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Determination of Thiosulfate in Refinery and Other Wastewaters

INTRODUCTION

Natural gas can contain hydrogen sulfide (H₂S) and carbon dioxide (CO₂). Because these gases (sour gases) are corrosive, they must be removed before the natural gas is fed into pipelines. This is usually accomplished by treating the gas with an amine solution. The amine-absorbed gases are then stripped from the amine solution so that it can be reused. Any anions introduced during this process can form heat-stable salts with the amine preventing its regeneration. Therefore, it is important to regularly determine the anion contents of these solutions to determine their efficacy for sour gas removal.¹

Thiosulfate and sulfate are two anions commonly found in these solutions. Thiosulfate is one of a group of anions classified as polarizable. These anions have large deformable electron clouds and are lightly hydrated and therefore hydrophobic. The group of polarizable anions includes perchlorate, chromate, thiocyanate, iodide, and thiosulfate. Due to their hydrophobicity, these anions elute from previously existing anion-exchange stationary phases with poor peak shapes and poor peak efficiencies, which compromises the chromatographic analysis. The addition of organic solvent to the eluent improves the peak shape and efficiencies but leads to increased eluent and waste disposal costs and reduces the sensitivity of conductivity detection.

The IonPac[®] AS16 is the first commercial anion-exchange column designed for the separation of polarizable anions. It is a high-capacity, hydroxide-selective anion-exchange column. The AS16 packing consists of a 9- μ M highly crosslinked macroporous resin bead functionalized with an anion-exchange layer of very hydrophilic quaternary ammonium groups. This construction allows polarizable anions to be eluted with high efficiency and good peak shape, without the addition of organic solvents (Figure 1).

The AS16 has been used for the determination of perchlorate in drinking water and high ionic strength matrices.^{2,3}

Because the IonPac AS16 column uses a hydroxide eluent, the EG40 Eluent Generator can be used for eluent generation. The EG40 produces high-purity carbonate-free KOH eluents via electrolysis. The use of hydroxide gradients for ion chromatography yields separations that allow the quantification of multiple analytes in difficult matrices. Unfortunately, many analysts have avoided hydroxide gradients due to the difficulty in preparing hydroxide eluents with low amounts of contaminating carbonate ion. Variability in the amount of hydroxide eluent carbonate causes irreproducible, and sometimes poor, chromatography. Adjusting the current of the EG40 controls the KOH concentration. Therefore, reproducible gradients can be produced without a gradient pump and without manual eluent preparation. The analyst can now easily use gradient chromatography to quantify analytes in difficult matrices. This Application Note shows that thiosulfate can be determined in refinery and other waste waters using an IonPac AS16 column, EG40-generated eluent gradients, and suppressed conductivity detection.

EQUIPMENT

Dionex DX-500 IC system consisting of:

- GP50 Gradient Pump
- CD20 Conductivity Detector
- AS40 Automated Sampler
- LC30 Chromatography Oven
- EG40 Eluent Generator with an EluGen[®] Hydroxide Cartridge

PeakNet[™] Chromatography Workstation

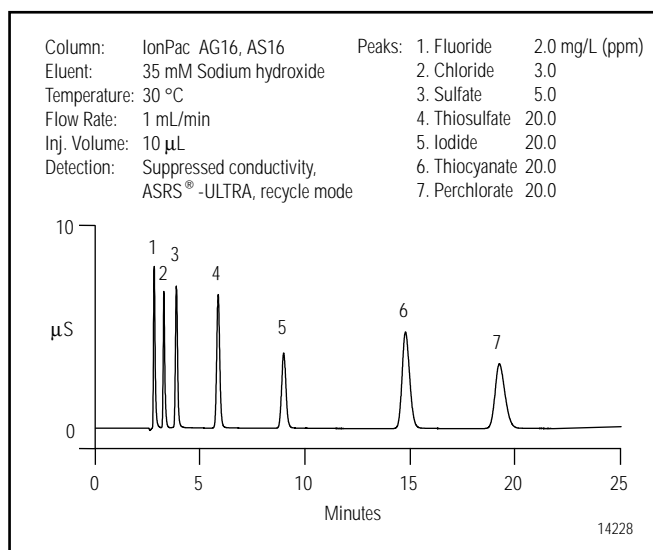


Figure 1. The new IonPac® AS16 for polarizable anions.

SYSTEM SET-UP

To ensure a quiet baseline, the following steps must be taken during the system setup. One thousand psi of backpressure must be added to the degas module on the eluent generator. (Refer to the EG40 Manual, P/N 031373, for details on adding backpressure to the degas module.) The final system backpressure should be in the range of 2400 to 2600 psi. A conditioned anion trap column (ATC) should be installed after the proportioning valve. A rise in background during gradient elution indicates that the ATC needs regeneration. (For instruction on ATC conditioning and regeneration, refer to the EG40 Manual, P/N 031373). Prior to sample analysis, determine a system blank by analyzing 100 µL of deionized water using the chromatographic method described below. An equilibrated system has a background conductance from 1–4 µS with the peak-to-peak noise typically 9–10 nS and no peaks eluting with the same retention time as thiosulfate.

STANDARDS

One thousand mg/L standards of 17 anions were prepared using the compounds and masses listed in Table 1. The mixed standard whose separation is shown in Figure 2 was prepared by mixing appropriate volumes of the 1000 mg/L standards. To determine method linearity for thiosulfate, the 1000-mg/L standard was diluted to prepare 1, 2, 5, 10, 20, 35, 50, and 100 mg/L standard solutions. Deionized water (DI H₂O), Type I reagent grade, 18 MΩ-cm resistance or better was used to feed the EG40, prepare all standards, and dilute samples.

Table 1 Amounts of Compounds Used to Prepare 1 L of 1000 mg/L Anion Standards

Anion	Compound	Mass (g)
F ⁻	Sodium fluoride	2.210
C ₂ H ₃ O ₂ ⁻	Sodium acetate	2.305
C ₃ H ₅ O ₂ ⁻	Sodium propionate	1.315
CHO ₂ ⁻	Sodium formate	1.511
ClO ₂ ⁻	Sodium chlorite • 2H ₂ O	2.409
BrO ₃ ⁻	Sodium bromate	1.179
Cl ⁻	Sodium chloride	1.648
NO ₂ ⁻	Sodium nitrite	1.499
NO ₃ ⁻	Sodium nitrate	1.371
CO ₃ ²⁻	Sodium carbonate	1.766
SO ₄ ²⁻	Sodium sulfate	1.479
I ⁻	Potassium iodide	1.310
S ₂ O ₃ ²⁻	Sodium thiosulfate • 5H ₂ O	2.375
CrO ₄ ²⁻	Sodium chromate • 4H ₂ O	2.172
PO ₄ ³⁻	Potassium phosphate, monobasic	1.433
AsO ₄ ³⁻	Sodium arsenate • 7H ₂ O	2.404
SCN ⁻	Sodium thiocyanate	1.396
ClO ₄ ⁻	Sodium perchlorate	1.231

SAMPLES

Samples were diluted so that thiosulfate was in the calibrated concentration range.

CONDITIONS

Columns: IonPac AS16 Analytical 4 x 250 mm (P/N 055376)
IonPac AG16 Guard 4 x 250 mm (P/N 055377)

Eluent: Potassium hydroxide

Eluent Source: EG40

Flow Rate: 1.0 mL/min

Temperature: 30 °C

Detection: Suppressed conductivity, ASRS®-ULTRA (4 mm), AutoSuppression® recycle mode. Power setting—300 mA

System Backpressure: 2600 psi

Background Conductance: 1–4 µS

RESULTS AND DISCUSSION

Figure 2 shows a separation of the 17 anions listed in Table 1. This separation includes inorganic anions (e.g., chloride), organic acid anions (e.g., acetate), oxyhalides (e.g., bromate), and six polarizable anions (iodide, thiosulfate, chromate, thiocyanate, arsenate, and perchlorate). The separation was accomplished using a multi-step hydroxide gradient that started at a low KOH concentration (1.5 mM). This or any gradient is easily executed by the EG40, allowing the analyst to quickly tailor the separation to resolve the analytes of interest in minimal time. We used the method in Figure 2 to determine thiosulfate in two wastewater samples. For routine analysis of thiosulfate in these samples, a much shorter method could be easily developed.

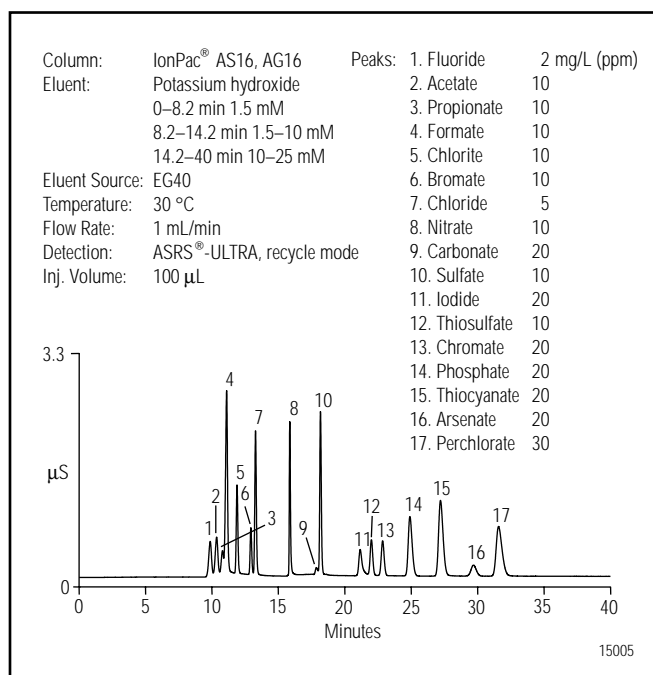


Figure 2. Separation of polarizable anions and inorganic anions using gradient elution.

The linearity of this method for thiosulfate was ascertained by making duplicate 100-µL injections of 1, 2, 5, 10, 20, 35, 50, and 100-mg/L thiosulfate. Figure 3 shows that the method is linear between 1 and 100 mg/L thiosulfate. A wider range was not tested.

Figure 4 shows the analysis of a refinery wastewater. The sample was diluted 1 to 5 so that the thiosulfate was in the calibrated range. Note the excellent peak shape for thiosulfate. Because the eluent was generated by the EG40, the baseline was flat, which facilitates reproducible integration.

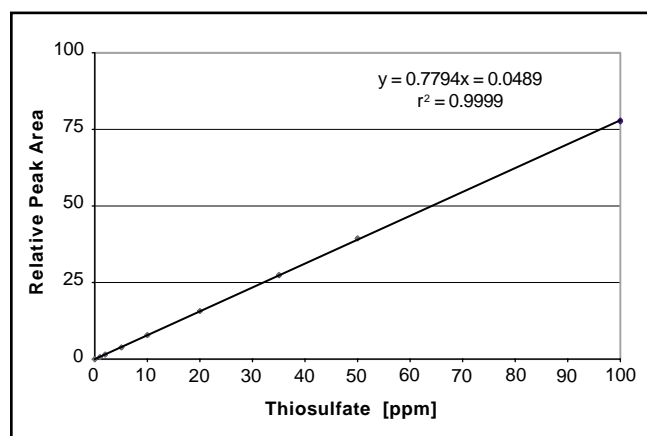


Figure 3. Thiosulfate linearity.

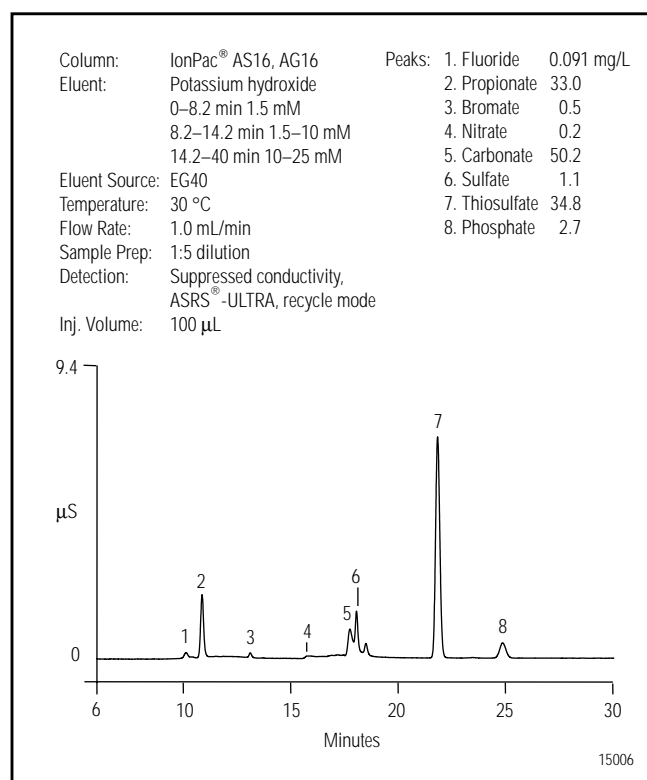


Figure 4. Determination of thiosulfate and inorganic anions in refinery wastewater.

Another wastewater sample was diluted 1 to 250 and analyzed with the same method (Figure 5). The sulfur in this sample is in a higher oxidation state compared to the sulfur in the refinery waste sample. The sample in Figure 5 has a sulfate content that is over twice the thiosulfate content compared to the refinery waste sample in which the thiosulfate content is over 30 times the sulfate content.

SUMMARY

The method described in this Application Note can be used to determine thiosulfate in industrial wastewaters. This method uses EG40-generated eluents, which improves method reproducibility. The IonPac AS16 can be paired with the EG40 to quickly develop methods for determining polarizable anions in a variety of matrices.

REFERENCES

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2. Dionex Application Note 134, “Determination of Low Concentrations of Perchlorate in Drinking and Ground Waters by Ion Chromatography”.
3. Jackson, P. E.; Laikhtman, M.; Rohrer, J. S. J. *Chromatogr. A* **1999**, *850*, 131–135.

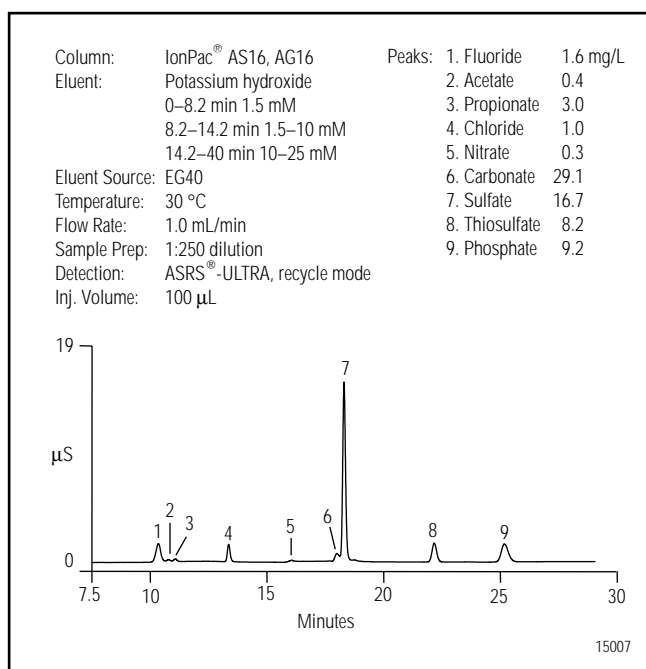
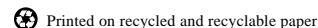


Figure 5. Determination of thiosulfate and inorganic anions in wastewater.



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