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Determination of boron in produced water using the carminic acid assay



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ABSTRACT

Using the carminic acid assay, we determined the concentration of boron in oilfield waters. We investigated the effect of high concentrations of salts and dissolved metals on the assay performance. The influence of temperature, development time, reagent concentration, and water volume was studied. Ten produced and flowback water samples of different origins were measured, and the method was successfully validated against ICP-MS measurements. In water-stressed regions, produced water is a potential source of fresh water for irrigation, industrial applications, or consumption. Therefore, boron concentration must be determined and controlled to match the envisaged waste water reuse. Fast, precise, and onsite measurements are needed to minimize errors introduced by sample transportation to laboratories. We found that the optimum conditions for our application were a 5:1 mixing volume ratio (reagent to sample), a 1 g L⁻¹ carminic acid concentration in 99.99% sulfuric acid, and a 30 min reaction time at ambient temperature (20 °C to 23 °C). Absorption values were best measured at 610 nm and 630 nm and baseline corrected at 865 nm. Under these conditions, the sensitivity of the assay to boron was maximized while its cross-sensitivity to dissolved titanium, iron, barium and zirconium was minimized, alleviating the need for masking agents and extraction methods.

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1. Introduction

Produced water [1] is a byproduct of hydrocarbon production. It is estimated that 210 million barrels of water are produced per day in the United States [2] alone. The scale of such volumes is both an environmental concern and an opportunity for new sources of water as numerous oil-producing regions are also water stressed. Therefore, there is a rising interest in repurposing the produced water for irrigation and industrial applications [3–5].

The fate of produced water is an environmental and economic decision determined by the composition of the waste product [6]. Produced waters are complex fluids, with their chemical composition varying greatly from well-to-well and also during the life-cycle of a well. They usually contain a high salt content, Total Dissolved Solid levels (TDS) of up to 40% [7], and organic matter, which make them toxic for the environment.

One species of particular interest is boron [8]. In produced water, boron can range from less than 5 mg L⁻¹ to more than 400 mg L⁻¹. Because boron is commonly used as a crosslinker, its concentration in flowback water can be much higher than that in

formation water [9]. Boron is an essential nutrient. Deficiency or excess of boron is known to impair the development of crops and plants [10,11], and affect the reproductive system of living organisms [12]. Environmental regulations vary from country to country [13], with recommended concentrations ranging from 0.5 mg L⁻¹ to 5 mg L⁻¹ for Saudi Arabia and Canada, respectively; the World Health Organization currently suggests 2.4 mg L⁻¹ for human consumption [4]. Before reuse, water treatment is often required. Boron removal from waste water is a very active field of research, in which technology reviews are published regularly [4,13–16]. Removal of boron is a costly process with varying degrees of efficiency. Early measurement of boron concentration would help in identifying the potential use of the water, reducing stress on treatment facilities and determining whether the treatment is sufficient.

1.1. Boron measurements

Conventional boron measurement techniques are reviewed in detail in Sah et al. [17,18]. Laboratory measurement techniques such as inductively coupled plasma-mass spectrometry (ICP-MS) and atomic flame spectroscopy represent the state-of-the-art in characterization of water. They are accurate, precise, and suitable for determining trace amounts of boron (< 1 mg L⁻¹), though

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without dilution factors of up to 10,000, their operating envelope is limited for oilfield samples. Because of their size, cost and requirement for a highly skilled operator, these instruments are not fit for use in remote field locations. Electrochemical techniques such as ion-selective electrode (ISE) and ion chromatography (IC) work based on conversion of boron to tetrafluoroborate (BF_4^-) prior to detection [19,20]. These techniques enable automated measurement of boron between 1 and 100 mg L^{-1} in complex matrix samples, but suffer from interferences from several ions, notably a high sensitivity to chloride content. Furthermore, the use of excess hydrofluoric acid (HF) to force the conversion introduces a safety hazard for field deployment of this technique [21,22].

To assess the quality of field water samples, onsite measurement of boron is needed. The challenge lies in developing a simple standardized method for which the sample preparation and operator involvement are minimized in order to reduce measurement errors. The method must be capable of measuring boron from less than 1 mg L^{-1} to more than 500 mg L^{-1} in waters with unknown matrices and most often rich in salts, metals, chloride, and sulfates. Currently, most oilfield water samples are sent for analysis to a regional support laboratory where standard measurements such as ICP-MS are conducted. Shipping samples poses risks such as deterioration due to contamination and bacterial growth leading to inaccurate results. The shipping process can take days, which delays operational decisions. Table 1 reviews the main boron measurement methods encountered in the literature and their simplified figures of merit. The methods are also assessed for their readiness for measurement in produced water and in the field.

Very few methods are adaptable for onsite measurement and for the range of boron encountered in the oilfield. The only commercial method for boron measurement available for field use is a manual spectrophotometric technique (Hach Company, Hach Method 10252) with limited published data on sensitivity and interferences.

1.2. Colorimetric methods

We examined the existing literature and reviewed absorption- and fluorescence-based spectrometric methods for their sensitivity to boron, selectivity, operating range, response time, chemical preparation, and shelf life.

Numerous spectrometric assays for determining boron in aqueous media exist. Fluorimetric methods such as Alizarin Red S and chromotropic acid are regarded as more sensitive than colorimetric assays but more susceptible to matrix interferences and reaction conditions such as temperature and pH [23]. Their use is, therefore, restricted to samples with known matrices and low boron contents ($< 1 \text{ mg L}^{-1}$). Boron in aqueous solutions forms a weak acid ($\text{pK}_a=9.5$); consequently, direct titration with a base is neither precise nor accurate [24]. The addition of a polyalcohol (or polyol) such as mannitol, sorbitol, or glycerol [25] to the boric acid creates a strong acid complex that can be precisely titrated with a conductivity electrode [26], a pH electrode [24,27,28], or a colorimetric indicator [29,30]. However, interferences due to precipitation with metal ions [24] and false negatives caused by the presence of organic compounds such as polyhydroxy have been reported [31].

The curcumin method [32], although highly sensitive and with a reported shelf time of more than 2 months [33], is cross-sensitive to numerous species (e.g., F, Fe, Mo, Ti, W, Ge, and Be), and requires multiple manipulation steps including extraction of water via distillation, evaporation, or solvent extraction in a rigorously controlled environment [34–36].

The azomethine-H [37] assay and its numerous derivatives [38–48] presents the advantages of working in buffered aqueous

media, being highly sensitive and easy to automate. Instruments with sampling rate of up to 60 sample/hour have been reported [44,45,47,49–56]. However, azomethine-H methods suffer from a short reagent shelf life [48], multiple stages of chemical preparation [42], a narrow working pH range [40], a high temperature sensitivity, and a high cross-sensitivity to other metals and divalent cations if used without masking agents. Gross et al. [38] also reported that the method failed to quantify the boron adsorbed in dissolved organic matter or suspended solids without a prior digestion step.

Solvent boron extraction is a popular but laborious technique that trades water interference for ion-specific limitations [57,58]. Fluoroborate-dye complexes are also well-studied colorimetric assays [19,29], with restrictions similar to solvent extraction, ISE, and IC methods.

The above-cited methods require substantial sample preparation either by extracting the boron or by removing or by masking the interfering species. They are not ideal candidates for field determination of boron in produced, flowback, and formation water where the concentration of the analyte of interest can span three orders of magnitude in metals and salt rich-matrices. The preparation of the reagents and the implementation of the specific assays are also laborious and ill fitted to the oilfield environment. Long shelf life is also critical for testing in remote geographical regions that may not have routine access to supplies.

1.3. The carminic acid assay

The spectrophotometric carminic acid method for the determination of boron is the least sensitive method to interferences [59,60]. Its simple single-step preparation and good performance make it a promising candidate for field use with produced water.

Carminic acid ($\text{C}_{22}\text{H}_{20}\text{O}_{13}$, 492.39 g mol^{-1}) is an anthraquinone dye derived from cochineal. It exists as eight quinoid tautomers [61], most commonly referred to 1,2,4,7-tetrahydroxy-3-(β -, D-glucopyranosyloxy)-5-methyl-9,10-anthraquinone-6-carboxylic acid.

Because of the shift of tautomeric equilibria taking place upon pH change in the medium and the nature of the metal forming a complex with carminic acid, a wide range of absorption spectra exists. For a given pH and wavelength, the fluorometric or colorimetric determination of a specific analyte is possible. In aqueous media, the determination of tungsten, molybdenum [62–65], beryllium [66], iron (II), vanadium (IV), uranium (VI) [61], and boron [67,68] have been demonstrated. The last required a tightly controlled neutral pH and the use of isolation methods to eliminate interferences.

In concentrated sulfuric acid ($> 90\%$), the absorption of the carminic acid–boron complex increased greatly at wavelengths between 575 and 660 nm. First proposed by Evans and McHargue [69] in 1947, the carminic acid method has been adopted by a number of researchers for the routine determination of boron in a wide range of media including soil, fresh and sea water, plants, steel, and alloys [70–72]. The literature is rich in variations of this assay, with often contradictory reported performances [59,73–88]. In attempts to standardize the method, Callicoat and Wolszon [79], Gupta and Boltz [81], and Samsoni [86] studied the factors affecting the sensitivity and precision of the carminic acid method. Some commonalities emerged from these efforts such as: greater than a month reagent shelf life, an optimum detection wavelength between 615 and 628 nm, an optimum water content of 4–5%, and the high influence of the water ionic content or acid concentration on the sensitivity and development time. But mainly, the findings were different and occasionally contradictory: e.g. the recommended concentrations of carminic acid spanned from 0.1 to 1 g L^{-1} , the development time ranged from 30 min to 6 h, and,

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