Rapid Analysis of SO$_2$ to Determine Catalyst Efficiency using Micro GC Fusion

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Outline

• Introduction
• Micro GC Fusion in the Field
• Micro GC Fusion Configuration
• Micro GC Fusion Setup
• Micro GC Fusion Method and Data
• Linearity and Repeatability
• Conclusion
Introduction

• Sulfuric acid (H$_2$SO$_4$) is one of the most produced chemicals in the world

• Worldwide, over 180 million tons are consumed on a per year basis (based on data from 2004)$^1$

• Sulfuric acid is generated from SO$_2$, which can by obtained by$^1$:
  • Burning elemental sulfur with air
  • Smelting and roasting metal sulfides
  • Decomposing contaminated sulfuric acid catalyst

Figure 2.7 U.S. production of sulfur and sulfuric acid. (Source: Lowenheim and Moran, Chemical and Engineering News, Chemical Economics Handbook)

Figure 2.8 U.S. prices of sulfur and sulfuric acid. (Source: Lowenheim and Moran and Chemical Marketing Reporter)
The most common way to generate sulfuric acid is by the following reaction, called the Contact Process\(^1\)

\[
SO_2(g) + \frac{1}{2} O_2(g) \rightarrow SO_3(g)
\]

Since \(O_2\) is not enough to oxidize \(SO_2\) to \(SO_3\), a catalyst (usually vanadium or platinum based)\(^1\) is used.

The \(SO_3\) is reacted with strong sulfuric acid with a small amount of water to produce strengthened \(H_2SO_4\), which consumes the water and produces additional \(H_2SO_4\)\(^1\)

\[
SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)
\]

\(SO_3\) is not reacted with pure water because the reaction is so exothermic, the resulting \(H_2SO_4\) would be a vapor that is expensive and difficult to condense\(^1\)
Micro GC Fusion in the Field

• Catalyst manufacturers will often send people into the field to analyze the gas stream at the inlet of the converter bed (high percent SO$_2$) and the outlet (low percent SO$_2$)
  • A linear instrument is required, due to the high concentration range

• A transportable instrument allows for several samples to be conducted around different sites of the H$_2$SO$_4$ plant
  • Up to 15 measurements are taken at a single plant per day

• Micro GC Fusion can meet both the analysis requirement and the transportability requirement
Micro GC Fusion Features

- Micro GC Fusion hardware features include:
  - Temperature programmable columns for fast temperature ramping
  - Additional heated zones to minimize ambient temperature effects
  - Optional integrated sample conditioner
  - Lightweight chassis
Micro GC Fusion Features

- Micro GC utilizes a modular architecture
- Each module is its own GC:
  - MEMs based injector
  - Resistively heated fused silica capillary columns
  - MEMs based $\mu$TCD
Micro GC Fusion Features

• Micro GC Fusion utilizes a web-based User Interface (UI)
  • Front panel display
  • Direct Ethernet connection to a computer
  • Direct Ethernet connection to a LAN hub for remote access
  • Wi-Fi enabled
  • License free
  • Works with any platform (ex. Windows, Apple, Android)
  • On board solid state drive for data storage
Micro GC Fusion Configuration

- Two module configuration:
  - Module A – 12m RT-Q-Bond, variable volume injector
  - Module B – 12m CPSil19CB, large variable volume injector

- Calibration gas:
  - 12% SO₂ in air
    - 6% SO₂ in air (syringe dilution)
    - 0.996% SO₂ in air (syringe dilution)
  - 100 ppm SO₂ in air

- Historically on the 3000 Micro GC, the CPSIL19CB column was used because previous PLOT Q columns were unsuitable for this application
The method was designed to elute all compounds within 60 seconds.
Micro GC Fusion Method – CPSil19CB

- The method was designed to elute all compounds within 60 seconds.
Chromatogram Overlay – RT-Q-Bond

12% SO2 in air
6% SO2 in air
0.96% SO2 in air
100 ppm SO2 in air
100 ppm SO2 in air
CPSi19CB Chromatogram

6% SO2

Water

Retention Time (s)

3,000k
2,500k
2,000k
1,500k
1,000k
500k
0k

Retention Time (s)
Chromatogram Overlay – CPSi19CB

12% SO2 in air

6% SO2 in air

0.96% SO2 in air

100 ppm SO2 in air

Water
Linearity and Repeatability

- Micro GC Fusion has excellent linearity from 100 ppm to 12%

Repeatability Test: 10 runs of 12% SO₂ in air connected via SilcoSteel tubing

<table>
<thead>
<tr>
<th>Component</th>
<th>No. Runs</th>
<th>Area (uV)</th>
<th>RT (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12% SO₂ on Rt-Q-Bond</td>
<td>10</td>
<td>0.43</td>
<td>0.14</td>
</tr>
<tr>
<td>12% SO₂ on CPSil19CB</td>
<td>10</td>
<td>1.39</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Concerns and Future Development

• The present of high percentage SO$_3$ poses a problem for GC analysis
  • SO$_3$ is dangerous and corrosive, and not suitable for GC analysis
  • Violent reaction with water can create sulfuric acid, not great for GC columns!

• Questions from the field include:
  1. How to remove SO$_3$ from the gas line
  2. If SO$_3$ is present is such quantity that it cannot be removed, how does the presence of SO$_3$ affect the chromatography? The integrity of the columns or internal components?
Conclusions

• Micro GC Fusion demonstrates excellent linearity for SO$_2$ from 100 ppm to 12% on both RT-Q-Bond and CPSil19CB

• Micro GC Fusion demonstrations excellent retention time and area repeatability

• RT-Q-Bond offers better repeatability and separation when compared to CPSil19CB
  • CPSil19CB has a faster analysis time, which may be desired for some users

• Further information must be gathered to determine the affects of SO$_3$ on Micro GC Fusion
References

   https://books.google.com/books?id=tRAb2CniRG4C&printsec=frontcover#v=onepage&q&f=false

   https://books.google.com/books?hl=en&lr=&id=gbHeBwAAQBAJ&oi=find&pg=PA1&dq=Survey+of+Industrial+Chemistry&ots=0q8Qlk58RP&sig=KvfebWUqr4BwWdU-KwVv1p_3tDs#v=onepage&q=sulfuric&f=false
More Information

- Application Note available from www.INFICON.com

INFICON Advances in Micro Gas Chromatography

APPLICATION NOTE
Rapid Analysis of SO₂ to Determine Catalyst Efficiency using Micro GC Fusion®

INTRODUCTION
Sulfuric acid is one of the most produced chemicals in the world. Almost 185 million tons are consumed per year on a worldwide basis. 1 In the United States alone, billions of pounds are produced and sold for a variety of uses including the formulation of fertilizers, insecticides and detergents. To generate sulfuric acid, sulfur dioxide (SO₂) is oxidized to generate sulfur trioxide (SO₃), which when reacted with water, forms sulfuric acid (H₂SO₄). The majority of sulfuric acid is manufactured using this process.

Catalysts facilitate the oxidation of SO₂. The analysis of SO₂ at the inlet and outlet of the catalytic bed determines the conversion efficiency and performance of the catalyst. A percent level of SO₂ is introduced at the catalytic bed inlet. After the catalytic conversion of SO₂ to sulfuric acid, the concentration of the SO₂ exiting the bed outlet is often around 100 ppm. Since sample integrity may be compromised due to the decay encountered transporting the sample to an analysis lab, it is preferable to obtain accurate results quickly and reliably on-site.

Gas chromatography (GC) can be used to accurately analyze a wide concentration range of SO₂. Micro GC Fusion is a small, portable GC capable of analyzing SO₂ across a broad linear range. The microelectromechanical systems (MEMS) based thermal conductivity detector (TCD) in Micro GC Fusion is able to accurately measure a wide concentration range of compounds in less than 60 seconds.

EXPERIMENTAL
Micro GC Fusion is configured with a 12 m Rtx-Q-Bond column and a variable volume injector. The Rtx-Q-Bond column was selected due to the excellent separation of the SO₂ peak from the neighboring water peak. A variable volume injector allows a broad concentration range of samples to be analyzed.

Two calibration gas standards from Air Liquide® are used. The first standard contains 12% SO₂ in air to mimic the initial concentration of SO₂ at the catalytic bed inlet. The second standard contains 100 ppm of SO₂ in air to mimic the concentration of SO₂ exiting the bed. The method was designed to elute SO₂ quickly, while maintaining separation of the water peak.

The 12% SO₂ and 100 ppm SO₂ calibration gases were introduced using a 100 ml gas tight syringe. The syringe was then used to dilute the 12% SO₂ calibration gas to 6% and 0.96%, which were also introduced into the instrument. (See Table 1.) Multiple injections of each concentration were analyzed.

A calibration curve was created by plotting the average area counts and concentrations of each of the four calibration standards.

Ten consecutive runs were conducted using the 12% SO₂ calibration gas standard to calculate the relative standard deviation (%RSD) for peak area and retention time. This calibration gas was connected directly to the sample inlet with 1/16 in. Restek SilcoNert® tubing.

RESULTS
In less than 60 seconds, SO₂ is separated from the solvent peak (air) and water. (See Figure 1.) Chromatograms corresponding to four calibration standards concentrations are displayed in Figure 2.

The calibration curve shows excellent linearity of SO₂ concentrations ranging from 100 ppm to 12%. (See Figure 3.)

The %RSD calculations for both retention time and area show excellent repeatability. Over ten runs, the %RSD is 0.14% for retention time and 0.43% for area count. (See Table 2.)

CONCLUSION
The 12 m Rtx-Q-Bond column analyzes 100 ppm to 12% SO₂ at the inlet and outlet of the catalytic bed with excellent linearity and precision. Analysis can be conducted within 60 seconds directly on-site to monitor the conversion efficiency and performance of the catalyst to optimize sulfuric acid production efficiency.