}^{-1} \text{ NaBH}_4$ for a 1 mm Au electrode and $0.516 \text{ mA mM}^{-1} \text{ NaBH}_4$ for a 6 mm electrode. This method cannot be used for absolute qualitative analysis of BH_4^- , but can be employed for its semi-quantitative or quantitative analysis, depending on the NaBH_4 concentration range in an aqueous solution. Therefore, it is proposed to serve as a simple and relatively inexpensive complement to other qualitative methods such as ^{11}B NMR.

NaBH_4 determination in alkaline medium was also studied using SWV with a Au working electrode.⁴⁰ This method gives much sharper and better separated peaks compared to CV and polarography and resulted in a limit of detection of $3 \times 10^{-5} \text{ M}$, much lower compared to those obtained with the spectrochemical and titrimetric methods. Au was found to be the most suitable electrode material for the voltammetric determination of BH_4^- . The Au CV peak current gave a linear response by the use of a standard addition method at a concentration level of 10^{-5} M NaBH_4 . Au electrodes were found to give rise to more satisfactory results compared to Pt, Ni and Pd electrodes due to the fact that Pt and Pd electrodes oxidise the BH_4^- at the transpassive oxide formation region and the electrocatalytic activity of the Ni electrode becomes very low as the medium is made more alkaline due to the formation of non-conducting Ni hydroxides. Moreover, Au electrodes are known to be relatively inactive with respect to BH_4^- hydrolysis accompanied by H_2 evolution.

Infrared spectroscopy

BH_4^- can display a characteristic infrared (IR) spectrum due to the vibration of its B–H covalent bonds. For a non-linear

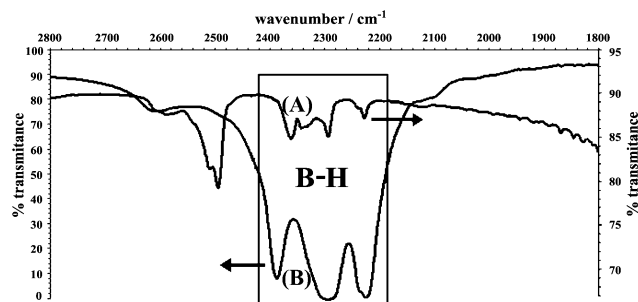


Fig. 5 IR spectra of the electrosynthesis reaction product obtained in aqueous medium (A) with the IR spectra of pure NaBH_4 (B).²⁰

Table 2 Characteristic B–H bond vibration bands in borohydride infrared spectra

	Frequency/cm ⁻¹
NaBH ₄ (ref. 20)	2225, 2293, 2359
NaBH ₄ (ref. 51)	2224, 2291, 2386
NaBH ₄ (ref. 69)	2200–2640
NaBH ₄ (ref. 70)	2229, 2305, 2400
NaBH ₄ (ref. 71)	2213
NaBH ₄ (ref. 72)	2217, 2284, 2404
NaBH ₄ (ref. 73)	2218, 2283
NaBH ₄ (ref. 74)	2115, 2168

polyatomic ion as the BH₄⁻ ion, 9 modes of vibration are expected according to the rule of the $3N - 6$ modes of vibration, where N is the number of atoms. Experimental studies performed in order to identify these vibrating bands of BH₄⁻ group have shown that three B–H stretching vibration bands observed in the NaBH₄ synthesis^{20,69} reaction product (Fig. 5) are in good agreement with the characteristic wavenumbers for the B–H bond vibrations reported in the literature (Table 2). However, it was argued that the IR spectroscopy method for BH₄⁻ monitoring has the disadvantage of being time-consuming, as sample preparation (complete drying of the sample followed by preparation of KBr/sample pellet) requires time.²⁰

Recently, Fourier transform infrared spectroscopy (FTIR) has been proposed as a method for determination of NaBH₄ and its purity.⁵¹ FTIR spectra of NaBH₄ samples showed well-defined sharp bands. A single peak due to the wagging band of BH₄ could be observed at 1126 cm⁻¹, with three distinct and sharp bands at 2224, 2291 and 2386 cm⁻¹, and a small contribution at 2594 cm⁻¹ due to stretching modes of the BH₄ group. The three well-defined bands correspond to a mixture of stretching modes involving different H atoms of the BH₄ moiety, while the small one at 2594 cm⁻¹ corresponds to the single stretching mode of B–H₃. FTIR methodology has the advantage of assessing the purity of NaBH₄ in the solid state, so previously mentioned problems related to the competition of BOR and the hydrolysis process in aqueous solutions are here avoided. Additionally, FTIR spectra can be successfully employed for the assessment of the presence of BO₂⁻. Namely, the NaBO₂ band appears at 1437 cm⁻¹ which does not overlap with those of NaBH₄. Thereafter, FTIR signals represent good fingerprints for qualitative detection of NaBH₄ and NaBO₂. Quantitative analysis attempts were performed using the Lambert–Beer law based on the ratio between NaBH₄ and NaBO₂. This FTIR NaBH₄ determination procedure is based upon a calibration curve, so the calculated results can slightly differ from the real value. Still, when assessing the NaBH₄ purity by FTIR, voltammetry and the iodometric method, it can be noticed that the standard deviation is much smaller in the case of FTIR than in cases of voltammetric and iodometric methods. Analysis of an old NaBH₄ sample by FTIR gave a purity of 81 mol% (range: 78–83%, number of measurements $n_x = 5$), while voltammetry gave a value of 86.3 mol% (range: 76.4–92.9%, $n_x = 5$) and the iodometric method value of 82.8 wt.% (range: 75.0–89.1%, $n_x = 6$). Still, the proposed FTIR analysis, due to its simplicity along with the above mentioned advantages, can be efficiently used for the

analysis of the purity of solid NaBH₄ and quality control purposes.

Nuclear magnetic resonance spectroscopy

NMR analysis, specifically ¹H and ¹¹B NMR, for the identification of NaBH₄ present in a system, *i.e.* qualitative analysis of samples, has been attempted.^{47–50} The magnetic equivalence of all four H atoms in NaBH₄ implies that there will be only one resonance in the ¹H NMR spectrum. However, due to the presence of the magnetically active boron nucleus, the signal will be split by the coupling to this boron nucleus. Indeed, ¹H NMR analysis of NaBH₄ (ref. 47) revealed four equally intense singlet peaks due to the coupling with ¹¹B. These signals appear at –0.882 ppm (–52.92 Hz), 0.462 ppm (27.72 Hz), 1.803 ppm (108.18 Hz) and 3.149 ppm (188.94 Hz). Furthermore, there are seven peaks of equal intensity that result from coupling with boron isotope ¹⁰B. These peaks are not as intense as those corresponding to coupling with ¹¹B because the natural abundance of ¹⁰B (19.6%) is much less than that of ¹¹B (80.4%). The appearance of the ¹H resonance splitting into a four-line multiplet by coupling to ¹¹B (spin $I = 3/2$) and a seven-line multiplet for ¹⁰B ($I = 3$) is in accordance with the rule that multiplicity, *i.e.* the number of lines in a multiplet, is equal to $2nI + 1$, with n , the number of neighbouring protons, being 1 for both isotopes.

When performing ¹¹B NMR analysis in a solution where BH₄⁻ is not the only species with boron present, the peaks appear at different locations due to the effect of the electronegativity of the adjacent atoms. Thus, in the case of a solution of BH₄⁻ and BO₂⁻ in the presence of the standard boron trifluoride diethyl etherate (BF₃·Et₂O), the spectrum will show 3 peaks, where the order will be BF₃·Et₂O, BO₂⁻ and BH₄⁻ from the lower to the higher chemical shift. The reason why this particular order is observed is because the more electronegative the adjacent atom is, then the more deshielded the boron nucleus will be. This will decrease the necessary magnetic field to apply in order for the nucleus to achieve resonance. With the electronegativity order of fluorine, oxygen and hydrogen atoms as follows, $F > O > H$, then the order of appearance in the ¹¹B NMR spectra should be BF₃ > BO₂⁻ > BH₄⁻. Expected chemical shifts of NaBH₄ for the ¹¹B NMR are –38.7 in water, –42.2 in diglyme, and –25.3 in dimethylether (DME), relative to BF₃·Et₂O.⁷⁵

Recently, solution-state ¹¹B NMR analysis was used for following the BH₄⁻ hydrolysis process, determination of its mechanism and products.⁴⁸ It was suggested that the relative area under each spectral peak can be calibrated to give the molar concentration of a certain boron-containing species. Different chemical shifts of BH₄⁻ and B(OH)₄⁻ species make possible the distinguishability of different species in the spectrum. *In situ* NMR analysis enables following the transformation of BH₄⁻ to B(OH)₄⁻ in time, with individual concentrations of these ions being determined.

Conclusions

The analytical techniques for identification and quantification of the NaBH₄ presence are summarised herein and the most

relevant among them are described in detail. Some of these methods are around sixty years old but new endeavours in the field resulted in the development of promising new techniques. Until recently, the most commonly employed techniques for BH_4^- quantitative analysis were the hydrogen evolution method and the iodate method. Another gasometric method, named hydride hydrolysis method, has been developed and successfully tested. Electrochemical methods, potentiometry and voltammetry have shown to be potentially good alternatives for BH_4^- analysis due to their high sensitivity. For the identification of the presence of the borohydride, other techniques were tested such as ^{11}B NMR and ^1H NMR and IR spectroscopy. The two groups of techniques often complement each other and they are combined in order to obtain accurate qualitative and quantitative results. Based on the above overview and analysis of the existing analytical methods for NaBH_4 monitoring, it is clear that further work is needed in developing accurate NaBH_4 sensing tools. We anticipate that the most likely route to take is further development of the electroanalytical methods as they fulfil the requirements of low cost, rapidness, simplicity and accuracy, and enable direct monitoring of NaBH_4 in a reaction system.

Acknowledgements

The authors would like to thank Fundação para a Ciência e a Tecnologia (FCT, Portugal) for postdoctoral research grants no. SFRH/BPD/63226/2009 (D.M.F. Santos) and SFRH/BPD/77768/2011 (B. Šljukić).

References

- 1 *Sodium Borohydride Digest*, ed. J. Yamamoto, Rohm and Haas, USA, 2003.
- 2 D. M. F. Santos and C. A. C. Sequeira, *Renew. Sust. Energy Rev.*, 2011, **15**, 3980.
- 3 H. I. Schlesinger and H. C. Brown, Methods of preparing alkali metal borohydrides, *US Pat.*, 2534533, 1950.
- 4 H. I. Schlesinger, H. C. Brown, B. Abraham, A. C. Bond, N. Davidson, A. E. Finholt, J. R. Gilbreath, H. Hoekstra, L. Horvitz, E. K. Hyde, J. J. Katz, J. Knight, R. A. Lad, D. L. Mayfield, L. Rapp, D. M. Ritter, A. M. Schwartz, I. Sheft, L. D. Tuck and A. O. Walker, *J. Am. Chem. Soc.*, 1953, **75**, 186.
- 5 H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, 1953, **75**, 215.
- 6 U. B. Demirci and P. Miele, *C. R. Chim.*, 2009, **12**, 943.
- 7 J. Ma, N. A. Choudhury and Y. Sahai, *Renew. Sust. Energy Rev.*, 2010, **14**, 183.
- 8 C. P. de Leon, F. C. Walsh, D. Pletcher, D. J. Browning and J. B. Lakeman, *J. Power Sources*, 2006, **155**, 172.
- 9 Y. Kojima, Y. Kawai, H. Nakanishi and S. Matsumoto, *J. Power Sources*, 2004, **135**, 36.
- 10 *Lange's Handbook of Chemistry*, ed. J. A. Dean, McGraw-Hill, New York, 15th edn, 1999.
- 11 M. E. Indig and R. N. Snyder, *J. Electrochem. Soc.*, 1965, **109**, 1104.
- 12 R. Jasinski, *Electrochem. Technol.*, 1965, **3**, 40.
- 13 *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. J. I. Kroschwitz, John Wiley & Sons, New York, 4th edn, vol. 4, 1992.
- 14 G. Broja and W. Schlabacher, Process for the production of alkali metal borohydrides, *DE Pat.* 1108670, 1959.
- 15 F. Schubert, K. Lang and W. Schlabacher, Process for the production of borohydrides, *DE Pat.* 1067005, 1959.
- 16 W. Büchner and H. Niederprüm, *Pure Appl. Chem.*, 1977, **49**, 733.
- 17 Z. P. Li, N. Morigasaki, B. H. Liu and S. Suda, *J. Alloys Compd.*, 2003, **349**, 232.
- 18 Y. Kojima and T. Haga, *Int. J. Hydrogen Energy*, 2003, **28**, 989.
- 19 Z. P. Li, B. H. Liu, N. Morigasaki and S. Suda, *J. Alloys Compd.*, 2003, **354**, 243.
- 20 D. M. F. Santos and C. A. C. Sequeira, *Int. J. Hydrogen Energy*, 2010, **35**, 9851.
- 21 Y. Sun and Z. Liang, Electrochemical process for preparing borohydride, *CN Pat. Appl.* 1396307A, 2003.
- 22 L. J. Guilbault, E. A. Sullivan, N. M. Sullivan and N. L. Weinberg, Electrolytic method for producing borohydride, *US Pat.*, 20050224364, 2005.
- 23 W. D. Davis, L. S. Mason and G. Stegeman, *J. Am. Chem. Soc.*, 1949, **71**, 2775.
- 24 J. A. Krynsky, J. E. Johnson and H. W. Carhart, *Anal. Chem.*, 1948, **20**, 311.
- 25 D. A. Lytle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, 1952, **24**, 1843.
- 26 S. W. Chaikin, *Anal. Chem.*, 1953, **25**, 831.
- 27 H. Dong, H. Yang, X. Ai and C. Cha, *Int. J. Hydrogen Energy*, 2003, **28**, 1095.
- 28 Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai and H. Hayashi, *Int. J. Hydrogen Energy*, 2003, **27**, 1029.
- 29 I. E. Lichtenstein and J. S. Mras, *J. Franklin Inst.*, 1966, **281**, 481.
- 30 E. H. Jensen, *A study on sodium borohydride, with special reference to its analytical application in organic chemistry*, Nyt Nordisk Forlag, Arnold Busck, Copenhagen, 1954.
- 31 A. R. Shah, D. K. Padma and A. R. Vasudeva Murthy, *Analyst*, 1972, **97**, 17.
- 32 H. C. Brown and A. C. Boyd Jr, *Anal. Chem.*, 1955, **27**, 156.
- 33 T. Freund, *J. Inorg. Nucl. Chem.*, 1959, **9**, 246.
- 34 B. Elamin and G. E. Means, *Anal. Chim. Acta*, 1979, **107**, 405.
- 35 E. L. Gyenge and C. W. Oloman, *J. Appl. Electrochem.*, 1998, **28**, 1147.
- 36 R. L. Pecsok, *J. Am. Chem. Soc.*, 1953, **75**, 2862.
- 37 J. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, 1965, **87**, 1692.
- 38 S. Amendola, P. Onnerud, M. T. Kelly and M. Binder, *Talanta*, 1999, **49**, 267.
- 39 M. V. Mirkin and A. J. Bard, *Anal. Chem.*, 1991, **63**, 532.
- 40 H. Çelikkan, H. Aydin and M. L. Aksu, *Turk. J. Chem.*, 2005, **29**, 519.
- 41 K. A. Kobe and F. H. Kenton, *Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 76.

- 42 D. A. Werner, C. C. Huang and D. Aminoff, *Anal. Biochem.*, 1973, **54**, 554.
- 43 C. A. Bunton, S. K. Huang and C. H. Paik, *Tetrahedron Lett.*, 1976, **17**, 1445.
- 44 C. N. Rudie and P. R. Demko, *J. Am. Oil Chem. Soc.*, 1979, **56**, 520.
- 45 W. H. Hill, J. M. Merrill, R. H. Larsen, D. L. Hill and J. F. Heacock, *AIHAJ*, 1959, **20**, 5.
- 46 J.-F. Biemann and H. J. Callot, *Bull. Soc. Chim. Fr.*, 1968, **3**, 1159.
- 47 R. Hanson, M. Grandbois and K. Shafer, *Magnetic susceptibility and multinuclear NMR*, <http://ed.augie.edu/~rrhanson/E9report.html>.
- 48 J. Hannauer, U. B. Demirci, C. Geantet, J. M. Herrmann and P. Miele, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3809.
- 49 L. Yu and M. A. Matthews, *Int. J. Hydrogen Energy*, 2011, **36**, 7416.
- 50 J. Andrieux, U. B. Demirci, J. Hannauer, C. Gervais, C. Goutaudier and P. Miele, *Int. J. Hydrogen Energy*, 2011, **36**, 224.
- 51 S. Botasini and E. Méndez, *J. Power Sources*, 2012, **197**, 218.
- 52 B. Šljukić, R. O. Kadara and C. E. Banks, *Anal. Methods*, 2011, **3**, 105.
- 53 B. Šljukić, C. E. Banks, A. Crossley and R. G. Compton, *Anal. Chim. Acta*, 2007, **587**, 240.
- 54 B. Šljukić, C. E. Banks, C. Salter, A. Crossley and R. G. Compton, *Analyst*, 2006, **131**, 670.
- 55 J. H. Wee, *J. Power Sources*, 2006, **155**, 329.
- 56 D. M. F. Santos and C. A. C. Sequeira, *J. Electroanal. Chem.*, 2009, **627**, 1.
- 57 D. M. F. Santos and C. A. C. Sequeira, *Electrochim. Acta*, 2010, **55**, 6775.
- 58 S. C. Amendola, P. Onnerud, M. T. Kelly, P. J. Petillo, S. L. Sharp-Goldman and M. Binder, *J. Power Sources*, 1999, **84**, 130.
- 59 E. Gyenge, *Electrochim. Acta*, 2004, **49**, 965.
- 60 G. Denuault, M. V. Mirkin and A. J. Bard, *J. Electroanal. Chem.*, 1991, **308**, 27.
- 61 R. Retnamma, A. Q. Novais and C. M. Rangel, *Int. J. Hydrogen Energy*, 2011, **36**, 9772.
- 62 H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, 1962, **84**, 1493.
- 63 M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, NACE International, Houston, TX, 2nd edn, 1974.
- 64 *Standard Potentials in Aqueous Solution*, ed. A. J. Bard, R. Parsons and J. Jordan, Marcel Dekker, New York, 1985.
- 65 M. W. Chase Jr, *Nist-janaf Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data*, Monograph 9, Am. Chem. Soc., Washington, DC, 1998.
- 66 M. V. Mirkin, H. Yang and A. J. Bard, *J. Electrochem. Soc.*, 1992, **139**, 2212.
- 67 J. B. McLafferty, J. C. Tokash, Y.-C. Zhang, W. J. Coulson and D. D. Macdonald, *ECS Trans.*, 2007, **2**, 19.
- 68 S. Colominas, J. B. McLafferty and D. D. Macdonald, *Electrochim. Acta*, 2009, **54**, 3575.
- 69 C. J. H. Schutte, *Spectrochim. Acta*, 1960, **16**, 1054.
- 70 E. Pretsch, T. Clerc, J. Seibl and W. Simon, *Tables of spectral data for structure determination of organic compounds*, Springer-Verlag, Berlin, 1983.
- 71 T. J. Tague Jr and L. Andrews, *J. Am. Chem. Soc.*, 1994, **116**, 4970.
- 72 G. Renaudin, S. Gomes, H. Hagemann, L. Keller and K. Yvon, *J. Alloys Compd.*, 2004, **375**, 98.
- 73 *Spectral database for organic compounds*, National institute of advanced industrial science and technology of Japan, <http://riodb.ibase.aist.go.jp/riohomee.html>.
- 74 J. Sirak, J. Graham, N. Heston, G. Ihas and G. Labbe, *Trapping and Matrix Isolation of Chemical Species in Solid Hydrogen. Research Program: Research Experiences for Undergraduates*, Department of Physics, University of Florida, 2004.
- 75 ¹¹B NMR chemical shifts, San Diego State University, <http://www.chemistry.sdsu.edu/research/BNMR/6.html>.