

# Improved Analysis of Sulfur-Containing Anions from Polysulfide Matrix by Suppressed Ion Chromatography

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## ABSTRACT

Sulfur-containing inorganic anions are commonly encountered in soil sediments, hot springs, and lake waters. They are also frequently used in many industrial applications. Their speciation and quantitation are very important to the understanding of those processes. However, due to their redox chemistry, many sulfur-containing species can readily react with each other, decompose over time, or be oxidized in the presence of air. They are also very sensitive to the solution pH, which would affect the distribution of the species over time. All these make the determination of these sulfur-containing anions a very challenging task. Currently, both wet chemistry and ion chromatography are used for the sulfur speciation. In this poster, we will focus on the analysis of sulfur-containing species in polysulfide matrix with suppressed ion chromatography. The presence of large amount of polysulfide complicates the determination of sulfur-containing species. Various sample pretreatment techniques were evaluated, and an optimized pretreatment method will be shown for improving the analysis of sulfur-containing anions in polysulfide matrix by suppressed ion chromatography.

## INTRODUCTION

Lime sulfur is a mixture of calcium polysulfide formed through the reaction of calcium hydroxide and sulfur, and is an aqueous solution with reddish-yellow color.

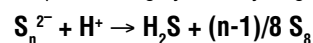
$S^{2-} + 4 S \rightarrow S_5^{2-}$
$S^{2-} + 5 S \rightarrow S_6^{2-}$
$S^{2-} + 6 S \rightarrow S_7^{2-}$
$S^{2-} + 7 S \rightarrow S_8^{2-}$

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Lime sulfur is used as a spray to control fungi, bacteria, and insects. It is also used for remediation of hexavalent chromium in chromite ore processing residue (COPR).

- Typically lime sulfur solutions are strong alkaline
- When acidified, it can produce highly toxic hydrogen sulfide



- It can also react with sulfite to form thiosulfate

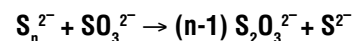


Table 2 lists the possible inorganic sulfur-containing anions present in lime sulfur-based aqueous streams or solutions.

Anion	Formula
Sulfide	$S^{2-}$
Sulfite	$SO_3^{2-}$
Sulfate	$SO_4^{2-}$
Polysulfide	$S_n^{2-}$
Thiosulfate	$S_2O_3^{2-}$
Thiocyanate	$SCN^-$
Dithionate	$S_2O_6^{2-}$
Polythionate	$S_xO_6^{2-}$

## CURRENT METHODS FOR DETECTION OF SULFUR CONTAINING ANIONS

- Iodometry (Sulfide)
- Direct current polarography (Sulfide)
- Differential pulse polarography (Sulfide)
- Spectrophotometry after derivatization with Methyl Blue (Sulfide)
- Spectrophotometry after derivatization with Ellman's reagent (Sulfite)
- Ion chromatography with suppressed conductivity (Sulfite, Sulfate, Thiosulfate)
- Ion chromatography with Electrochemical Detection (Sulfide)
- Ion-pair chromatography (Polythionate)

Figure 1 showed the direct analysis of a diluted polysulfide solution with an IonPac® AS19 4 mm column. The polysulfide solution was not stable, as shown by the overlay of chromatograms from run 1 (red) and run 12 (blue). The amount of thiosulfate and sulfate increased over time while the amount of sulfite decreased over the same period. The distinct yellow color has faded away.

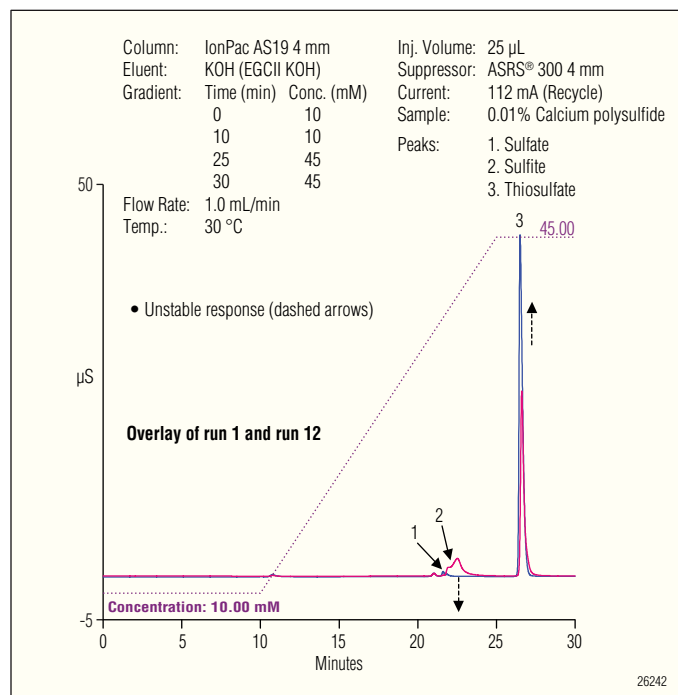


Figure 1. Direct injection with AS19 chemistry.

Figure 2 showed the direct analysis of a diluted polysulfide solution spiked with base. The polysulfide solution was also not stable in the basic solution, as shown by the overlay of chromatograms from run 1 (red) and run 12 (blue). The amount of thiosulfate, sulfate, and sulfite increased over time. Again, the distinct yellow color from polysulfide faded away.

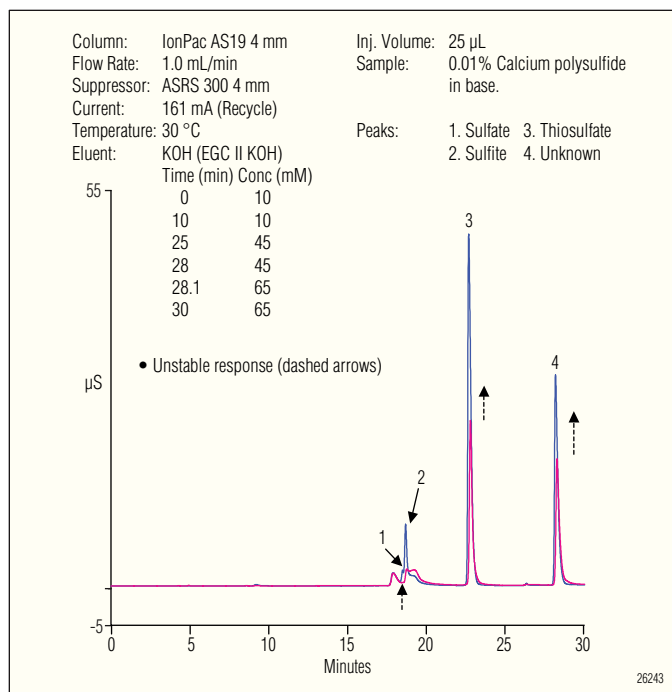
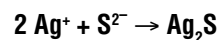


Figure 2. Base effect polysulfide sample was spiked with base.

## REMOVAL OF POLYSULFIDE WITH SILVER CARTRIDGE

- An OnGuard® II sample pretreatment cartridge was investigated for matrix removal.
- The OnGuard II line of disposable sample pretreatment cartridges is designed to remove matrix interferences such as phenols, metals, cations, anions, or hydrophobic substances that are encountered in many ion chromatography applications. These cartridges have wide pH stability and allow low level ion analysis.
- Silver cartridge was chosen for this application due to the high affinity of silver ions for sulfide species.



- The diluted sample was pushed through the cartridge.

Figure 3 showed the direct analysis of a thiosulfate solution after the passage through a silver cartridge. The thiosulfate peak was completely removed, as shown by the overlay of chromatograms before (red) and after (blue) the passage.

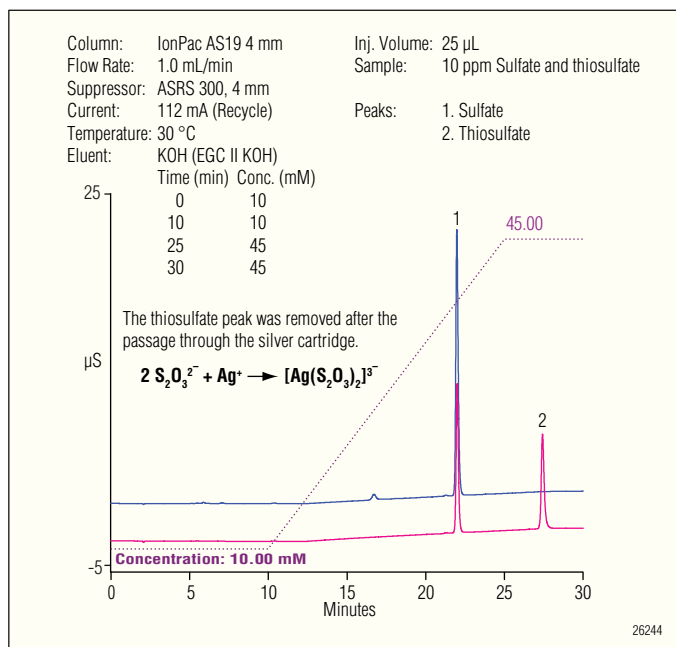


Figure 3. Effect of Ag cartridge.

Figure 4 showed the direct analysis of a diluted polysulfide solution after the passage through a OnGuard H cartridge. The sample was much more stable, as shown by the overlay of chromatograms from run 1 (blue) to run 23 (red). Only the amount of sulfite showed noticeable increase, while the amount of thiosulfate and sulfate were largely unchanged over time. The yellow color from polysulfide was removed after the passage through the cartridge.

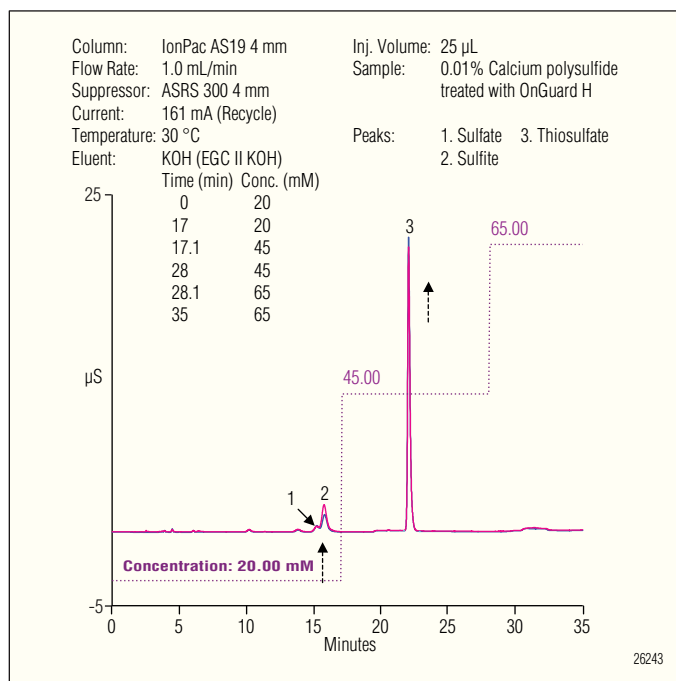


Figure 4. Effect of OnGuard H cartridge.

Figure 5 showed the direct analysis of a diluted polysulfide solution with electrochemical detection before (red) and after (blue) the passage through an OnGuard H cartridge. The large polysulfide peak was removed with the OnGuard H cartridge.

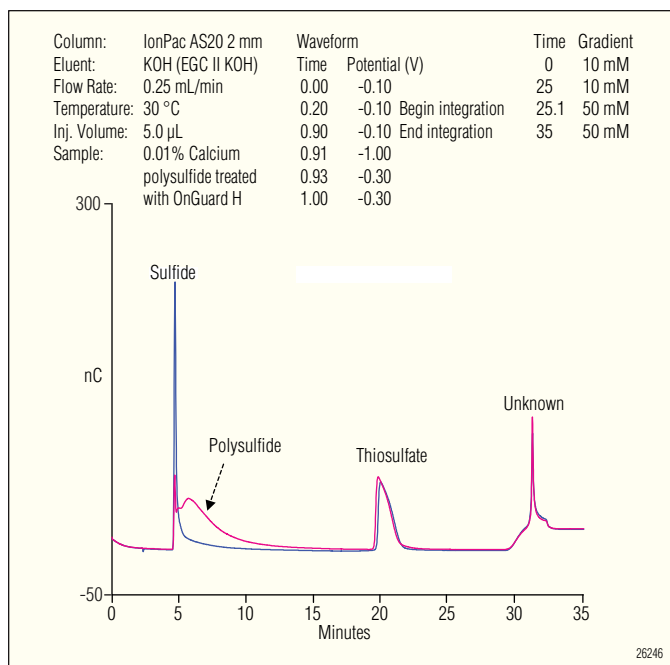


Figure 5. Electrochemical detection.

## NEW SAMPLE PRETREATMENT STEPS PRIOR TO SUPPRESSED ION CHROMATOGRAPHY

- Dilute the polysulfide containing sample 1000 times.
  - Typically present as a 10% aqueous solution
- Push the diluted samples through the OnGuard H and OnGuard Na cartridges sequentially. These two cartridges have been pre-rinsed with at least 20 mL of DI water each.
- Directly inject the pre-treated samples into the IC system.

Figure 6 showed the direct analysis of a diluted polysulfide solution after the passage through a OnGuard H and a OnGuard Na cartridge with an AS17-C column. The AS17-C column provided better resolution between the sulfite and sulfate peaks, which facilitated their quantitation.

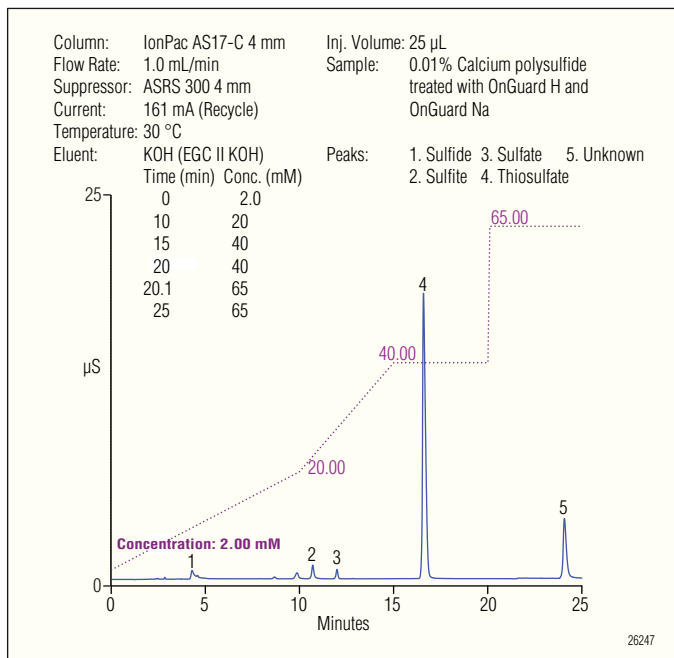


Figure 6. Polysulfide analysis.

## CONCLUSIONS

### Current Methods

- The diluted polysulfide samples are not stable.
- Quantitation of trace levels of sulfur-containing species is unreliable.
- The use of silver cartridge can remove sulfide, but it also removes thiosulfate.

### OnGuard SPE Based Treatments

- The OnGuard II H cartridge is capable of removing polysulfide species from the solution. However, the resulting solution is acidic and many sulfur-containing species are not stable in the presence of acid.
- Combination of OnGuard II H and Na cartridge treatment sequentially stabilizes the sample and yields more stable response.
- The new pretreatment approach provides a more reliable approach for analyzing sulfur containing anions in polysulfide matrix.

### Ion Chromatography

- The AS17-C column provides good separation for sulfur speciation.

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