



Watergenics AISRAS: addressing the problem of sudden changes in ion concentrations with real-time spectroscopy

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Abstract

Our study compares the performance of real-time augmented in-situ Raman spectroscopy (AISRAS) with real-time electric conductivity (EC) measurements, spectrophotometry (HACH) and laboratory ion chromatography—the latter serving as the most reliable reference. We measure sulfate in post-lignite-mining-influenced river water at a test site located in the Lusatia region of eastern Germany.

The ion chromatography tests serve as the reference and the other methods are compared to it. The results suggest that AISRAS performs considerably better than EC and HACH. The former tends to overestimate sulfate concentrations and the latter tends to underestimate them. Like AISRAS, EC measurements were continuous (20-minute intervals) but did not cover some sudden sulfate concentration changes suggested by the other two methods.

Keywords: Real-time analysis, sulfate, environmental monitoring, surface water monitoring, raman spectroscopy

Introduction

In the aftermath of the Oder River Fish die-off in the summer of 2022, the European Commission called for further improvements in water quality monitoring and risk management (European Commission 2023). Our research on real-time Augmented In-situ Raman Spectroscopy (AISRAS) addresses these objectives. The innovation of this approach lies in its ability to provide real-time, in-situ concentration analyses of key chemical substances, such as sulfate, nitrate, carbonate, calcium, and iron. As such, it provides a comprehensive and cost-efficient real-time water quality assessment. While laboratory concepts and experiments to measure sulfate in aqueous solutions are known, not many market-ready solutions of in-situ-real-time-Raman spectroscopy exist (Kruus et al. 1985; Chi et al. 2007; Ben Mabrouk et al. 2012; Mabrouk et al. 2013; Qiu et al. 2019).

Real-time measurement of water quality enables rapid responses to changes in pollutant concentrations. In addition to emergency response, smart discharge

management is another application. Reliable data with high temporal resolution ensure that pollutant limits in water bodies are not exceeded at any time and that discharge rates can be optimized. Therefore, it is crucial to understand the reliability of the generated data points. Furthermore, real-time data can help identify additional contamination sources and increase the understanding of the discharge system. Therefore, we compare the performance of AISRAS with real-time electric conductivity (EC) measurements, spectrophotometry, and laboratory ion chromatography – the latter serving as the most reliable reference.

This study was carried out at a test site in the Lusatia region of Germany. The site is operated by Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft (LMBV), a state-owned company responsible for the remediation and environmental monitoring of the lignite mining legacy sites in the former territory of the German Democratic Republic (GDR). From the 1960s to the end of the 1980s, Lusatia was the major lignite mining area of the GDR.

The upper Spree River at this site is exposed to high concentrations of iron and sulfate causing regular discoloration of the river. This is caused by the recovery of the groundwater level in this post-lignite mining region. After the reunification of Germany, most of the mines were closed, and the remaining ones are scheduled to phase out of production by 2038.

During the period from 28/09/2022–08/10/2022, we investigated the performance of the AISRAS system in quantifying the dissolved sulfate concentration in the Spree at site SP0030/1180 Spremberg-Wilhelmsthal north of Spremberg. A lime dispensing facility is located adjacent to the measurement site.

The AISRAS sensor is based on the principle of conventional Raman spectroscopy. The Raman effect is used to quantitatively analyze substances using the analytical basis of the Lambert-Beer law by analyzing the scattering and absorption of a monochromatic laser light during interaction with the water sample. Raman scattering is an inelastic scattering as opposed to the elastic Rayleigh scattering. Due to the interaction of the monochromatic laser light with the matter, conventional Raman spectroscopy normally looks at the Stokes section. Energy is transferred from the light to the matter (e.g. molecules) during scattering, which shifts the bonds to a higher energy level. This light-matter interaction, usually in the form of lattice and bond vibrations, manifests itself in a shift in the frequency of the diffracted light or, in other words, in a shift in the wavelength

of the light. If the intensity of the inelastically scattered light is plotted against the change in energy relative to the irradiated laser light given in wave numbers (cm^{-1}), the Raman spectrum is obtained.

The Rayleigh scattering, which dominates with a factor of 106, is generally filtered out after the interaction with the matter by so-called Notch filters. An additional general problem in conventional Raman spectroscopy is fluorescence, i.e. long-wave interactions on the molecules within the laser beam path, which impair the Raman spectrum. In general, statistical methods are used to eliminate the fluorescence interaction with Raman scattering. This allows for observation of only the light quanta affected by the Raman effect.

Material and Methods

The AISRAS sensor manufactured by Watergenics as shown in Fig. 1 A consists of:

- a reflection chamber (Fig. 1 B) submersible into the liquid containing a self-cleaning mechanism to mitigate precipitation and biofouling,
- a fiber optic cable to transmit the laser signals from and to the emitter and sensor,
- a main body comprising named emitter and sensor, computing and broadcasting modules, as well as power supply.

Apart from the inherent property of spectrometric technologies to measure multiple substances/elements simultaneously, our approach aims to provide a continuous

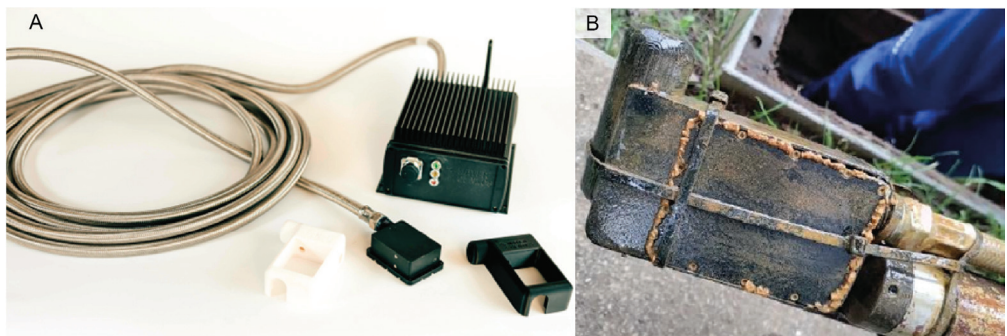


Figure 1 A – Watergenics AISRAS sensor system comprising reflection chamber, fibre-optical transmission, spectrometer and casing **B** – reflection chamber during the test trials (Photo: Watergenics)

measurement where data are processed in near-real-time and stored in a data lake environment.

Our system has a Level of Quantification (LoQ) for sulfate of 70 mg/L at a nominal error rate of 2%.

We compared the performance of the following measurement systems:

- Continuous measurements (20 min intervals) with the AISRAS system
- Continuous measurements (20 min intervals) of electric conductivity sensor operated by LMBV, SO₄-concentration is computed from EC with temperature adjustment and calibration curve. The computation process is well known and not covered further in this document.
- 3-times-daily spectrophotometry measurements with a HACH (Loveland, CO, USA) DR1900 (further abbreviated HACH)
- Laboratory analysis data from both the LMBV and the environmental agency of the state of Brandenburg (LfU); both used ion chromatography to estimate SO₄ concentrations (abbreviated LMBV Lab and LfU Lab, respectively)

In this study, we view the LMBV Lab measurements as “gold standard” or reference. The measurement from LfU is only used as a general validation because only one data point exists within the study period. We compare the remaining three methods against LMBV Lab to assess their respective performance.

In this study, we focus on a qualitative assessment of the real-time data, assess the offset between the different methods, and conduct a regression analysis to aid the qualitative analysis. For the latter, the data were binned into 20-minute intervals to make a comparison of different methods possible.

Results and Discussion

Fig. 2 with Markings a–c shows the measurements of all compared methods over the study period while Fig. 3 shows the summarized results as a boxplot. From both the real-time data and the boxplot multiple observations can be made:

1. All methods appear to follow the same general trend. We interpret this as a confirmation that all methods generally perform and none of the methods was dysfunctional.
2. The two real-time methods can display sudden changes in sulfate concentrations expectedly well – as seen on the \approx 50 mg/L drop-and-rise over the course of September 30 (Marking a). This illustrates how real-time methods can allow for quick responses in discharge management. While an ion-chromatographic measurement can be run in under an hour, times for sampling and travelling from and to the sample site must be considered, as such only one laboratory measurement is executed per day. In the case of September 30, a possible reaction to lab data could only have taken place in the afternoon of that day – when the SO₄ concentration was already increasing again.
3. However, not all sudden changes are captured by both methods as seen on October 3 (Marking b). AISRAS shows a considerable drop in SO₄ concentration, while EC does not show this drop at all. The LMBV Lab and HACH measurements on that day support that this drop actually occurred.
4. Compared to LMBV Lab during the test period, HACH seemed to underestimate SO₄ concentrations and EC seemed to overestimate them. HACH on average underestimated SO₄ concentration by 33 mg/L and EC overestimated by 56 mg/L. These differences are statistically significant while the difference between AISRAS and LMBV Lab is not significant (based on two-sided t-test with $\alpha = 0.01$, assumed normality, homogeneity of variances is confirmed by F-test). In case of the HACH-deviation, a temperature inconsistency could be responsible for the lower results of the spectrophotometric data. This is plausible as the water temperatures ranged 12–14 °C and air temperatures ranged 4–17 °C. The water temperatures mark the lower end of the prescribed

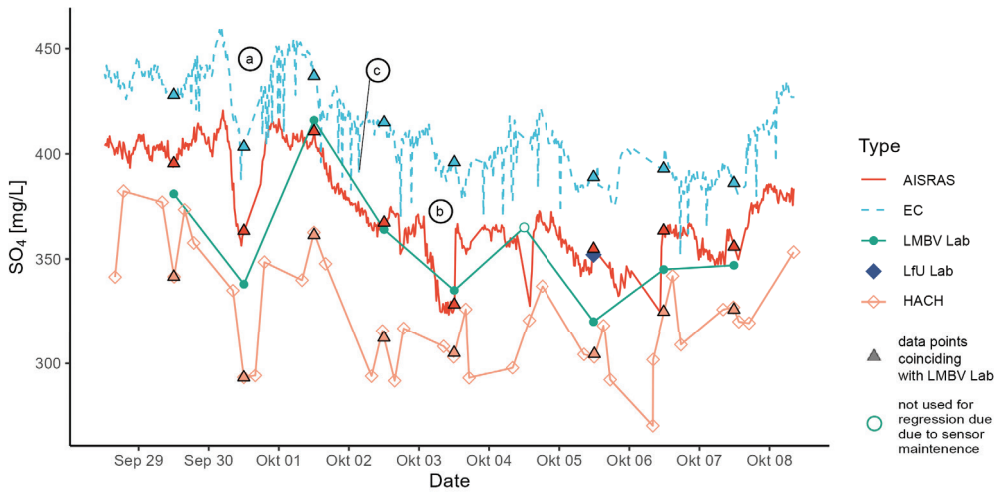


Figure 2 Raw data of all compared methods at the location; numbered markings relate to the text

temperature interval of 15–25 °C for this method. Furthermore, turbidity effects may have had an influence.

- During the test period, in contrast to AISRAS, EC shows irregularly occurring “low-spikes” (e.g. Marking c). These spikes may have occurred during the test period (and not before and after) because the EC sensor was not maintainable during that time. EC and AISRAS had been installed next to each other to allow comparable results without disturbing each other. Due to that, there was simply not enough room for EC sensor maintenance to take place. In light of this observation, these results may illustrate the necessity for EC sensor maintenance, which is not necessary for AISRAS.

Further assessing the association behaviour between the methods, Fig. 4 A-C shows linear regressions for AISRAS, HACH, and EC against LMBV Lab measurements. The plots show both a linear regression in the form of $y = mx + n$ (solid line) and a linear regression forced through the origin in the form of $y = mx + 0$ (dashed line). The latter follows the assumption that no offset is present. Ideally, all methods would be close to a regression with $m = 1$ and $n = 0$. For the first regression type, the methods perform relatively similarly with EC showing the highest offset n and the lowest value for m while AISRAS shows the

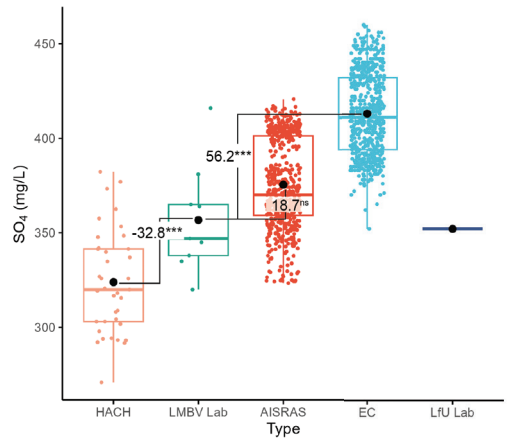


Figure 3 Boxplot of all compared measurement methods, black lines connecting the boxes indicate mean deviation to the LMBV Lab measurements; ***-significant at $\alpha = 0.01$, ns-not significant

value for m closest to 1.

In an application environment, multiple sensor data are not present – there, the practitioner’s question is: “Is the measurement trustworthy?”. A continuously measuring device should be as close to the lab measurements as possible: The equation would then be close to $y = mx$ with $m = 1$. In terms of this metric, AISRAS shows the best performance followed by HACH and EC (Note that R^2 is generally

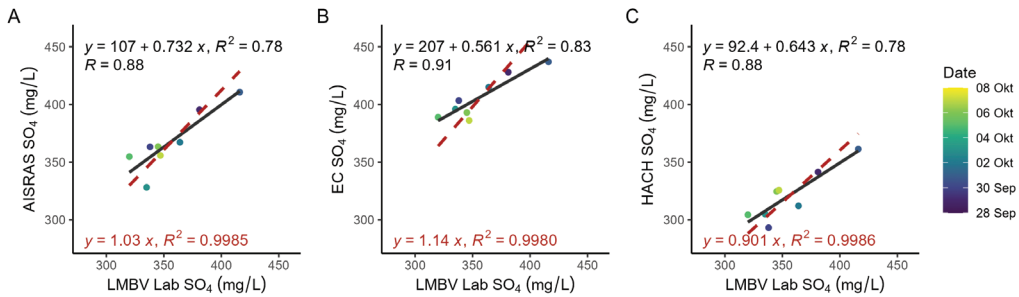


Figure 4 AISRAS (A), EC (B), and HACH (C) sensors plotted against LMBV Lab SO_4 analysis; all plots show a regular linear regression (solid line) with R^2 ; regression coefficient R , as well as linear regression forced through the origin (dashed line)

high for regressions that are forced through the origin and should not be compared to R^2 of normal linear regressions).

Summary

The key findings of our study indicate that AISRAS is an effective method to detect sulfate in real-time and with a high temporal resolution. The AISRAS data show a lower deviation from the lab data than the “traditional” EC data and could capture plausible variations that EC did not capture.

During the test period, the EC data generally appeared to overestimate sulfate concentrations with the calibration used at the test site. Outside the test period, e.g. in 2022, EC did not show such high overestimation (internal communication with LMBV and not part of this study). Furthermore, AISRAS does not rely on historical calibration curves to estimate SO_4 concentrations and does not suffer from measurement alterations due to auxiliary ion concentrations in the water. The HACH spectrophotometry data are slightly underestimated compared to the LMBV Lab data. The reason for this could be related to the fact that it was used on the lower end of its calibrated temperature range. Regarding EC, the reasons for the deviation were limited to the test period and remain to be investigated in a longer-term comparison between EC and AISRAS planned for 2024.

While the study illustrates the use of AISRAS for continuous sulfate measurements, the method can be used for the simultaneous estimation of other ions such as nitrate, carbonate, calcium, and iron—providing accurate and high-resolution insights into the chemical status of a water body. The technology has been in operation at several test sites for now, including active mining sites in Sweden, legacy mining sites in Germany, France, and Chile, and water treatment facilities in Ghana and France. As such AISRAS can enhance our understanding of the intricate interplay between the various ions in aquatic systems, providing an essential tool for environmental monitoring and management.

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