

Sulfur Dioxide Analysis Using the Agilent 990 Micro GC

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Introduction

Sulfuric acid is one of the most important chemicals in the world. It is widely used for manufacturing fertilizers, pigments, dyes, drugs, explosives, detergents, and inorganic salts and acids. It is also used in petroleum refining and metallurgical processes.

The most important process for making sulfuric acid is the contact process. During this process, sulfur is burned in air to make sulfur dioxide (SO_2). Then, the SO_2 is converted to sulfur trioxide (SO_3) by oxygen (O_2). The reaction of SO_2 and O_2 is reversible, and usually a catalyst is used to speed up the reaction to increase the amount of SO_3 created.

During the contact process, the concentration of SO_2 should be monitored before and after its reaction with O_2 to track the conversion rate of SO_2 . The O_2 concentration also needs to be monitored to ensure that SO_2 and O_2 are in the right ratio to make SO_3 . The Agilent 990 Micro GC provides fast and accurate measurement of SO_2 and O_2 , which helps control the SO_3 manufacturing process.

Experimental

Channel 1: A 10 m, Agilent CP-Molesieve 5 Å, backflush channel, with retention time stability (RTS) option for O₂ analysis. The backflush option and RTS is used to protect the Molesieve 5 Å column from moisture, CO₂, SO₂, and other contaminants. This is beneficial to the long term RT repeatability and column performance of Molesieve 5 Å column.

Channel 2: A 12 m, Agilent CP-Sil 19CB backflush channel for SO₂ analysis.

Figure 1 shows the chromatogram of the O₂ analysis on channel 1. Figure 2 shows the chromatogram of the SO₂ and moisture (H₂O) analysis on channel 2. During manufacturing, H₂O is present as moisture in the gas mixture of O₂ and SO₂. Figure 2 shows that SO₂ and H₂O can effectively be separated on the CP-Sil 19CB column at the tested concentration. Their peak resolution in this chromatogram is 3.6, and SO₂ can accurately be quantitated. In the reaction gas, the concentrations of SO₂ and H₂O are sometimes as high as 10%. With such high concentration, the peaks broaden, and the resolution gets worse. Under these circumstances, it is necessary to use a filter to remove the moisture from the reaction gas before analyzing SO₂. The signal-to-noise ratio (S/N) for 35 ppm SO₂ under the applied test conditions is 98, and the calculated detection limit is 1.1 ppm.

Table 1. Test conditions for the Agilent CP-Molesieve 5 Å and the Agilent CP-Sil 19CB channels.

Channel Type	10 m, Agilent CP-Molesieve 5 Å, Backflush	12 m, Agilent CP-Sil 19CB, Backflush
Injector Temperature	110 °C	110 °C
Column Pressure	200 kPa	220 kPa
Column Temperature	80 °C	50 °C
Carrier Gas	Helium	Helium
Backflush Time	7 seconds	0 seconds
Injection Time	40 ms	40 ms

Table 2. SO₂ calibration gas standard.

Compounds	Concentration
SO ₂	0.1%
N ₂	Balance

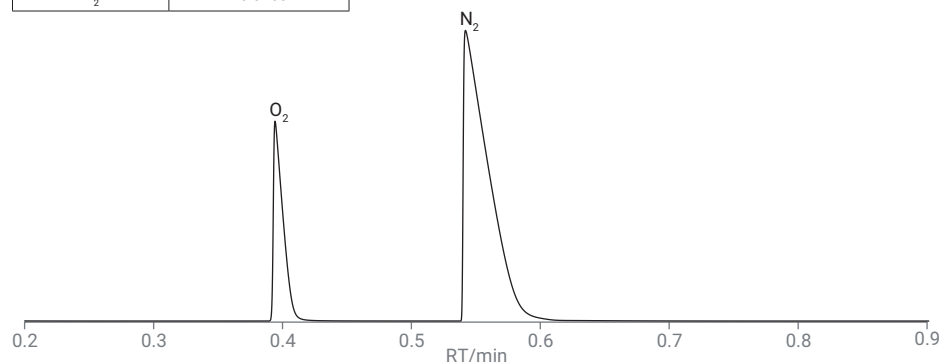


Figure 1. O₂ analysis on the Agilent CP-Molesieve 5 Å channel.

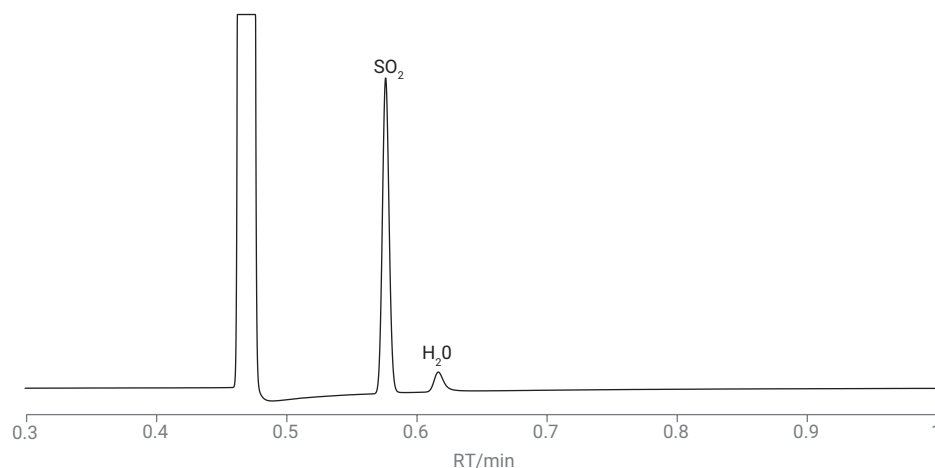


Figure 2. SO₂ and H₂O analysis on the Agilent CP-Sil 19CB channel.

The instrument repeatability was evaluated by 10 injections of calibration standard (1,000 ppm SO₂ and lab air). Table 3 shows the RT and area RSD for O₂ and SO₂. The RT RSD% is less than 0.1% and the area RSD% is lower than 1%.

Conclusion

This study demonstrates the application of the Agilent 990 Micro GC for SO₂ and O₂ analysis, which can be used for performance evaluation of the catalyst or the process control in sulfuric acid manufacturing. With the specially selected column channel, Agilent CP-Sil 19CB, 0.1% SO₂ and H₂O can be resolved with resolution greater than 3. Oxygen is analyzed on a molecular sieve channel with backflush option. The quantitation precision was evaluated by 10 consecutive analyses of calibration standard and lab air with RT repeatability less than 0.1% and area repeatability less than 1%, demonstrating excellent instrument performance for reliable qualification and quantitation of SO₂ and O₂.

Table 3. RT and area repeatability of SO₂ and O₂ on two analytical channels.

	SO ₂		O ₂	
	RT (min)	Area (mv × s)	RT (min)	Area (mv × s)
	0.576	1.689	0.395	74.520
	0.576	1.704	0.395	74.622
	0.575	1.700	0.395	74.598
	0.575	1.721	0.395	74.616
	0.575	1.697	0.395	74.596
	0.575	1.694	0.395	74.608
	0.576	1.669	0.395	74.592
	0.576	1.684	0.395	74.568
	0.576	1.680	0.395	74.568
	0.575	1.716	0.395	74.617
Average	0.576	1.695	0.395	74.592
RSD%	0.09	0.93	0.002	0.041