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FACT SHEET FOR TRACE LEVEL SO_2 MONITORING METHOD

Introduction

Trace levels of sulfur dioxide (SO_2) 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 SO_2. 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 SO_2 is based on the principle that SO_2 molecules absorb ultraviolet (UV) light and become excited at one wavelength (for SO_2, 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 SO_2 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 SO_2 Analyzer, TEC manufactures the Model 43C-TLE trace level Pulsed Fluorescence SO_2 analyzer, and Ecotech manufactures the EC9850T Trace SO_2 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.teledyne-api.com/products/index.asp
http://www.thermo.com/
http://www.ecotech.com.au

Trace Level Modifications

A number of modifications are made to the standard SO_2 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 SO_2 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 SO_2 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 SO_2 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 SO_2. 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-SO_2 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 (H_2O).

Another potential source of interference experienced by the fluorescence method for detecting SO_2 is water vapors (H_2O). In ambient applications, the interference from H_2O is negligible. In situations where the concentration of H_2O 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 SO_2 Analyzers

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

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 SO_2 measurements. A prototype of the 100EU is expected to be available early in 2005.