



## Determination of boron contained in a cementitious matrix used for the transport or the storage of radioactive waste



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### ABSTRACT

Neutron shielding materials, containing boron as the neutron absorbing element, are used as a biological protection in nuclear materials storage and transportation casks. In the present work, boron in the form of colemanite powder ( $\text{Ca}_2\text{B}_6\text{O}_{11}\cdot 5\text{H}_2\text{O}$ ), was incorporated in a cementitious matrix. Localized quantification of boron is required to confirm that a homogeneous distribution in the matrix has been achieved. The elemental analysis of a neutron-shielding cement matrix containing boron in minor quantities (less than 1 to 2 wt% of boron) was made.

The elemental analysis of mineral materials requires dissolution in most cases. The first challenge encountered was the determination of a dissolution protocol that leads to total dissolution of materials, namely cement, colemanite and other minerals, without losing volatile compounds such as borates. The next challenge was the elemental analysis itself. Numerous elements are present in the obtained solutions and could interfere with boron determination. Different boron titration techniques are reviewed out in order to choose the most suitable.

In practice, the quantification of boron using an ICP-AES was very satisfactory but a second titration technique was needed to confirm ICP-AES results. The titration of boron using the carminic acid assay was chosen. In order to remove interfering ions, a simple laboratory made purification device was set up. A protocol was developed in order to measure the boron concentration by the carminic acid assay. This led to consistent data with ICP-AES results.

## 1. Introduction

Boron is widely used in the glass industry and ceramics industry as fluxes. It is studied in natural sciences as it is necessary for the development of plants (Keren, 1996). Boron is also essential in the nuclear industry thanks to its ability to absorb neutrons (Machiels and Lambert, 2009; Yazar and Bayülken, 1994; Okuno and Iikura, 2014). Each year, approximately 980 000 nuclear material packages are transported in France alone. Several sectors are concerned: nuclear industry (12%), health, certification, industry or research (IRSN, 2014). Robatel Industries, a nuclear subcontractor, has been developing containers for transportation and storage of radioactive wastes which include cementitious materials containing boron used as neutron and thermal protections. These cementitious materials containing boron participate in the biological protection of surrounding people. A lack of boron in any region of the material could enable neutrons to escape from the cask and irradiate people. The neutron shielding effect of the

cementitious material thus requires an homogeneous distribution of boron within the cement matrix while its initial content is fairly low (< 1 to 2 wt%). Therefore, a reliable boron determination technique is thus necessary to check the homogeneity of boron distribution within the whole container. This also implies using a reliable dissolution technique in order to dissolve the entire mineral sample prior to analysis. A review of the current dissolution and determination techniques for boron is presented in the next paragraph. Then, the results concerning the sample analysis on a cementitious matrix with a low boron content are discussed.

## 2. State of the art

### 2.1. Dissolution techniques

Two main approaches can be distinguished for dissolution of mineral samples: dry digestion by fusion and wet digestion. The goal of

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those techniques is to dissolve the whole sample so that all elements are in ionic form in an aqueous medium. This is an essential requirement to measure concentrations accurately.

Dry digestion consists of mixing a powder of the sample to be analyzed with a flux powder. The most common fluxes are alkali metal salts: ( $\text{Na}_2\text{CO}_3$ ;  $\text{K}_2\text{CO}_3$ ). A eutectic mixture containing 0.59 mole of  $\text{Na}_2\text{CO}_3$  and 0.41 mole of  $\text{K}_2\text{CO}_3$  is often used for its low melting point (709 °C). Lithium metaborate ( $\text{LiBO}_2$ ) or lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) are also widely used but are not suitable for the present case where boron determination is required. The powder mix is fired above the melting point in a Pt crucible in order to obtain a liquid where all the components should be nicely dissolved. After cooling, the melt can be dissolved with deionized water or alternatively acidic and basic solutions. Salts can precipitate at this stage, which can be separated from the solution by filtration or centrifugation. A solution containing all the dissolved elements from the sample powder and the fluxes is then obtained. The elements are in ionic form in the aqueous solution (Vernet and Govindaraju, 1993). The quantity of fluxes is ten times higher than the quantity of dissolved matter, which introduces many ions in the solution to be titrated. These ions may participate in matrix effects. Depending on the melting temperature, the temperature can be raised over 900 °C for roughly 1 h, which causes risks of boron volatilization in several forms like  $\text{B}_2\text{O}_3$ ,  $\text{HBO}_2$ ,  $\text{BO}$  (Wei et al., 1995; Snyder et al., 2006). Dry digestion using  $\text{Na}_2\text{CO}_3$  is however used by several authors (Keren, 1996; Gupta, 1966). Wilde (1973) mixes  $\text{NaF}$  and  $\text{Na}_2\text{CO}_3$  to form  $\text{BF}_4^-$  which concentration can be then measured using an ion selective electrode (ISE). Dry digestion applied to boron containing materials can lead to the formation of vitreous phases above 800 °C. Those phases are quite difficult to dissolve, like borosilicate glass.

Wet digestion is based on the use of acids or bases in different concentrations: sulfuric acid, nitric acid, hydrochloric acid, perchloric acid, hydrofluoric acid or aqua regia. The use of other chemicals can be noted like  $\text{CO}_2$  saturated water to form carbonic acid (Alkan et al., 1990; Davies et al., 1990) or ammonium chloride (Kum et al., 1994). In order to accelerate the dissolution, temperature and concentration can be increased. Other techniques can be used such as ultrasonic agitation, digestion in micro-wave devices (Çelik et al., 2017; Kuru et al., 2018), decomposition bombs (Skoog et al., 2004). Wet digestion shows advantages compared to dry digestion. Indeed, it is simpler and the absence of heat treatment reduces volatilization risks. Moreover, without fluxes, potentially interfering ions are discarded. Boric acid  $\text{H}_3\text{BO}_3$  volatilization can occur in boiling water (Skoog et al., 2004).  $\text{BF}_3$  volatilization is possible if boron reacts with HF but this phenomenon can be avoided by the addition of mannitol (Lécuyer et al., 2002; Luo et al., 2018). Industrial production of boric acid is based on the dilution of boron-rich minerals as colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11}\cdot 5\text{H}_2\text{O}$ ) in hot sulfuric acid  $\text{H}_2\text{SO}_4$  (boiling point 340 °C (Çelik et al., 2017)) (Davies et al., 1990; Çetin et al., 2001). During this dissolution, gypsum is formed by the reaction of calcium contained in colemanite with sulfate from sulfuric acid (Çetin et al., 2001; Bayca, 2013). Dissolution of colemanite with sulfuric acid can be accelerated by ultrasonic agitation (Okur et al., 2002) or using micro-wave reactors (Bayca, 2013). Bakhtar et al. (1989) developed a complex process of dissolution using hydrogen peroxide, hydrochloric acid and diluted fluorhydric acid to solubilize rocks including colemanite. They concluded colemanite can be dissolved in HCl 6M, without using HF, but the titration of the solution obtained gave too low concentrations of boron. Their method was reused by Ilić (Ilić, 1996) and gave better results than dry digestion ones. Another difficulty encountered is the unavailability of a mineral boron standard with certified boron concentration (Ilić, 1996). Dissolution of colemanite has been reported by several authors but dissolution of colemanite contained in minor quantities in cementitious materials like mortars or concretes has not been documented to our knowledge.

## 2.2. Boron determination techniques

Boron determination in drinking water has been described in numerous studies (Floquet et al., 2016; Bin Darwish et al., 2015; Kmiecik et al., 2016) using the techniques reported here. However, boron determination in a solid material is more complex; boron determination in minerals has been studied but not when the mineral is included in small quantities in a cement matrix as it is the case in the present study. Finding an adequate digestion process is the first step but a suitable method for the measurement of boron concentration in our materials is necessary. The literature suggests several techniques as detailed below.

The colorimetric titration by spectrophotometry of the complex formed between boric acid ( $\text{B}(\text{OH})_3$ ) and carminic acid ( $\text{C}_{22}\text{H}_{20}\text{O}_{13}$ ) has been widely used and often quoted as a reference technique (Kuru et al., 2018; Floquet et al., 2016; Callicoat and Wolszon, 1959; Brown, 1970). This assay is only possible in concentrated  $\text{H}_2\text{SO}_4$  medium, which is quite hazardous for the operator and difficult to perform. This assay is efficient, 5% precision has been reported (Okur et al., 2002) and has been developed for the purpose of determining boron concentration in water (Rodier et al., 2009). If interfering ions are present in the solution to titrate, overestimation of boron concentration can be observed (Çelik et al., 2017). Separation of boron is then necessary (Callicoat et al., 1959). Other assays for boron determination can be found in the literature such as titration of boron by complexation with curcumin ( $\text{C}_{21}\text{H}_{20}\text{O}_6$ ) (Berger and Troug, 1939), Azomethine-H ( $\text{C}_{17}\text{H}_{12}\text{NNaO}_8\text{S}_2\cdot \text{xH}_2\text{O}$ ) (Keren, 1996) or even methylene blue (Chu et al., 1990).

X-ray fluorescence (XRF) is one of the most used techniques for elemental analysis but the low atomic mass of boron implies the use of additional devices which are complex and expensive. This technique has the advantage of being applied to bulk samples, pressed pellets or glass beads. Common XRF devices can determine concentrations of elements for which the atomic number  $Z$  is greater or equal to 6 whereas for boron  $Z = 5$ . Another problem is to prepare calibration standards whose elemental composition is close to that of the sample to analyze (Rouessac and Rouessac, 1992). Schuster et al. (1988) showed that boron is also difficult to detect because of its proximity with oxygen atoms (often in  $\text{H}_3\text{BO}_3$  or  $\text{B}_2\text{O}_3$  forms). Indeed, the  $\text{K}\alpha\text{III}$  line of oxygen obscures the signal of the  $\text{K}\alpha\text{I}$  line of boron which is used for XRF analysis of boron. Schuster et al. managed to develop a multilayer filter made of carbon and tungsten that significantly reduces the  $\text{K}\alpha\text{III}$  line of oxygen. Thus, determinations of boron concentration by XRF have been done with a precision of 0.2 wt% in 5 min in borophosphosilicate glass (these glasses contain around 0 to 5 wt% of B).

Inductive Coupled Plasma - Mass Spectrometry (ICP-MS) allows the measurement of very low concentrations (Kuru et al., 2018). With an ElectroThermal Vaporization (ETV) device for introducing the sample, the detection limit of boron has been found to be  $0.2 \text{ ng mL}^{-1}$  which is 3 orders of magnitude lower than with ICP Atomic Emission Spectroscopy (ICP-AES) (Wei et al., 1995). ICP-MS with ETV is suitable for boron concentrations around  $5\text{--}100 \text{ ng mL}^{-1}$  and has been developed to measure traces of boron in semiconductors. The authors claim a precision better than 5% when measuring  $50 \text{ ng mL}^{-1}$  boron. In addition to the ETV system, these performances have been enhanced by the addition of mannitol. The complex between boron and mannitol multiplied the boron signal by a factor 84 and facilitated vaporization and transport of boron to the plasma. More generally, it is admitted that losses of boron through volatilization are reduced or at least limited when complexation with mannitol occurs. It was shown that sensitivity of boron determination using ICP-MS was multiplied by 40 due to mannitol (Gaillardet et al., 2001). Another interest of ICP-MS is to permit isotopic ratio measurements. In the case of boron, the ratio is  $^{11}\text{B}/^{10}\text{B}$ . This ratio is widely used in the nuclear field because only  $^{10}\text{B}$  is able to absorb neutrons. Other fields are interested in this ratio, for example it is measured in marine sediments to determine the evolution of sea water pH at the geologic time scale (Lécuyer et al., 2002). This application led to the development of a purification protocol of boron-

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