Continuous Infrared Analysis of N$_2$O in Combustion Products

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Nitrous oxide (N$_2$O) levels in the atmosphere are increasing, potentially contributing to the greenhouse effect and depletion of stratospheric ozone. From a limited data base, combustion sources have been identified as a major anthropogenic source of N$_2$O. However, the existing data base (obtained by traditional grab sampling techniques followed by gas chromatographic analysis) is in question due to the discovery of a sampling artifact. A continuous on-line N$_2$O analyzer would enable and facilitate the accurate characterization of combustion sources over a range of operating conditions, and also aid in the development of an appropriate sampling technique. This paper addresses the development of a continuous measurement technique, and the evaluation and initial use of a field prototype continuous N$_2$O analyzer developed at the UCI Combustion Laboratory in cooperation with a major Instrument manufacturer. The analyzer is capable of measuring N$_2$O levels down to a few ppm. The analyzer has been evaluated and used to study the N$_2$O emissions from a pulverized coal-fired boiler. The N$_2$O levels found with the analyzer are substantially lower than levels previously attributed to such sources. Initial N$_2$O measurements made with the analyzer suggest that N$_2$O levels are not a substantial fraction of the NO levels, as previously suggested.

Attention has recently focused on the emission of nitrous oxide (N$_2$O) from fossil fuel combustion processes. Although the emissions and emission formation mechanisms of NO, (NO + NO$_2$) are relatively well documented, the data base on nitrous oxide formation and control is small, with relatively limited information available in the literature. N$_2$O is suspected to have a two-fold effect in the atmosphere. In the troposphere, the species is stable with a lifetime of approximately 150 years.$^1$ Here N$_2$O is a likely contributor to the greenhouse effect$^2,3$ with the global mean concentration increasing between 0.2 and 0.4 percent a year.$^2$ The stability of N$_2$O facilitates its transport to the stratosphere. In the stratosphere, N$_2$O is the largest source of nitric oxide, which subsequently results in the destruction of ozone (O$_3$).$^4$ Hence, an increase in N$_2$O emissions is expected to translate to an increase in O$_3$ depletion.

Anthropogenic sources, including the use of chemical fertilizers and the combustion of fossil fuels,$^3$ are estimated to comprise one-third of the total N$_2$O produced.$^1$

Using the limited data available, which are based on grab sampling techniques, N$_2$O production was originally estimated to be between 20-25 percent of the NO$_x$ levels.$^4,6$ At these levels, combustion sources have been considered to be the largest source of anthropogenic nitrous oxide$^4,5$ with flue gas concentrations normally varying between 1 and 200 ppm.$^5$ Measurements from pilot scale facilities have been reported to be as high as 400 ppm.$^7$

However, recent findings suggest that grab samples containing NO, SO$_2$, and condensed H$_2$O produce N$_2$O as an artifact.$^8,9$ As a result, the N$_2$O levels reported to date may be higher than the levels actually produced directly by pulverized coal combustion systems. Providing a valid grab sampling technique is available, the method is tedious, making the complete characterization of a combustion source difficult.

An accurate, on-line continuous N$_2$O measurement technique is needed to (1) obtain reliable measurements in the field; and (2) assess the extent to which combustion sources directly produce N$_2$O. The present paper reports an investigation of means by which N$_2$O can be continuously monitored in combustion effluents. The goal is to identify, evaluate, and demonstrate a measurement method which is susceptible to minimal interferences and yet relatively simple, compact, reliable, and suitable for both field and laboratory use.

Approach

In addition to gas chromatography, various analytical techniques have the capability of measuring nitrous oxide concentrations.$^5$ These include: Tunable Diode Laser System, Fourier Transform Infrared Spectroscopy (FTIR), and Infrared (IR) Analyzers.

A Tunable Diode Laser System allows for continuous monitoring with the potential of avoiding interferences from other species in the combustion products due to the very fine spectral resolution of the technique. Major disadvantages (system cost and the requirement of cryogenic cooling) render the technique difficult for field application. An FTIR analyzer has the potential of providing sufficient accuracy. However, FTIR is moderately expensive, and while providing relatively rapid sampling and analysis, is not truly a continuous analysis method.

In comparison, infrared (IR) analyzers are relatively simple and inexpensive, and Non-Dispersive InfraRed (NDIR) analyzers are routinely used for continuously measuring CO, CO$_2$, and SO$_2$ in combustion systems. Since N$_2$O is an active infrared species, an analyzer based on IR analysis is a logical starting point in developing a simple analysis system. Be-
cause N₂O has a number of clearly defined peaks in its absorption spectrum, the particular methodology selected as a point of departure in the present study was selective NDIR at a specific, single wavelength (versus nonselective NDIR).

**Experimental Apparatus**

To assess the viability of continuous N₂O analysis in combustion effluents with a selective, single wavelength NDIR technique, and especially its sensitivity to interfering gases, a variable wavelength infrared analyzer (Foxboro Miran 1A) was used (Figure 1). Assuming the suppression of excessive interferences from other gases, the instrument can be calibrated to detect and measure a specific, infrared-active gas over a fairly wide concentration range.

A parametric variation was conducted with the Miran 1A using simulated combustion products. High Purity gases were blended to investigate (1) linearity of the analyzer with respect to N₂O (as a function of absorption wavelength, pathlength, and slit width); and (2) interferences from NO, NO₂, CO, CO₂, SO₂, and H₂O. These interferences were evaluated over the gas concentration ranges listed in Table 1.

**Results**

The infrared absorption spectrum of N₂O (obtained with an FTIR) is shown in Figure 2 and exhibits IR absorption peaks at 4.5, 7.8, and 17.0 microns, the primary N₂O absorption lines being 4.5 and 7.8 microns. As a result, these two lines were selected to evaluate the linearity of the analyzer to N₂O. Pathlengths were chosen at each wavelength to provide sensitivity to N₂O while maintaining linearity between N₂O and IR absorption. Slit width (spectral bandwidth) was chosen to minimize interferences from the other IR gases expected to be present in the effluent. Once the linearity of the instrument response to N₂O was verified, interference curves for CO₂, CO, NO, NO₂, and SO₂ were generated by observing the response of the analyzer to the introduction of various gas mixtures.

Typically N₂O levels of 400 ppm resulted in absorption of 20–25 percent. Figure 3 compares the interferences found for the species expected in combustion products. At a wavelength of 4.5 microns, the principal interfering species are CO₂ and CO. At 7.8 microns, NO₂ and SO₂ are the primary interfering species. For combustion gases generated from a relatively low sulfur coal in a moderately low NOₓ combustion environment, the N₂O measurement would be high by approximately 22 ppm at 4.5 microns and 6 ppm at 7.8 microns, and for combustion gases from a high sulfur coal with high NOₓ levels, by approximately 37 ppm at 4.5 microns and 17 ppm at 7.8 microns (assuming no corrections for interferences). Measurement error, at both wavelengths, can be further reduced by correcting for SO₂, CO₂, CO, NO₂, and NO interferences. (Note that the error introduced by interferences is less at 7.8 microns than at 4.5 microns; as a result, all further work with the Miran 1A was carried out at 7.8 microns.)

**Table 1. Concentration ranges used to generate interference curves. Maximum values used to normalize the values for Figure 3.**

| Species | Concentration ranges | minimum | maximum |
|---------|----------------------|---------|---------|
| CO₂     |                      | 0 %     | 25 %    |
| CO      | 0 ppm                | 500 ppm |
| NO₂     | 0 ppm                | 125 ppm |
| NO      | 0 ppm                | 1250 ppm|
| SO₂     | 0 ppm                | 5000 ppm|
8.5 microns. To date, the 7.8-8.5 micron region has been adapted for analysis with the HORIBA Model VIA-500. The analyzer uses two Luft-placeable optical filters to allow the instrument to measure emissions from 6 to 1 ppm for a low sulfur, low NOx fuel and from 17 to 1 ppm for a high sulfur, high NOx fuel (assuming no corrections have been made for interferences).

The results described above outline the requirements and criteria for a continuous analyzer utilizing infrared absorption for measuring N2O in combustion effluent. The key points from this study are as follows:

- The 7.8 micron region in the infrared is most suitable for measuring N2O in combustion products.
- At 7.8 microns, the primary interfering species are SO2 and NOx.
- SO2 and NOx can be readily removed from the sample stream ahead of the analyzer without affecting N2O levels.
- A precision of better than 3 percent can be achieved based on reported N2O levels from coal combustion products.

Based on these criteria, a field prototype instrument was designed and built in cooperation with a major instrument manufacturer. The evaluation of the prototype continuous N2O analyzer is described below. In addition, recent field measurements from two coal-fired utility boilers are presented to establish (1) the instrument performance in the field; and (2) representative emission levels of N2O from practical coal-combustion sources.

Prototype Analyzer Description

The prototype analyzer was built by HORIBA Ltd. as an adaptation of the HORIBA Model VIA-500. The analyzer is a nondispersive infrared analyzer utilizing a 500 mm sample cell. A schematic of the analyzer is shown in Figure 5. Replaceable optical filters allow the instrument to measure N2O either in the optical region around 4.5 microns, or 7.8-8.5 microns. To date, the 7.8-8.5 micron region has been used. To minimize interferences, the analyzer uses two Luft-type detectors, containing N2O, in series. The first, or primary detector, senses N2O and any interfering gases that absorb in the 7.5-8.5 micron region. Since the first detector absorbs all of the radiation from the N2O bands, the radiation reaching the second detector is only that due to interfering species. The second detector then senses the interfering species and electronically compensates for their effect.

The initial specifications for the analyzer included two ranges: 0 to 250 ppm and 0 to 500 ppm. This specification was made at the time N2O concentrations up to 400 ppm were anticipated, prior to the identification of an artifact associated with the use of grab samples.6,9 However, the analyzer is capable of operating on a 0 to 25 ppm full scale range with sufficient signal-to-noise ratio to detect 0.5 ppm changes in N2O level.

Prototype Analyzer Characterization

Simulated combustion products were used for the initial evaluation of the prototype continuous N2O analyzer. High purity gases were blended to (1) verify the linearity of the instrument; and (2) quantify the extent of interferences from CO2, CO, NO, NOx, and SO2.

The linearity of the analyzer response to N2O was evaluated first. The analyzer responds linearly to N2O concentrations ranging between 0 and 250 ppm for the low range of the analyzer. The analyzer provides an excellent signal-to-noise level even at very low N2O levels (<1 ppm).

Subsequently, the extent of the interferences produced by typical coal combustion products was evaluated. Interference curves were generated for CO levels between 0 and 500 ppm; CO2, 0 and 20 percent; NO, 0 and 1250 ppm; SO2, 0 and 4000 ppm. In general, the results correspond to those obtained with the Miran 1A; SO2 is the primary interfering species. The analyzer utilized some construction materials that adsorb NOx, which precluded generation of an interference curve for this species.
Because of the NO2 adsorption within the analyzer and the extent of SO2 interferences, NO2 and SO2 removal from the sample stream is desirable.

**Field Application**

Upon completion of the initial laboratory evaluation and validation of the prototype analyzer, the analyzer was used to make measurements in utility boiler combustion effluents. This field effort was intended to (1) verify the suitability of the analyzer for field use; and (2) begin characterization of the N2O emissions from full scale combustion field sources, particularly pulverized coal fired utility boilers.

Two combustion engineering units burning pulverized coal were tested. Both units are tangentially-fired and rated at 790 MW (MegaWatts). For these measurements, the N2O analyzer was integrated into a continuous gas analysis system being used to make continuous measurements of O2, CO2, CO, NOx, and SO2 at the site. Figure 6 shows a diagram of the sampling system and illustrates the way in which the N2O analyzer was integrated into the existing system.

The gas samples were obtained from the ducts between the electrostatic precipitators and the stack. The gas samples were drawn through stainless steel probes, passed through a heated filter, dried in an ice bath, and transported through a ⅜ inch unheated sample line (approximately 300 feet in length), further dried through a refrigerated dryer, and then distributed to the analyzer. As shown in Figure 6, the sample for continuous N2O analysis was obtained downstream of the SO2 analyzer.

In addition to continuous analysis, grab samples for N2O were obtained at the inlet to the N2O analyzer and directly from the probes at the sample location (refer to Figure 6).

**Continuous N2O measurements.** The average values for the continuous gas measurements obtained at each unit are summarized in Table II. As seen in Table II, N2O levels from the continuous analyzer were low at each unit, less than 1 ppm. The NOx levels at both units ranged between 275 and 419 ppm. These measurements provide evidence that, at least from these two utility furnaces, direct N2O emissions from coal combustion are low and, in fact, not a large fraction of the NOx levels (e.g., N2O/NOx < 0.4 percent), as previously reported.

**Comparison to grab samples.** In addition to the continuous analysis of N2O, grab samples were obtained during

| Unit | Load (MW) | CO2 (%) | CO (ppm) | O2 (%) | NO (ppm) | N2O (ppm) | NO (ppm @ 3% O2) | N2O (ppm @ 3% O2) |
|------|-----------|---------|----------|--------|----------|-----------|------------------|------------------|
| 1 CE | 790       | 13.7    | >194     | 5.2    | 285      | <1        | 325              | <1               |
| 2 CE | 790       | 13.2    | 2.2      | 5.7    | 332      | <1        | 390              | <1               |

Table II. Data summary.
testing of the two units. The grab samples were obtained two ways; using a "standard" flask sampling technique, and the procedure suggested by Muzio and Kramlich. The "standard" sampling technique simply captures flue gas in a clean, dry glass sample flask. The method suggested by Muzio and Kramlich involves sampling into a flask containing 5 cc. of 10 N NaOH which effectively ties up the SO2 and increases the sample pH. As shown by Muzio et al., this inhibits generation of N2O in the sample flask.

Table III. Continuous vs. grab sample data (790 MW CE tangentially fired pulverized coal boiler).

| Sample location | NaOH (10N) | no NaOH | Continuous |
|-----------------|------------|---------|------------|
| stack           | <1<sup>b</sup> | 26      | <1         |
| CEM             | <1<sup>b</sup> | —       | <1         |

<sup>a</sup> Corrected to 3% O2.
<sup>b</sup> Detectability limit is 2 ppm.

Table III compares the results obtained with the continuous analyzer to those obtained from the sample flasks containing NaOH. The grab sample analyses showed N2O levels below 2 ppm, which is the detectability limit of the analytical technique. Agreement between the two different analysis methods is good. Table III also compares the two different grab sampling techniques. The N2O value obtained from the flask without NaOH is higher, once again indicating N2O generation in the sample flask.

Conclusions

The following conclusions can be drawn from the results discussed above:

- The continuous analyzer system designed and built for the detection of N2O is capable of N2O analysis in combustion effluents at levels down to a few ppm.
- Field tests of the continuous N2O analyzer demonstrated its suitability for continuous source testing.
- N2O measured with the continuous analyzer at two 790 MW pulverized coal fired boilers showed levels less than 1 ppm. These levels are substantially lower than the fraction of NO<sub>x</sub> levels suggested by data previously obtained using grab samples.
- The N2O levels were in agreement with grab samples using a grab sampling technique to inhibit N2O generation in the sample flasks.

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