

# Laser Induced Breakdown Spectroscopy (LIBS) for Rapid Monitoring of Metals in Produced Water and its Precipitates: A Preliminary Report

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## Background

Major challenges exist for the rapid analysis of produced and flowback water with traditional analytical approaches, especially in the context of on-site treatment and/or reuse of the water. Laser induced breakdown spectroscopy (LIBS) is one approach with the potential to overcome many of these challenges because of its transportability, no need for sample preparation, and semi-quantitative results.

We are developing LIBS methodology for the rapid characterization of barium and strontium in produced water and its precipitates. Treatment of produced or flowback water often involves precipitation to remove corrosives prior to reuse. The ability to rapidly characterize the produced water and/or its precipitates on-site would mean less downtime and improved treatment control. Our research applies the LIBS methodology in conjunction with a Sequential Precipitation Fractional Crystallization Process (SPFCP), technology developed by ProChemTech International, Inc. However, LIBS can be broadly applied for the analysis of metals associated with any treatment process.

## Laser Induced Breakdown Spectroscopy

LIBS is a form of emission spectroscopy in which a high energy laser ablates a small portion (ng or less) of a sample, creating a high temperature plasma. As the continuum radiation of the plasma cools, light from atomized and ionized species at characteristic frequencies can be detected for both qualitative and semi-quantitative results.

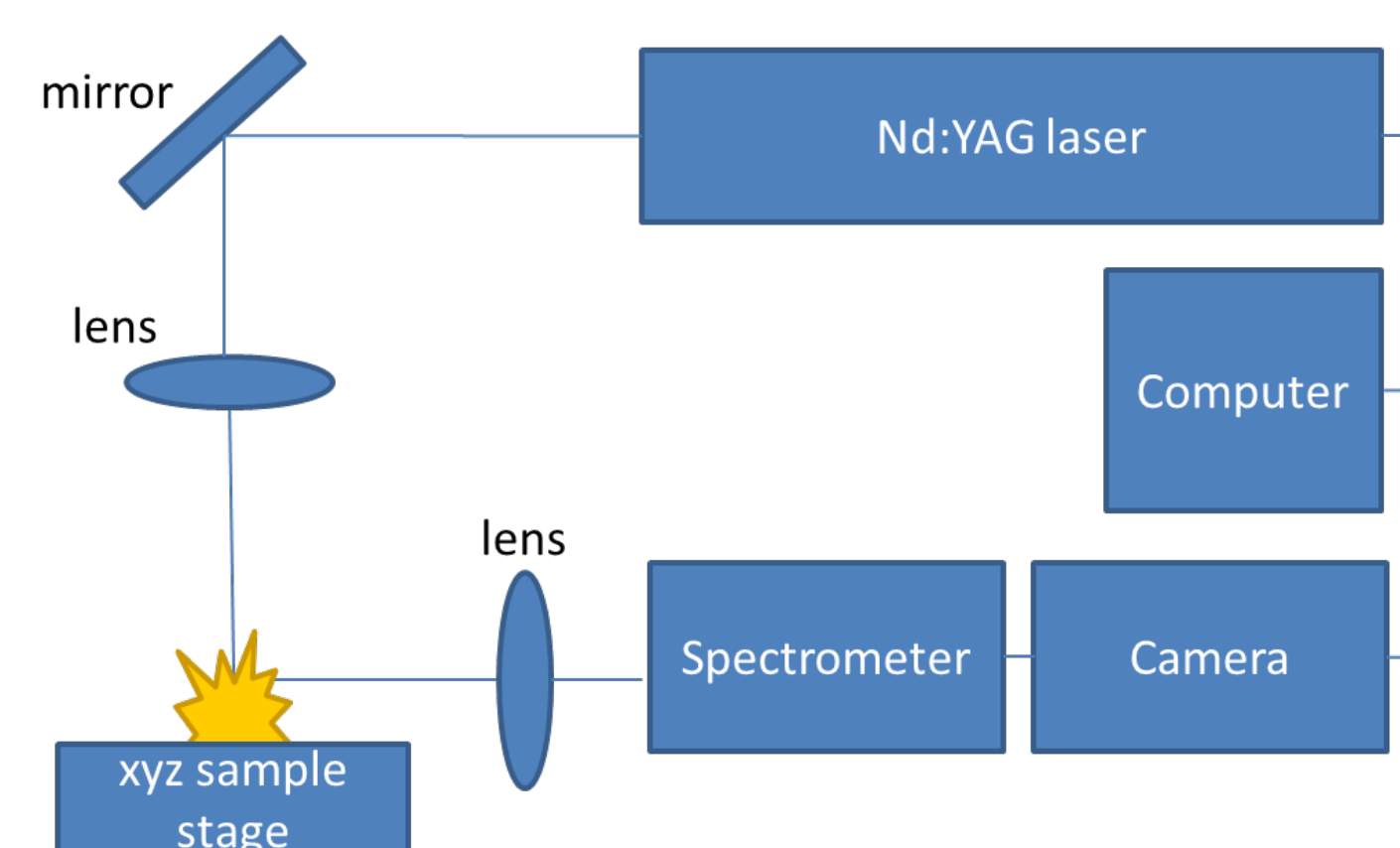


Figure 1. Schematic diagram of a LIBS system. Gated detection collects emission data after continuum light from plasma decays.



LIBS system (Photon-Machines, Inc.) with insert showing sample stage. Our system is equipped with a pulsed, Q-switched Nd:YAG laser (1064 nm, 10-500 mJ) and a broadband diode array spectrometer.

## Research Objective



Undergraduate Danielle Murtagh ('14) prepares a QC produced water sample.

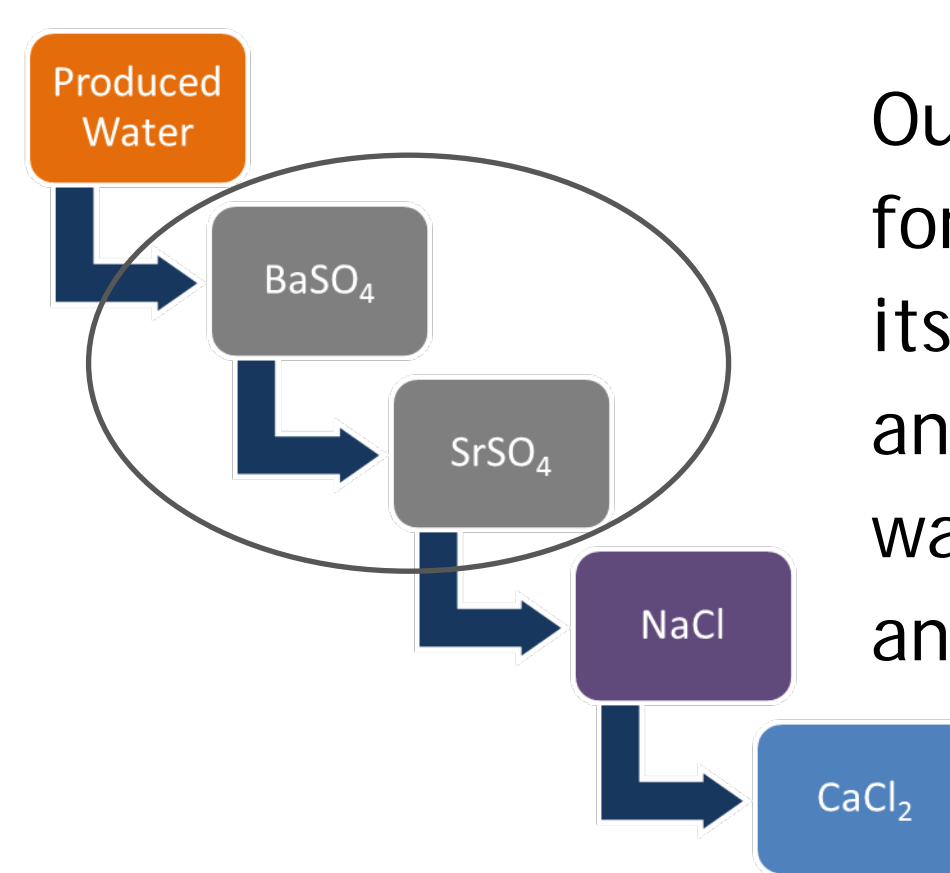


Figure 2. Sequential process utilized by SPFCP for the treatment of produced water with resource recovery. The product at each stage is a saleable chemical commodity.

Our goal is to establish LIBS methodology for the analysis of produced water and its precipitates. We use LIBS for rapid analysis on a project which explores ways to minimize co-precipitation of Ba and Sr in the SPFCP process.

## Results

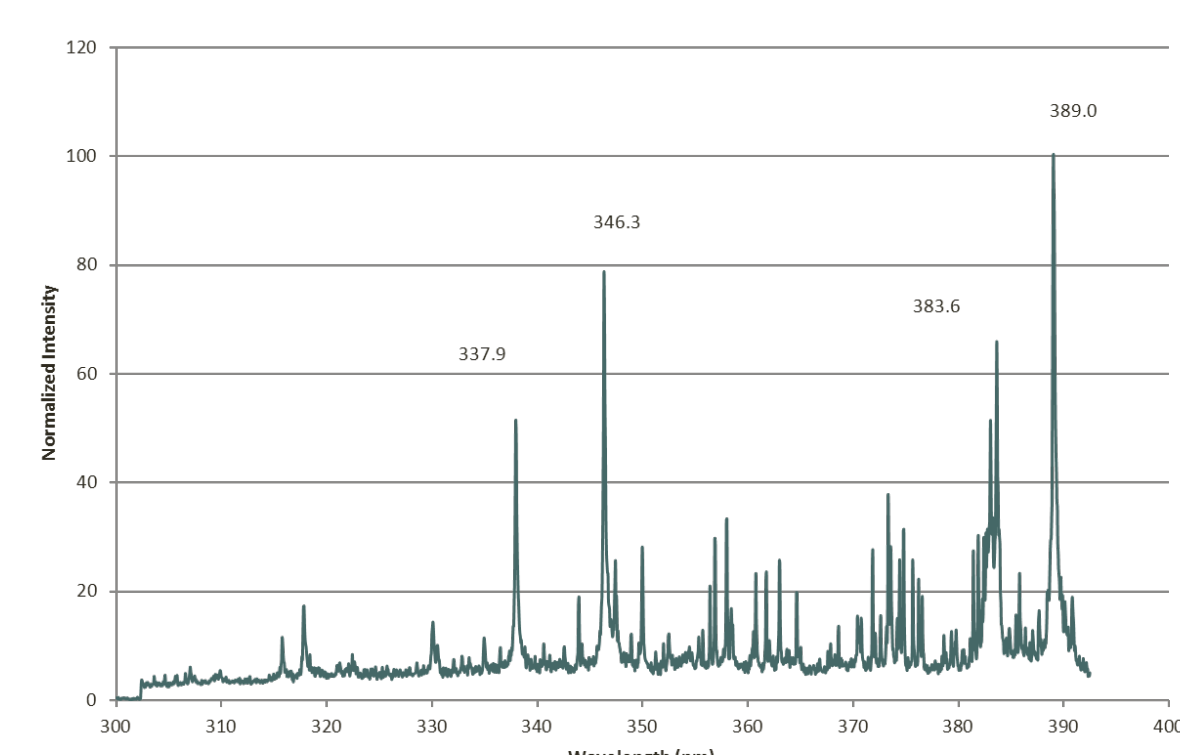


Figure 3. LIBS spectrum resulting from the analysis of produced water precipitate which demonstrates the complex spectra that are typical with LIBS. Multiple atomic and ionic emission transitions occur in the high temperature plasma from the laser ablation process. The transition at 389 nm is an intense, characteristic Ba emission line.

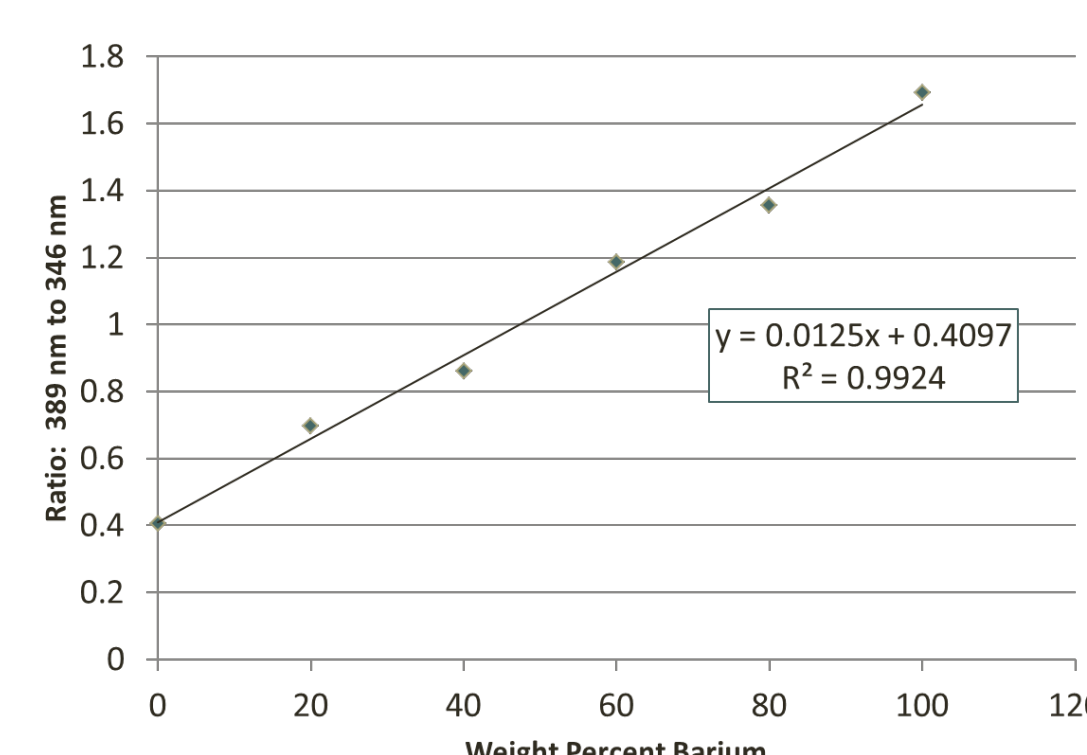


Figure 4. The ratio of a characteristic analyte emission line to that of a non-analyte can be used in quantification to mitigate the issues associated with matrix and plasma variability. We have successfully quantified Ba in precipitates using a ratio of 389 to 346 nm.

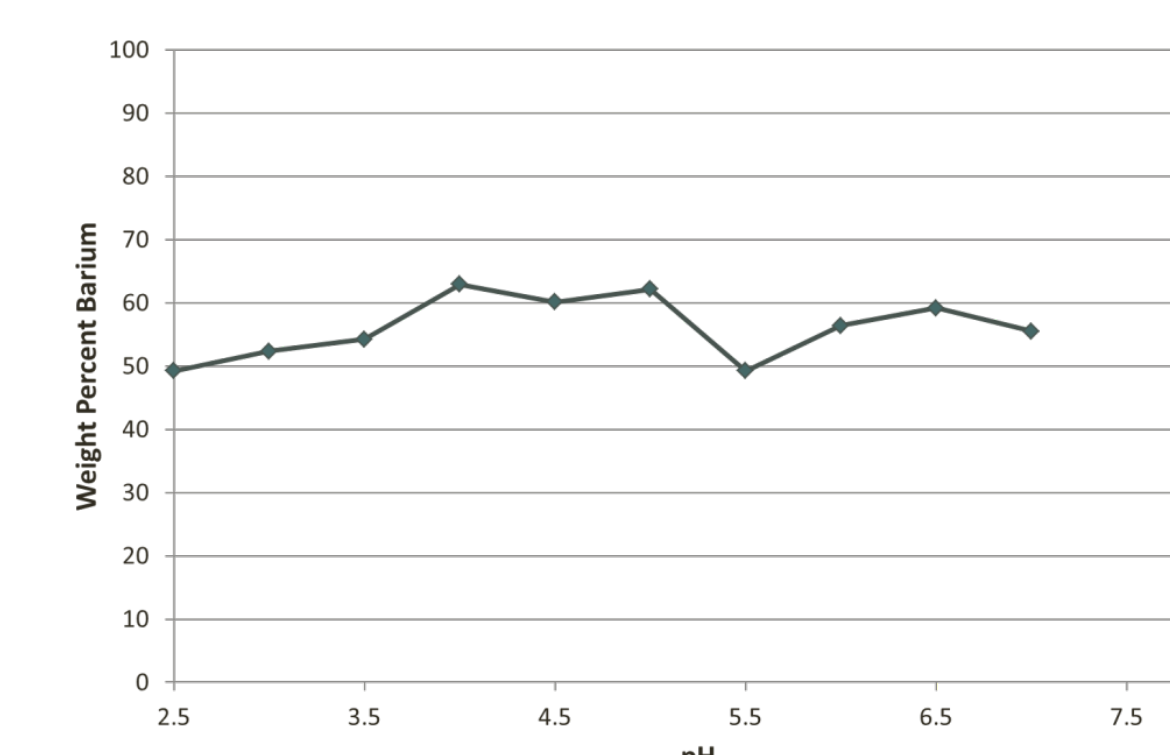


Figure 5. Barium sulfate concentration in produced water precipitates at various pH levels. The results confirm that significant co-precipitation occurs regardless of pH. We are currently testing various approaches to minimize co-precipitation.

## Pros & Cons of LIBS

Pros	Cons
Ease of use	Complex spectra
No sample preparation	Matrix interferences
Simultaneous multi-element analysis	Plasma heterogeneity
On-site & remote analysis possible	Challenging quantification

## Conclusions/Future Work

This preliminary work done at an undergraduate institution demonstrates the potential for LIBS in the analysis of precipitates from produced water. The lack of sample preparation is the clear advantage to this approach. Our results indicate that the challenges associated with quantification can be overcome, and we have established quality results for the analysis of barium.

Current work is focused on the quantification of strontium and optimization of the barium sulfate precipitation in the SPFCP process. We are exploring chemometrics for more sophisticated data analysis and experimenting with the direct analysis of produced water samples. Complementary analysis of produced water by FAAS and GC-MS supports our research on this topic.

## Traditional Analysis



Undergraduates Tyler Umstead ('14) and Lance Jubic ('15) optimize analysis of Ba and Sr by FAAS.

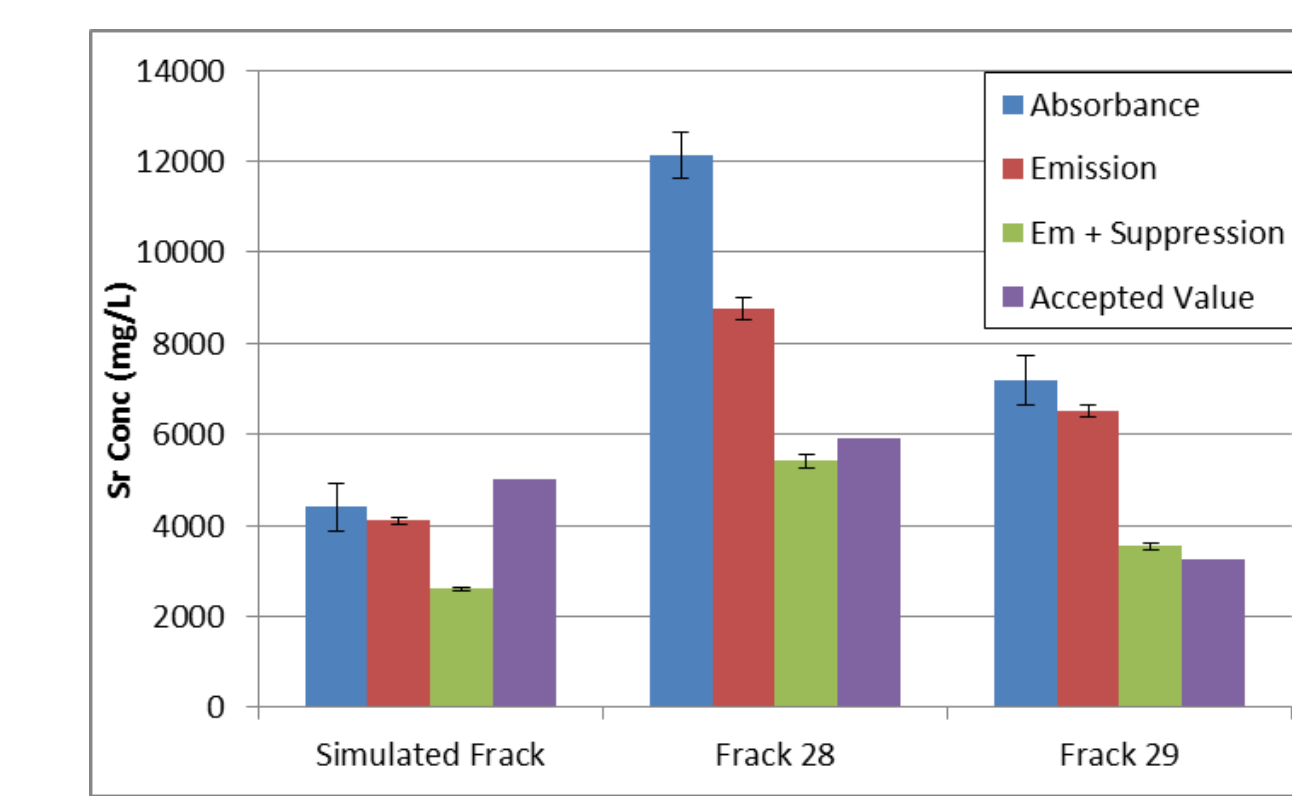
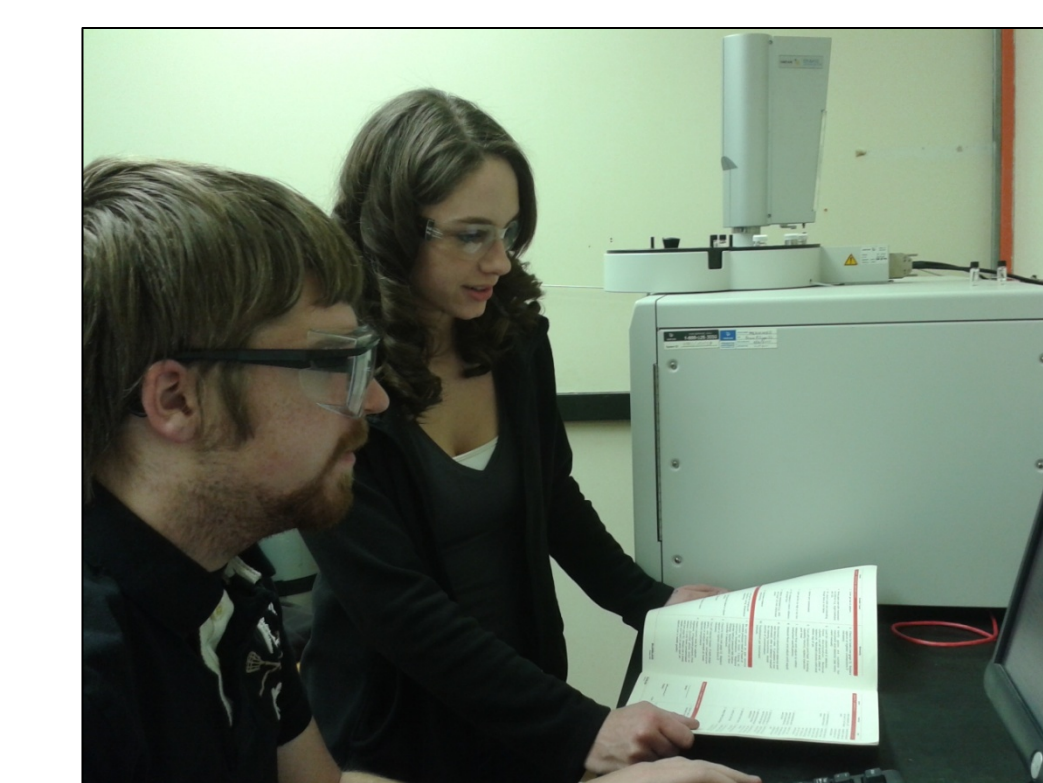


Figure 6. FAAS results can vary significantly depending on the methodology used. In this scenario, Sr results are most precise using emission spectroscopy with an ionization suppressor (KCl).

## Complementary Analysis of Organics



Undergraduates Gavin Steadman ('13) & Brittany Majors ('15) explore novel solid phase extraction & chemometric approaches for the analysis of organics by GC-MS.

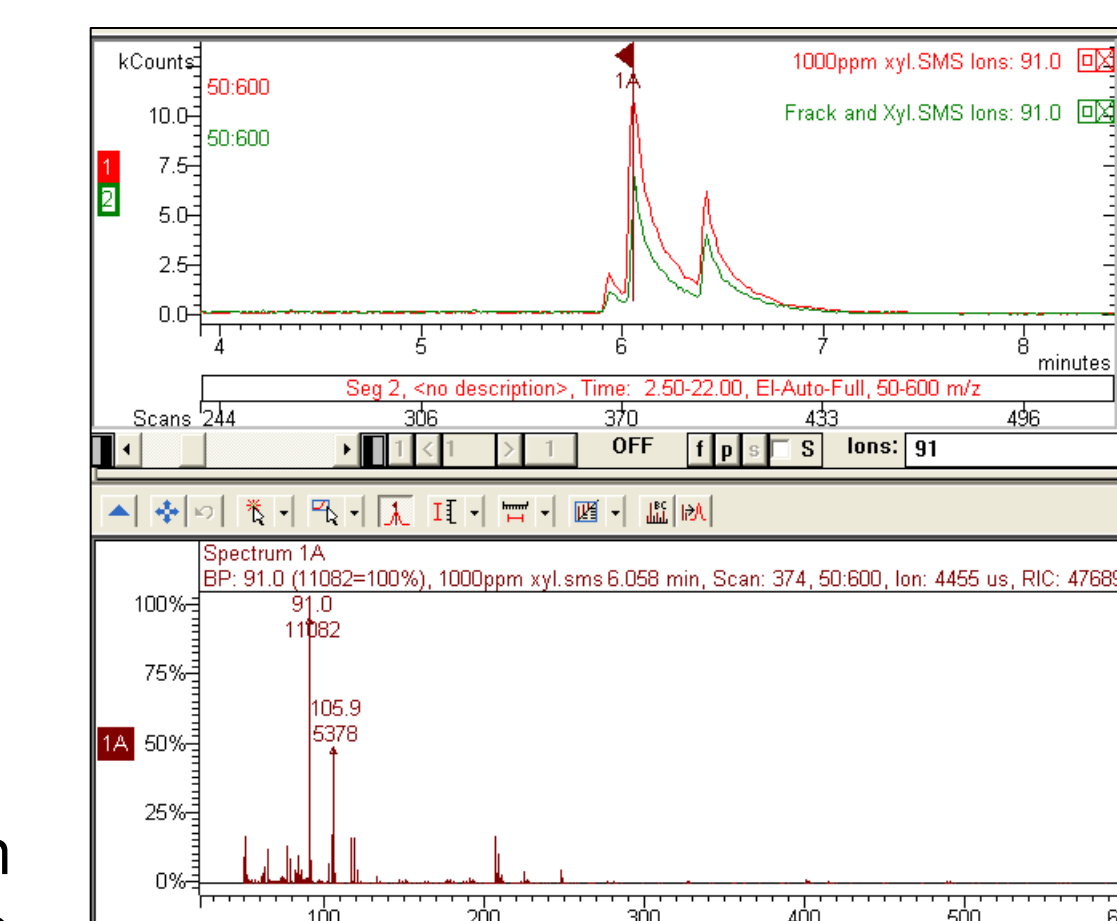


Figure 7. Spike recovery of xylenes from produced water in comparison with a xylene standard.

## Acknowledgments

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