Application Note 21
Simultaneous Determination of CO2 and H2S in Amine Scrubbing Solutions

PRINCIPLES OF OPERATION AND TYPICAL USE

This procedure is typically utilized for the analysis of amine solutions that are used to remove environmentally controlled emissions from flue gases. This method measures the amount of carbon dioxide (CO_2) and the amount of hydrogen sulfide (H_2S) in the scrubbing solution. This result is used along with other analyses to determine the amine scrubbing solution's efficiency and remaining capacity. This procedure may also be used for the analysis of “sour” water.

The system is composed of the CM5230 Acidification Module and the CM5016 C/S Coulometer. The Acidification Module is purged of atmospheric CO_2, SO_2 and H_2S with an inert carrier gas. After purging the system, an aliquot of the amine solution is injected into the sample flask. Acid is then added using the dispenser on the Acidification Module. The gases evolved from the acidification of the sample then pass into the special cell on the Sulfur analysis side of the coulometer where SO_2 and H_2S are absorbed into the solution and titrated.

CO_2 is not absorbed into the sulfur detector solution and provides no interference. The CO_2 enriched carrier gas is then routed to the cell on the Carbon analysis side of the instrument where it is absorbed and automatically titrated.

APPARATUS

CM5016 C/S Coulometer
CM5230 Acidification Module
Special, air-tight sulfur cell
Carbon cell

REAGENTS

1. Pre-Scrubber Solution: 40-45% (wt/vol) potassium hydroxide (KOH)
2. Post Scrubber Solution: 3% (wt/vol) silver nitrate ($AgNO_3$), acidified to pH 3
3. Acid: 2 to 4N Sulfuric Acid (H_2SO_4)
4. CM300-001 Carbon Cathode Solution
5. CM300-002 Carbon Anode Solution
6. CM300-003 Potassium Iodide (KI)
7. CM300-026 Sulfur Anode Solution
8. CM300-027 Sulfur Cathode Solution

9. External Carrier Gas (optional) (Note: An external carrier gas, such as nitrogen, helium, or CO_2-free air may be used in place of the "internal" air source of the Acidification Module if desired.)

PROCEDURE

ASSEMBLY

Assemble the Acidification Module and C/S Coulometer as instructed in their respective manuals. It is especially important to ensure that the special sulfur analyzer cell is leak free and that the flow from the acidification module always passes through the sulfur cell first. The cell solution on the carbon analyzer side of the instrument is adversely affected by sulfur compounds and passing the carrier gas through the sulfur analyzer first effectively removes all interfering compounds.

An optional solid silver or silver nitrate scrubber should be used in line between the sulfur coulometer and the carbon coulometer as an indicator of sulfur cell efficiency. Black precipitate in the silver nitrate solution or “graying” of the solid silver indicates that SO_2 or H_2S is not being properly absorbed into the sulfur cell solution.

Place a stir bar in a 100 ml sample flask and attach the flask to the bottom of the condenser on the Acidification Module. Secure the flask with the red locking ring. Place the flask and assembly into the heating and stirring port of the Acidification Module. Heating is not normally required so the condenser does not need to be connected to a cooling source. If an external carrier gas is used, adjust the pressure of the system to 2-5 psi. Set the flow to 100 ml/min. using the flow meter on the front of the Acidification Module. *(See FIGURE 2 for an example of the set-up and flow diagram.)*

ANALYSIS

Determine the background rate of the system by first analyzing a “Blank” sample. The instrument will use the saved blank value in calculating the final result values of subsequent analyses.

To perform an analysis, draw the sample into a syringe that is fitted with an injection needle. *(See note on "sample integrity".)* Usually 200 to 300 µl of sample is used depending on the sample's H_2S content*. Start the coulometer and inject the sample into the sample flask through the septum at the top of the sample column adapter. Add 5 to 10 ml of acid to flush the sample through the sample column line. The analysis endpoint will be automatically determined by the coulometer according to the user selectable settings saved within the instrument. All analysis data and parameters are saved to an SD Card. Data may also be printed to an optional printer or output to an external computer or LIMS.

****Note:*** *Due to lower H_2S solubility in the sulfur cell solution sample sizes should be adjusted to allow no more than 2500ug S per sample at a 100ml/minute flow rate.*

The weight of the sample can be determined in either of two ways. First, the syringe can be weighed before and after injection. The weight of the sample is determined by the difference between these two measurements. Second, if the density of the sample is known, the injection volume can be noted and the weight can be calculated. This method requires a volumetric syringe.

After a few samples are analyzed, the blank should be re-established and occasionally checked throughout the day. The sample flask does not need to be emptied until it is almost full.

Although calibration is not required, the instrument's performance can be checked using calcium carbonate ($CaCO_3$) and Sodium Sulfite (Na_2SO_3). This is done by weighing 10 to 15 mg of $CaCO_3$ and 5 to 10mg of Na_2SO_3 into a small Teflon cup and placing it in a 10 ml sample flask. The sample flask is connected to the bottom of the condenser, purged, and then acidified. Alternatively, the user

may use a liquid standard to verify the instrument's performance. To prepare a 10,000 mg C-S/L solution, weigh 3.237 g of sodium bicarbonate, 4.428 g of sodium carbonate and 3.931 g of sodium sulfite and transfer all to the same 100 ml volumetric flask. Bring to volume with reagent water. This solution should yield 2000ug C and 2000ug S when using a 200ul injection. *The user should establish acceptance criteria for whichever type of performance check is used.*

NOTE: Sample Integrity ... *Because of the ability of amine solutions to absorb CO_2 or release H_2S, sample handling is extremely important. The collection should be done so that the sample has as little contact with the air as possible. Ideally, the samples should be collected into bottles with septum tops. The septum top allows the sample to be drawn into the injection syringe without opening the sample bottle.*

RESULTS

Actual Results Using This System

Sample	Wt. Range	# of Runs	Theory %H_2S	Found %H_2S	Std. Dev.	RSD	Theory %CO2	Found %CO2	Std. Dev.	RSD
$CaCO_3$/ Na_2SO_3	5-15mg	7	26.74	26.54	0.089	0.36%	44.01	43.82	0.014	0.12%
Amine 1	400-1200mg	6	----	0.35	0.003	0.73%	----	0.63	0.006	0.96%
Amine 2	200-400mg	6	----	1.21	0.004	0.34%	----	2.30	0.005	0.22%
Amine 3	200-400mg	6	----	0.24	0.005	2.23%	----	1.28	0.010	0.82%

The analysis accuracy is normally limited to the precision of the sample volume measurement. The relative standard deviation for standard materials is better than 0.5%.

Assuming that the system is clean and that high purity water and acid are used, blank rates as low as 1 to 2 µg of carbon in 10 minutes are typical. Normally, blanks lower than 1 µg of carbon per minute are accepted.

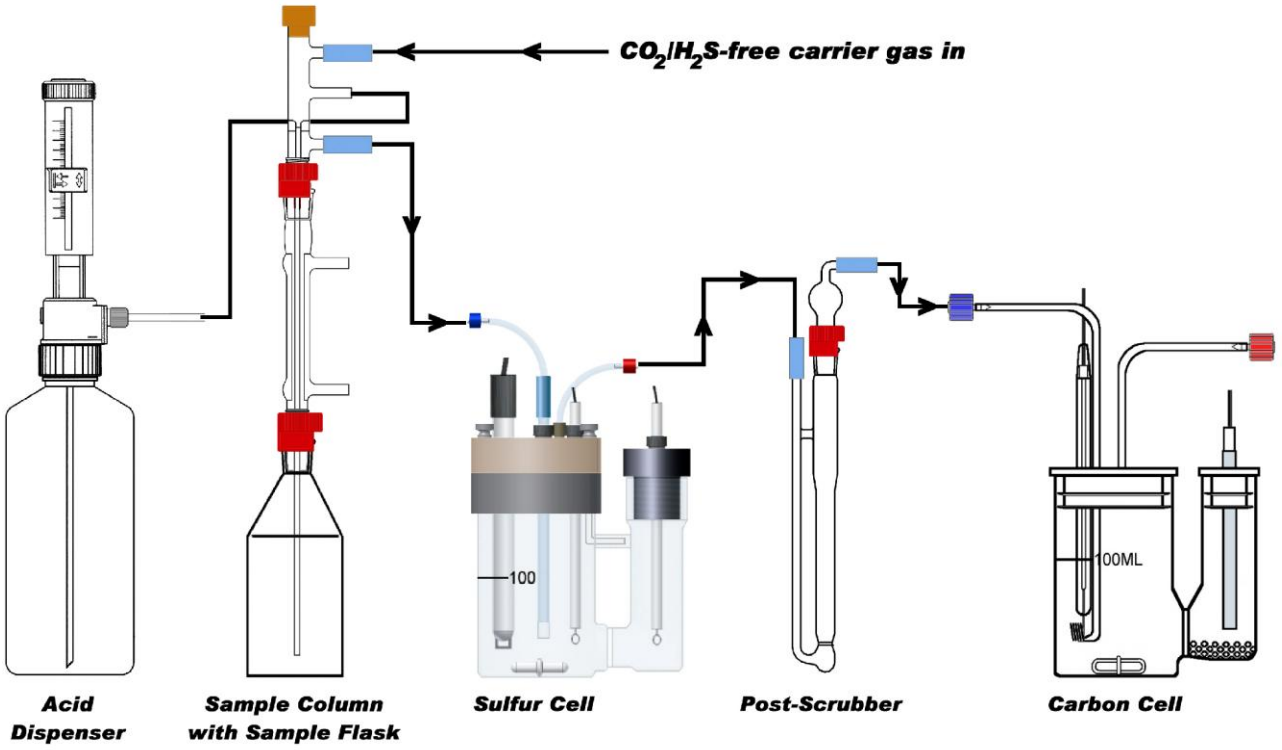

Figure 2 – CM540 Flow Diagram