

Determination of sulfide in mining leachates

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Summary

Metal precipitation and cyanide recovery in the SART process (sulfidization, acidification, recycling, thickening) depend to a great extent on the sulfide concentration. Among the flow injection analysis methods coupled to wet-chemical analyzers, the combination of a gas diffusion cell with an ion chromatograph (IC) plus subsequent direct spectrophotometric detection has proven to be one of the most convenient methods of sulfide analysis.

After acidification of the sample with sulfuric acid, the hydrogen sulfide produced continually enters the gas diffusion cell, where it selectively diffuses through the hydrophobic membrane into a non-UV-absorbing acceptor solution (4 mmol/L sodium carbonate solution, pH ≈ 12), where it is deprotonated to the IC-compatible hydrogen sulfide anion (HS⁻). In contrast, potentially interfering compounds, which can foul the column, are widely rejected by the membrane. Owing to the selectivity of the gas diffusion cell and the direct ultraviolet absorption of the hydrogen sulfide anion at 230 to 250 nm – no chromogenic post-column reagent is necessary – the overall analysis time is less than eight minutes. A linear five-point external calibration graph was obtained over the range of 0 to 20 mg/L with a coefficient of determination of 0.998. The limit of detection was 0.1 mg/L.

Successfully applied to sulfide analysis in mining leachates, the straightforward and widely interference-free online determination of sulfide is also an invaluable tool for numerous environmental and biogeochemical applications.

Introduction

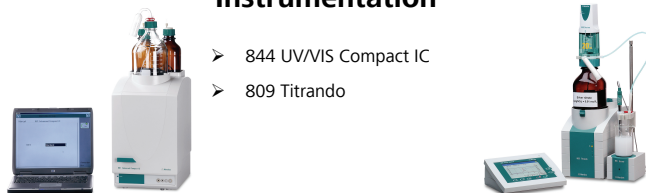
Sulfide is an effective reagent for the precipitation of copper and other base metals in both metal winning and environmental control. For an effective and economic operation of the SART process (sulfidization, acidification, recycling, thickening) control of the sulfide concentration is essential.

Normally sulfide is determined by acidifying the sample and collecting the H₂S gas through a membrane in a buffer. The collected gas is then determined spectrophotometrically at 230 nm or after the methylene blue reaction at 600 nm. This method is very time-consuming and prone to interferences by other substances present. Another problem is the fact that at a pH below 10 sulfide forms H₂S gas, which is very susceptible to evaporation. A direct measurement at the SART process is therefore preferable to offline measurements in the laboratory. As a further advantage, the online measurement provides faster and more accurate results.

This paper deals with the determination of sulfide anions via the coupling of a gas diffusion cell to an IC with subsequent spectrophotometric detection.

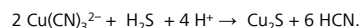
Instrumentation

- 844 UV/VIS Compact IC
- 809 Titrand



The SART process

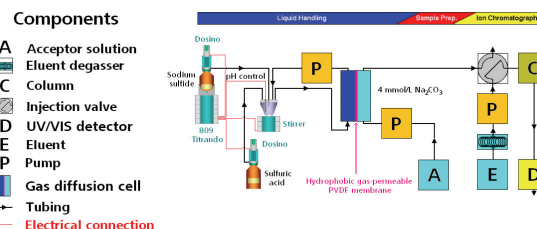
The SART process has been developed for use in the processing of gold-copper ores. Sulfide ions are used to precipitate cupric ions from cyanide leachates under weakly acidic conditions (pH ≈ 5):



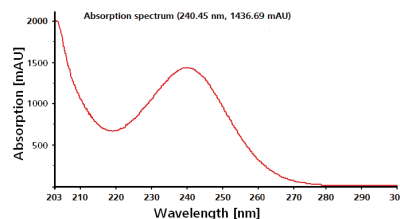
Due to the extremely low solubility of Cu₂S, this reaction results in a nearly complete precipitation of copper. The excellent solubility and the low vapor pressure of gaseous HCN at ambient temperatures result in a clear solution after the removal (by filtration or thickening) of the sulfide precipitate. After being treated with lime or caustic soda, this solution can be reused in the leaching process. The small part of the hydrogen cyanide gas that accumulates in the vapor phase is recycled by venting the gas phase to a caustic scrubber. Other metals such as cadmium, molybdenum, nickel and zinc are also precipitated as sulfides and can thus also be efficiently removed by the SART process.

Analytical setup with gas diffusion cell

After acidification, volatile hydrogen sulfide diffuses selectively from the sample stream (donor stream) through a hydrophobic gas-permeable membrane (Durapore Membrane, PVDF, GVHP04700, Millipore, USA) into a 4 mmol/L sodium carbonate acceptor solution. Potentially interfering species cannot pass the membrane.

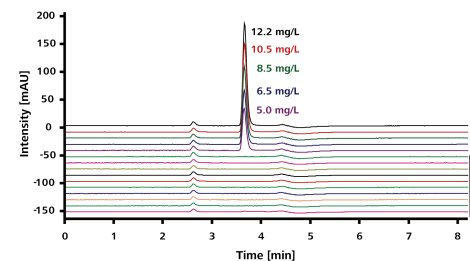


Absorption spectrum



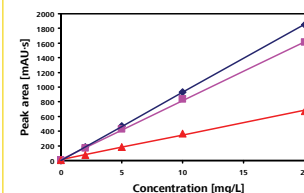
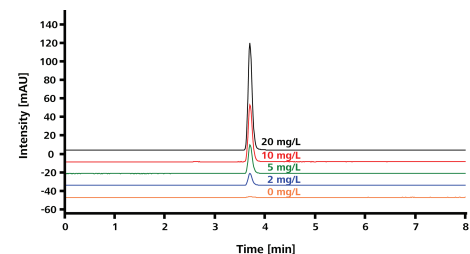
As many other inorganic ions (e.g. NO₃⁻, Br⁻, I⁻), the sulfide ion strongly absorbs at wavelengths below 250 nm. Since interfering ions cannot pass the membrane, HS⁻ can be sensitively determined by direct ultraviolet spectrophotometric detection at wavelengths between 230 and 250 nm.

Results



Sample Prep.: Gas diffusion cell, acceptor solution: 4 mmol/L Na₂CO₃, flow sample/acceptor solution: 1 mL/min
Column: Metrosep A Supp 1 – 250, 4.6 × 250 mm, 7 μm
Eluent: 4 mmol/L Na₂CO₃
Flow: 1.0 mL/min
Loop: 10 μL
Wavelength: 230 nm

Calibration with the gas diffusion cell



Concentration [mg/L]	Peak area [mAU]	Direct injection	Direct injection after acidification	Gas diffusion cell after acidification
0	0	0	0	0
2	184.9	172.1	75.7	
5	470.6	430.4	181.9	
10	930.8	860.9	374.6	
20	1863.0	1801.0	744.4	
Coefficient of determination	0.9998	0.9992	0.9992	

Unlike the direct injection of pure sulfide standards, the direct injection of the SART solution leads to severe column fouling (by e.g. Cu²⁺) due to the permanent absorption of sulfide. This problem can be overcome by the presented setup.

References

- (1) E.A. Guenther, K.S. Johnson and K.H. Coale, Direct ultraviolet spectrophotometric determination of total sulfide and iodide in natural waters, *Analytical Chemistry* **73**, 3481-3487 (2001).
- (2) I.G. Casella, M.R. Guascito and E. Desimoni, Sulfide measurements by flow injection analysis and ion chromatography with electrochemical detection, *Analytica Chimica Acta* **409**, 27-34 (2000).