FACT SHEET FOR TRACE LEVEL SO₂ MONITORING METHOD

Introduction

Trace levels of sulfur dioxide (SO₂) have been identified as precursors for particulate matter 2.5 (PM2.5). OAQPS began an effort to find analyzers capable of measuring background (trace) levels of SO₂. It was decided that these trace level analyzers must be rugged, precise, and accurate; also, they must be stable in the low parts per billion (ppb) ranges. Stability may eventually be necessary in the parts per trillion (ppt) ranges.

Principle of Operation

The current measurement of SO₂ is based on the principle that SO₂ molecules absorb ultraviolet (UV) light and become excited at one wavelength (for SO₂, the excitation wavelength is 214 nm), then decay to a lower energy state emitting UV light at a different wavelength (330 nm).

Literature Search

During an online literature search, three manufacturers of trace level SO₂ analyzers were identified - Teledyne-Advanced Pollution Instrumentation, Inc. (Teledyne-API), Thermo Electron Corporation (TEC), and Ecotech. Teledyne-API manufactures both the Model 100AS and Model 100ES Ultra Sensitivity Fluorescence SO₂ Analyzer, TEC manufactures the Model 43C-TLE trace level Pulsed Fluorescence SO₂ analyzer, and Ecotech manufactures the EC9850T Trace SO₂ Analyzer. The specifications for the four analyzers are provided in Table 1. The prices for these analyzers are in the range of $10,000 and $15,000. See the internet websites below for additional information on these analyzers, and vendor contacts in your area:

http://www.thermo.com/
http://www.ecotech.com.au

Trace Level Modifications

A number of modifications are made to the standard SO₂ analyzer to improve the detection limit for trace gas monitoring. Typical modifications may include the following:

- Increased intensity of the UV source, and
- The use of reflective UV source optical filter.
Calibration and Zero

The calibration systems for the Teledyne-API Model 100AS and 100ES, and the TEC Model 43C-TLE are very similar. Both models offer a zero/span valve option for controlling the flow of calibration gases generated from external sources. They also offer the option to perform quick zero and span checks through the use of an internal zero air and span gas generator. The span gas is created when zero air passes over a permeation tube containing liquid SO₂ under high pressure. Both manufacturers recommend performing a Level 1 calibration if the quick checks indicate a possible analyzer drift or malfunction.

Issues with the Method

1) Interference from NO and Hydrocarbons.

It is known that the fluorescence method for detecting SO₂ is subject to interference from a number of sources. The most common source of interference is from other gases that fluoresce in a similar fashion to SO₂ when exposed to UV light. The most significant of these is a class of hydrocarbons called poly-nuclear aromatics (PNA). Both manufacturers offer a hydrocarbon “kicker” that removes any PNA chemicals present in the sample gas before it reaches the sample chamber. Nitrogen oxide (NO) fluoresces in a spectral range close to SO₂. In applications where high levels of NO are expected, the Teledyne-API 100AS and 100ES offer an optional optical filter that improves the rejection of NO. The standard source UV optical filter in the 100AS and 100ES removes the wavelength of light needed to excite a specific non-SO₂ fluorescing gas. Also, the light given off by NO is outside of the bandwidth passed by the photomultiplier tube (PMT) optical filter.

2) Interference from water vapor (H₂O).

Another potential source of interference experienced by the fluorescence method for detecting SO₂ is water vapors (H₂O). In ambient applications, the interference from H₂O is negligible. In situations where the concentration of H₂O may be very high (typically found in stack applications), the 100AS offers the option of installing a dryer system. This system would remove any moisture from the sample gas prior to reaching the particulate filter.
Table 1. Summary of Commercially Available SO₂ Analyzers

<table>
<thead>
<tr>
<th>Instrument Make/Model</th>
<th>Lowest Range</th>
<th>LDL</th>
<th>Response Time</th>
<th>Zero Drift</th>
<th>Span Drift</th>
<th>Auto Ranging</th>
<th>Precision</th>
<th>Linearity</th>
<th>Nafion Dryer option</th>
</tr>
</thead>
<tbody>
<tr>
<td>API 100AS, 100ES</td>
<td>10 ppb</td>
<td>100 ppt</td>
<td>120 sec</td>
<td>&lt;0.2 ppb/day</td>
<td>&lt;0.5% per day</td>
<td>Yes</td>
<td>0.5% of reading</td>
<td>1% FS</td>
<td>Yes</td>
</tr>
<tr>
<td>Thermo 43C-TLE</td>
<td>10 ppb</td>
<td>100 ppt</td>
<td>110 sec</td>
<td>&lt;0.2 ppb/day</td>
<td>1% per week</td>
<td>Yes</td>
<td>1% of reading or 0.2 ppb</td>
<td>1% FS</td>
<td>No</td>
</tr>
<tr>
<td>Ecotech 9850T</td>
<td>Auto ranging 0-200ppb</td>
<td>200 ppt</td>
<td>120 sec</td>
<td>&lt;0.2 ppb/day</td>
<td>&lt;0.5% per day</td>
<td>Yes</td>
<td>± 2% of reading</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>

Note: The Teledyne-API 100ES is the newer of the two Teledyne-API models, designed on a different electronic platform, with the same user interface. The platform allows for the use of common parts, and easy upgrades. Teledyne-API is also developing the model 100EU analyzer; designed specifically for trace level SO₂ measurements. A prototype of the 100EU is expected to be available early in 2005.