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APPLICATION NOTE

Quantitative Analysis of Low Concentration Borate and Sulfate Solutions using a Portable Raman

Introduction

Boron is a semimetal found in the form of borax and other oxides [1]. The borax is made into boric acid (H_3BO_3), which is used in glass manufacturing, electronics, food preservatives, etc. [1, 2]. This process exploits different solubility behaviors of borax, H_3BO_3 and sodium sulfate (Na_2SO_4) between 0 and 100 °C [3].

Gravimetric analysis is used for quantifying desired constituents of mixed chemicals or solution by weight after separation [4]. This conventional method can monitor H_3BO_3 concentration [5] and Na_2SO_4 concentrations [6]. However, it has practical problems of laborious sample extraction preparation and data analysis, and it does not provide real-time information.

Waterflood injection in offshore oil production requires the removal from seawater and online monitoring of SO_4^{2-} to tens of ppm levels to prevent scaling and well souring.

This study demonstrates the performance of the **PTRam**, B&W Tek's Raman instrument for process development, in measuring low concentration H_3BO_3 and Na_2SO_4 solutions (<100 ppm).

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Experiment setup

Instruments and sample preparation

Raman spectra of:

a. Na_2SO_4 (ACS reagent ≥ 99.0%), H_3BO_3 (ACS reagent ≥ 99.5%) salts
b. single salt
c. mixed salt solution

were investigated using **PTRam** (BWS476-785H) with **fiber optic probe** (BAC100B-785-HT), configured with different sampling set ups for initial studies in sample vials and in situ measurements. Sampling was done with the **research-grade laboratory shaft** (RSS100-785) interfaced with a **vial holder** (NR-LVH), and for in situ measurements an **immersion shaft with sapphire-ball lens** (RIS100-HS-785-08). The instrument was controlled with **Vision** software. Table 1 summarizes the data collection methods.

Table 1. The data collection methods

Experiment	Integration Time	Laser Power	Average
Salt powders	Auto†	100%	1
Single salt	120s	100%	5, 8
Mixed salt	75s	100%	8

† 1501 ms for Na_2SO_4 and 3869 ms for H_2SO_4

Stock solutions of 225 mg/mL Na_2SO_4 and 5 mg/mL H_3BO_3 were prepared. Beakers lined with aluminum foil were filled with 500 mL of distilled H_2O. The immersion sapphire-ball shaft connected to the fiber-optic probe of the **PTRam** was placed into the water. Table 2 summarizes the concentration range and steps used for different experiments. Test samples were made using the stock solutions. All experimental parameters were optimized through preliminary studies.

Chemometric Analysis

Vision was used for both data collection and chemometric analysis. The data were treated with Savitzky-Golay 1st derivative, Raman Region Selection (860 – 890 cm^{-1} for H_3BO_3 or 960 – 1020 cm^{-1} for Na_2SO_4 and 1560 – 1800 cm^{-1} for H_2O), Standard Normal Variate, Mean Center, Partial Least Squares Regression (PLS1), Cross-Validation with Segment Size 4. The number of samples used for calibration and validation are given in Table 2.

Table 2. Range of concentration and concentration step per experiment (each spectrum are technical replicates)

Experiment	Concentration range (ppm)	Concentration step (ppm)	No. of samples	No. calibration spectra per concentration	No. Validation spectra per concentration
H_3BO_3 solution	0 – 80	20	5	5	10
Na2SO4 solution	0 – 80	20	5	5	10
H_3BO_3 in 1 g/L Na_2SO_4	0 – 80	20	5	5	10
Na_2SO_4 in 5g/L H_3BO_3	0 – 80	20	5	5	10

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Results

Boric acid salt and sodium sulfate salt have intense Raman bands at 880 cm^{-1} and 993 cm^{-1}, respectively.

Figure 2 and Table 2 & 3 summarizes the calibration curve, predicted values and limit of detection (LOD) of these Raman measurements for the single salt and mixed salt solutions. In single salt experiments, ca. 94% of the H_3BO_3 and Na_2SO_4 predictions were within ± 10 mg/L and ± 5 mg/L range of the actual concentration, respectively.

Table 3. LOD (in ppm) of H_3BO_3 and Na_2SO_4 solution

Solution	Factors	SEP†	LOD_{st}‡	LOD_{io}*
H_3BO_3 solution	2	4.6	15.2	14.5
Na_2SO_4 solution	2	3.1	10.2	6.9
H_3BO_3 in 1 g/L Na_2SO_4	2	10.1	33.3	31.6
Na_2SO_4 in 5 g/L H_3BO_3	2	3.5	11.6	7.8

*† SEP without bias correction; ‡ H_3BO_3 and Na_2SO_4 ppm; * BO_3^{3-} and SO_4^{2-} ppm*

The representative Raman bands for H_3BO_3 and Na_2SO_4 were well separated from each other and discernible at each concentration step (Figure 1).

The validation model of 0 – 300 mg/L H_3BO_3 (0 – 285.5 ppm BO_3^{3-}) in Na_2SO_4 solution had R^2 of 0.99 and SEP 10.1 ppm (Figure 3a). Likewise, validation model of 0 – 200 mg/L Na_2SO_4 (0 – 135.2 ppm SO_4^{2-}) in H_3BO_3 solution had R^2 of 0.99 and RMSE 3.5 mg/L (Figure 3b).

The quantification models were built using one measurement per concentration step. This was increased to two measurements per concentration step resulting in an improved model with lower SEP of H_3BO_3 (7.2 ppm) and LOD (23.8 ppm).

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Conclusion

The **PTRam** can successfully quantify H_3BO_3 and Na_2SO_4 concentrations in single salt and mixed salt solutions, with only minimum number of measurements for calibration curve. The LOD for H_3BO_3 and Na_2SO_4 solutions are ca. 15 mg/L (15 ppm BO_3^{3-}) and ca. 10 mg/L (7 ppm SO_4^{2-}), clearly demonstrating the ability for accurate quantitative analysis at low concentrations.

Figure 1A

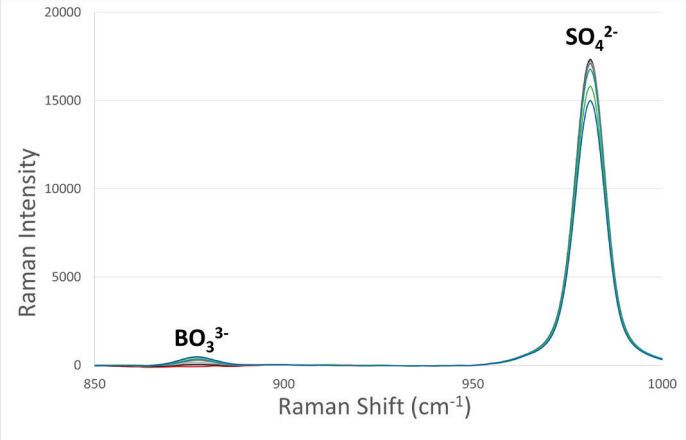

Figure 1B

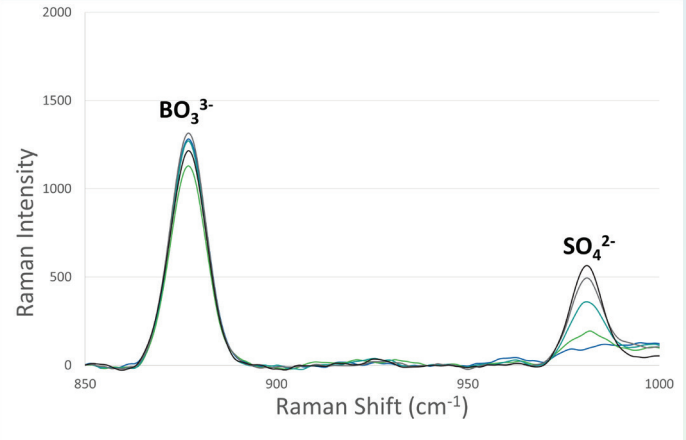

Figure 1 Raman band of H_2BO_3 vs(BO_3^{3-}) at 877 cm^{-1} in Na_2SO_4 solution (a) and Na_2SO_4 solution v1(SO_4^{2-}) at 981 cm^{-1} in H_2BO_3 solution (b). Concentration step, 50 mg/L.

Figure 2A: **Figure 2B:**

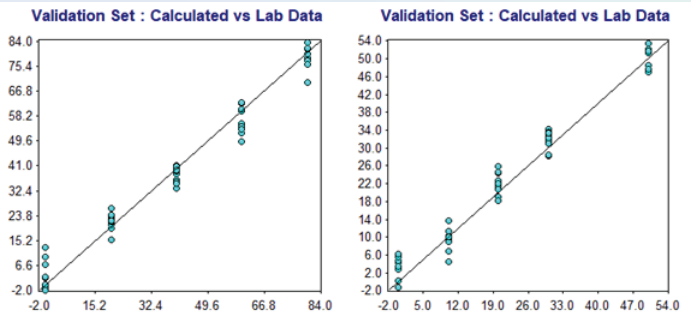

Figure 2. Validation model for H_2BO_3 (a), and Na_2SO_4 (b) single salt solution.

Figure 3A: **Figure 3B:**

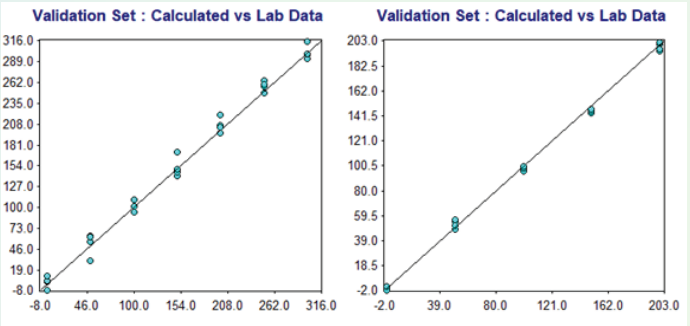

Figure 3. Validation model for H_2BO_3 in 5g/L Na_2SO_4 solution (a), and Na_2SO_4 in 1g/L H_2BO_3 solution (b)

Reference

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[5] Childs, M. P., 2016. Quantification of Boric Acid Concentration and Losses due to Vaporization in the PASTA Facility (Doctoral dissertation).

[6] ISO 3237:1975