Application Note AN-PAN-1063

Inline analysis of borate and sulfate solutions with Raman spectroscopy

Boron is a semimetal found in the form of borax (sodium tetraborate) and other oxides in nature [1]. Boric acid (H_3BO_3) is derived from borax and is used in several industrial applications such as glass manufacturing, electronics, detergents, food preservatives, and more [2].

Boric acid can be produced from borax through various processes. Sulfuric acid is mainly used during borax synthesis since it is considered to have minimal environmental impact.

In 2021, the boric acid market was estimated at US$ 706.52 million and is expected to reach US$ 1,169.89 million by 2030 [3]. As the market grows, so does the need for a more cost-efficient and environmentally friendly production process.

This Process Application Note shows the excellent performance of the PTRam, the single-channel Raman instrument for process development from Metrohm Process Analytics, while measuring boric acid and sodium sulfate solutions inline at low concentrations (<100 mg/L).

INTRODUCTION

There are several ways to manufacture boric acid from borax. Some of these processes use strong acids like nitric acid or chloric acid, however, production costs using these chemicals are high due to equipment wear. Out of these acids, sulfuric acid is primarily used (Reaction 1) since it is considered to have the smallest environmental footprint.

$$Na_2B_4O_7 \cdot 10H_2O \ + \ H_2SO_4 \rightarrow Na_2SO_4 + 4H_3BO_3 + 5H_2O$$

borax boric acid

Reaction 1. Boric acid can be produced from the reaction between borax and sulfuric acid.

Maximizing production efficiency and reducing costs in a boric acid refinery is possible by monitoring and controlling the sodium sulfate (Na_2SO_4) chemistry in the crystallization stage (Figure 1). If the reagent concentrations are outside of the set limits, chemical dosage is not controlled, waste increases, and production costs are higher.

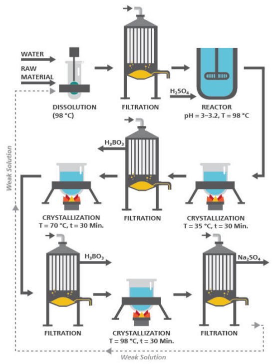

Figure 1. Schematic illustration of boric acid production from borax (adapted from [4]).

Gravimetric analysis is traditionally used for quantifying desired constituents of mixed chemicals or solutions by weight after separation [5]. This conventional method can monitor H_3BO_3 [6] and Na_2SO_4 concentrations [7]. However, practical challenges arise through laborious sample preparation methods and manual data analysis. Additionally, gravimetric analysis does not provide users with real-time process information.

For optimal boric acid production, multiple parameters must be monitored in a safer, more efficient, and faster manner. This is possible via inline process analysis with reagent-free spectroscopy (e.g., Raman).

Metrohm Process Analytics offers the PTRam Process Analyzer (Figure 2) which enables direct comparison of «real-time» spectral data from the process to a reference method (e.g., titration). This allows operators to create a simple, yet indispensable calibration model used to produce quantitative results during the boric acid manufacturing process.

Figure 2. The PTRam Analyzer is suitable for quantitative inline process analysis.

APPLICATION

Laser used: 785 nm. Samples of H_3BO_3 and Na_2SO_4 single salt and mixed salt solutions were taken for this study. Only a minimal number of reference measurements were required for calibration and modeling.

One of the many functions of Raman spectroscopy is its use for material identification. Most materials can be identified by their Raman signature, as they exhibit sharp, distinctive peaks serving as a molecular fingerprint. The spectrum contains information not only regarding sample composition, but also about the concentrations of its constituents, which are directly proportional to the intensity of the spectrum. Because of the spectral differences, Raman analyzers are known to be capable of identification and confirmation of chemical substances used in a variety of industries (e.g., semiconductors, food, pharmaceuticals, etc.).

RESULTS

In this application study, the boric acid salt and sodium sulfate salt exhibit intense Raman bands at 880 cm^{-1} and 993 cm^{-1}, respectively (Figure 3). The limits of detection (LODs) for H_3BO_3 and Na_2SO_4 solutions are 15 mg/L (15 mg/L BO_3^{3-}) and 10 mg/L (7 mg/L SO_4^{2-}) (Table 1). This clearly demonstrates the ability of inline Raman spectroscopy for accurate quantitative analysis at low analyte concentrations.

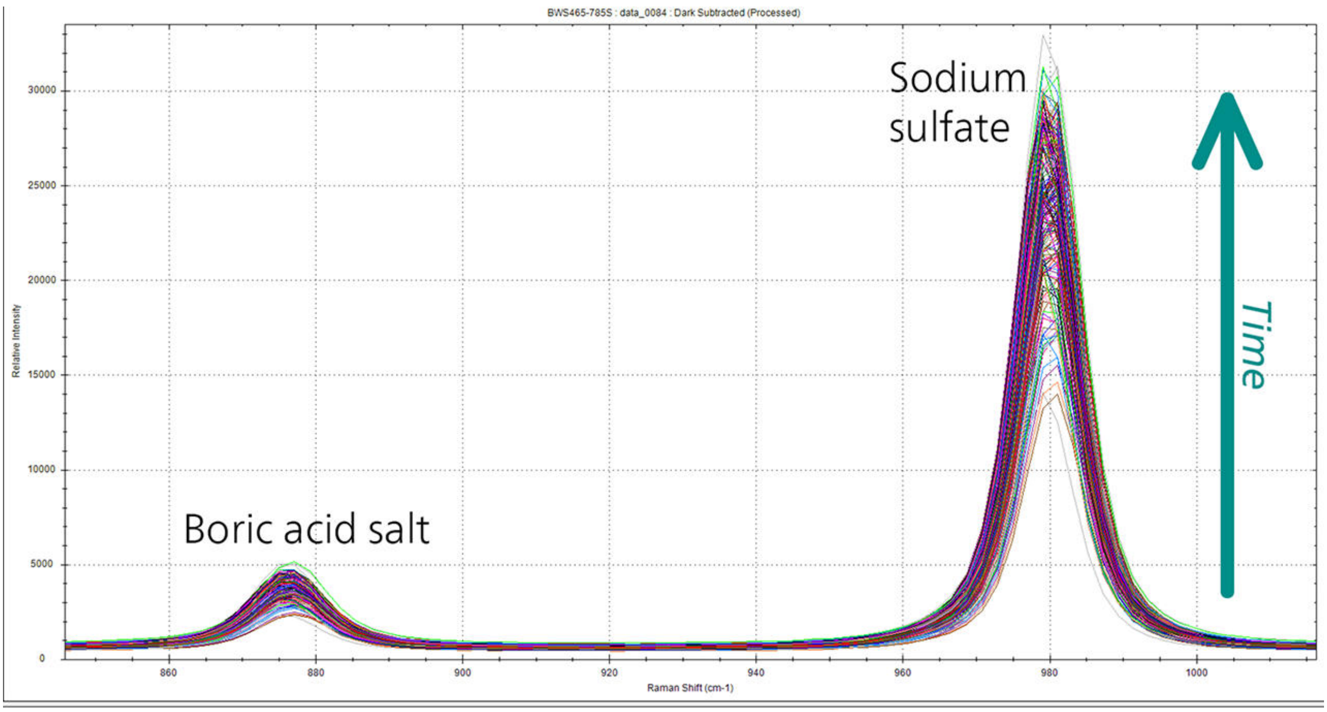

Figure 3. Raman spectra from the reaction stage. Boric acid salt (left) and sodium sulfate (right) exhibit clearly defined peaks.

Table 1. LOD (limit of detection in mg/L) of H3BO3 and Na2SO4 solutions with inline Raman spectroscopy.

† Standard Error of Prediction without bias correction; ‡ H3BO3 and Na2SO4, mg/L; * BO33- and SO42-, mg/L. st: salt weight. io: ion weight.

Parameters	Factors	Concentration range (mg/L)	SEP†	LOD_{st}‡	LOD_{io}*
H_3BO_3 solution	2	0–80	4.6	15.2	14.5
Na_2SO_4 solution	2	0–80	3.1	10.2	6.9
H_3BO_3 in 1 g/L Na_2SO_4	2	0–80	10.1	33.3	31.6
Na_2SO_4 in 5 g/L H_3BO_3	2	0–80	3.5	1.6	7.8

CONCLUSION

In conclusion, the use of Raman spectroscopy for inline analysis of borate and sulfate solutions presents significant advantages in the context of boric acid production. As the boric acid market expands, the demand for efficient and eco-friendly production intensifies. Inline analysis, facilitated by reagent-free spectroscopy techniques such as Raman, enables real-time monitoring of process parameters, as demonstrated by the PTRam Process Analyzer. By identifying distinctive molecular signatures and offering accurate quantitative results, Raman spectroscopy presents a robust approach for optimizing boric acid production, addressing challenges associated with traditional methods.

BENEFITS FOR RAMAN IN PROCESS

- Increased product throughput, reproducibility, production rates, and profitability.
- Gain insight into chemical reactions occurring in the manufacturing process.

REFERENCES

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CONTACT

Metrohm Česká republika s.r.o.
Na Harfě 935/5c
190 00 Praha

office@metrohm.cz

CONFIGURATION

PTRam Analyzer

The PTRam Analyzer is a process development 785 nm Raman analyzer designed for product and process development use in labs and pilot plants. It is a high performance, precise, robust, and reliable Raman system featuring self-calibration and automated performance validation to ensure validity of every measurement.

This single-sample channel system includes a lab fiber optic probe with an user-replaceable shaft. The PTRam is 19″ rack-mountable. The PTRam operates with Vision software and it can be connected with a 2060 Human Interface.