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Continuous Infrared Analysis of N₂O in Combustion Products

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Nitrous oxide (N₂O) 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 N₂O. 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 N₂O 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 N₂O analyzer developed at the UCI Combustion Laboratory in cooperation with a major instrument manufacturer. The analyzer is capable of measuring N₂O levels down to a few ppm. The analyzer has been evaluated and used to study the N₂O emissions from a pulverized coal-fired boiler. The N₂O levels found with the analyzer are substantially lower than levels previously attributed to such sources. Initial N₂O measurements made with the analyzer suggest that N₂O levels are not a substantial fraction of the NO_x levels, as previously suggested.

Attention has recently focused on the emission of nitrous oxide (N₂O) from fossil fuel combustion processes. Although the emissions and emission formation mechanisms of NO_x (NO + NO₂) are relatively well documented, the data base on nitrous oxide formation and control is small, with relatively limited information available in the literature.

N₂O 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 N₂O 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 N₂O facilitates its transport to the stratosphere. In the stratosphere, N₂O is the largest source of nitric oxide, which subsequently results in the destruction of ozone (O₃).⁴ Hence, an increase in N₂O emissions is expected to translate to an increase in O₃ 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 N₂O produced.¹

Using the limited data available, which are based on grab sampling techniques, N₂O 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, SO₂, and condensed H₂O produce N₂O as an artifact.^{8,9} As a result, the N₂O 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 N₂O measurement technique is needed to (1) obtain reliable measurements in the field; and (2) assess the extent to which combustion sources directly produce N₂O. The present paper reports an investigation of means by which N₂O 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, CO₂, and SO₂ in combustion systems. Since N₂O is an active infrared species, an analyzer based on IR analysis is a logical starting point in developing a simple analysis system. Be-

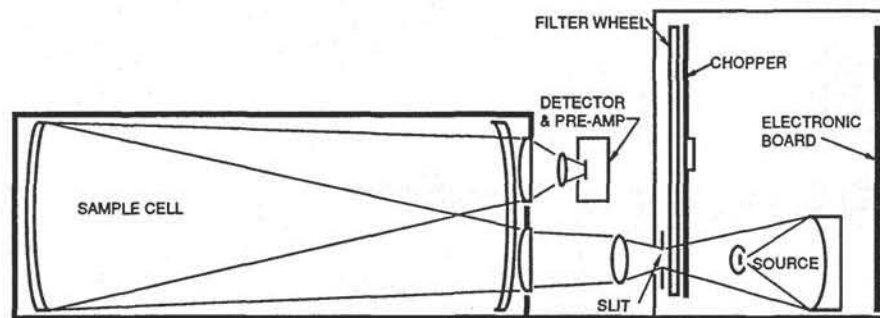


Figure 1. Analyzer (Miran 1A) schematic.

cause N_2O 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 N_2O 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 N_2O (as a function of absorption wavelength, pathlength, and slit width); and (2) interferences from NO , NO_2 , CO , CO_2 , SO_2 , and H_2O . These interferences were evaluated over the gas concentration ranges listed in Table I.

Results

The infrared absorption spectrum of N_2O (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 N_2O absorption lines being 4.5 and 7.8 microns.¹⁰ As a result, these two lines were selected to evaluate the linearity of the analyzer response to N_2O . Pathlengths were chosen at each wavelength to provide sensitivity to N_2O while maintaining linearity between N_2O 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 N_2O was verified, interference curves for CO_2 , CO , NO , NO_2 , and SO_2 were generated by observing the response of the analyzer to the introduction of various gas mixtures.

Typically N_2O 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 CO_2 and CO . At 7.8 microns, NO_2 and SO_2 are the primary

interfering species. For combustion gases generated from a relatively low sulfur coal in a moderately low NO_x combustion environment, the N_2O 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 NO_x 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 SO_2 , CO_2 , CO , NO_2 , 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.)

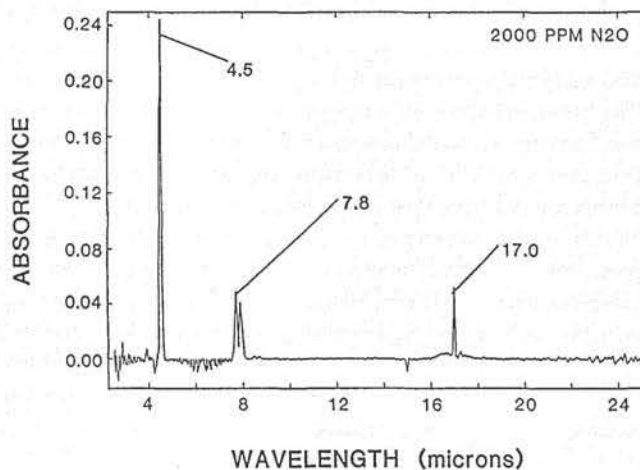


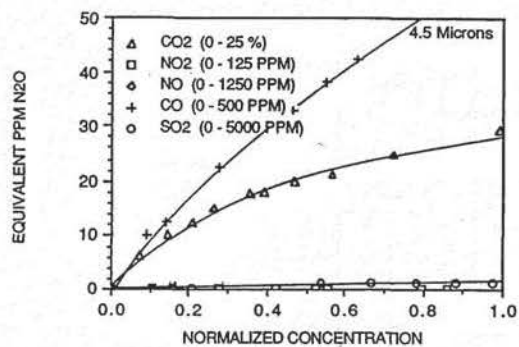
Figure 2. Infrared N_2O absorption spectra.

The effect of trace amounts of water, corresponding to a 1–2 degree Celsius dew point, was also evaluated. An initially dry gas blend was passed through an ice bath prior to analysis, simulating the amount of water anticipated to be present in actual samples if the gases were dried in a refrigerated dryer. Water interferences can be accounted for by either subtracting the effect of water after the measurement is made or passing the zero and calibration gases through an ice bath prior to analysis. Drierite was also put in series between the ice bath and the analyzer to remove the excess water prior to analysis with no effect upon nitrous oxide levels.

To further reduce the error introduced from the interferences at the 7.8 micron wavelength, sodium sulfite and sodium carbonate solutions were used to condition the sample by scrubbing the NO_2 and SO_2 , respectively. As shown in Figure 4, a sodium sulfite solution effectively removes the NO_2 and a sodium carbonate solution effectively removes the SO_2 from the sample while having essentially no effect upon nitrous oxide levels. By scrubbing the NO_2 and SO_2 from the sample, the over prediction of N_2O levels can be reduced

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

Species	Concentration ranges	
	minimum	maximum
CO_2	0 %	25 %
CO	0 ppm	500 ppm
NO_2	0 ppm	125 ppm
NO	0 ppm	1250 ppm
SO_2	0 ppm	5000 ppm



(a) 4.5 microns

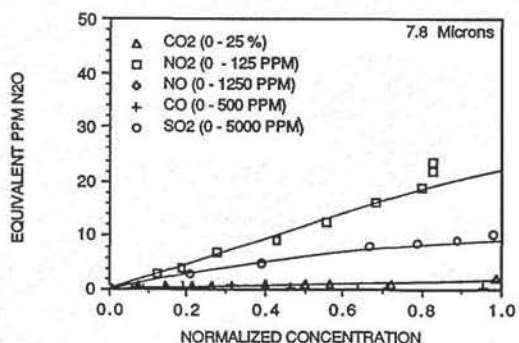


Figure 3. N₂O interferences at 4.5 microns and 7.8 microns.

from 6 to 1 ppm for a low sulfur, low NO_x fuel and from 17 to 1 ppm for a high sulfur, high NO_x 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 NO₂.
- SO₂ and NO₂ 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 field prototype instrument including both instrument performance and sensitivity to interferences 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 7.8–8.5 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.^{8,9} 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, NO₂, 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 (< a few ppm).

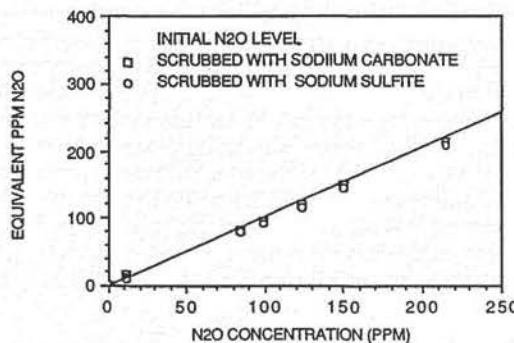
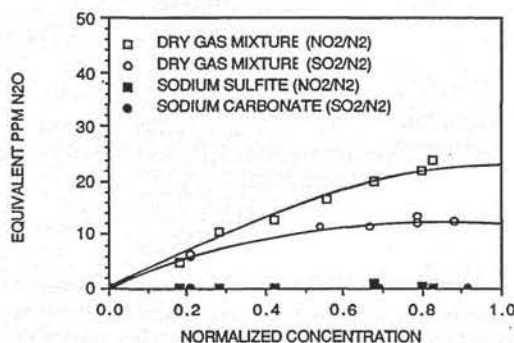


Figure 4. Reduction of NO₂ and SO₂ by conditioning the sample with sodium sulfite and sodium carbonate scrubbing solutions and the effect of conditioning on N₂O levels.

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 NO₂, which precluded generation of an interference curve for this species.

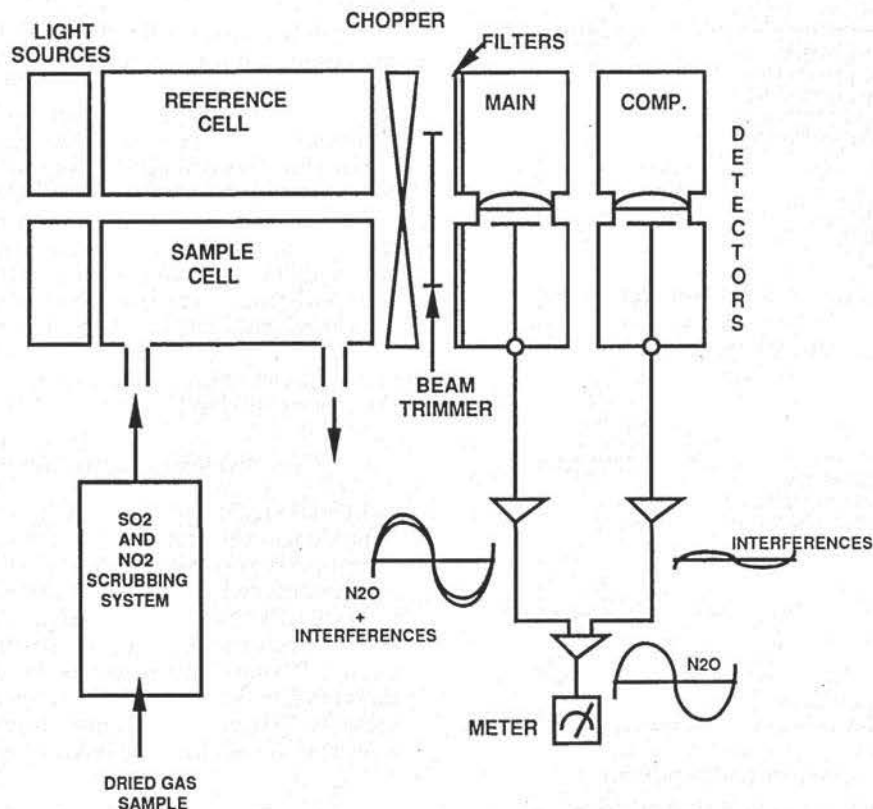


Figure 5. Field prototype analyzer schematic.

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, NO_x, 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 sam-

ples were drawn through stainless steel probes, passed through a heated filter, dried in an ice bath, and transported through a 3/8 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 NO_x 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 NO_x levels (e.g., N₂O/NO_x < 0.4 percent), as previously reported.

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

Table II. Data summary.

Unit	Load (MW)		as measured, dry basis					NO (ppm @ 3% O ₂)	N ₂ O (ppm)
	rated	test	CO ₂ (%)	CO (ppm)	O ₂ (%)	NO (ppm)			
1 CE -tangentially fired	790	750	13.7	>194	5.2	285	<1	325	<1
2 CE -tangentially fired	790	650	13.2	2.2	5.7	332	<1	390	<1

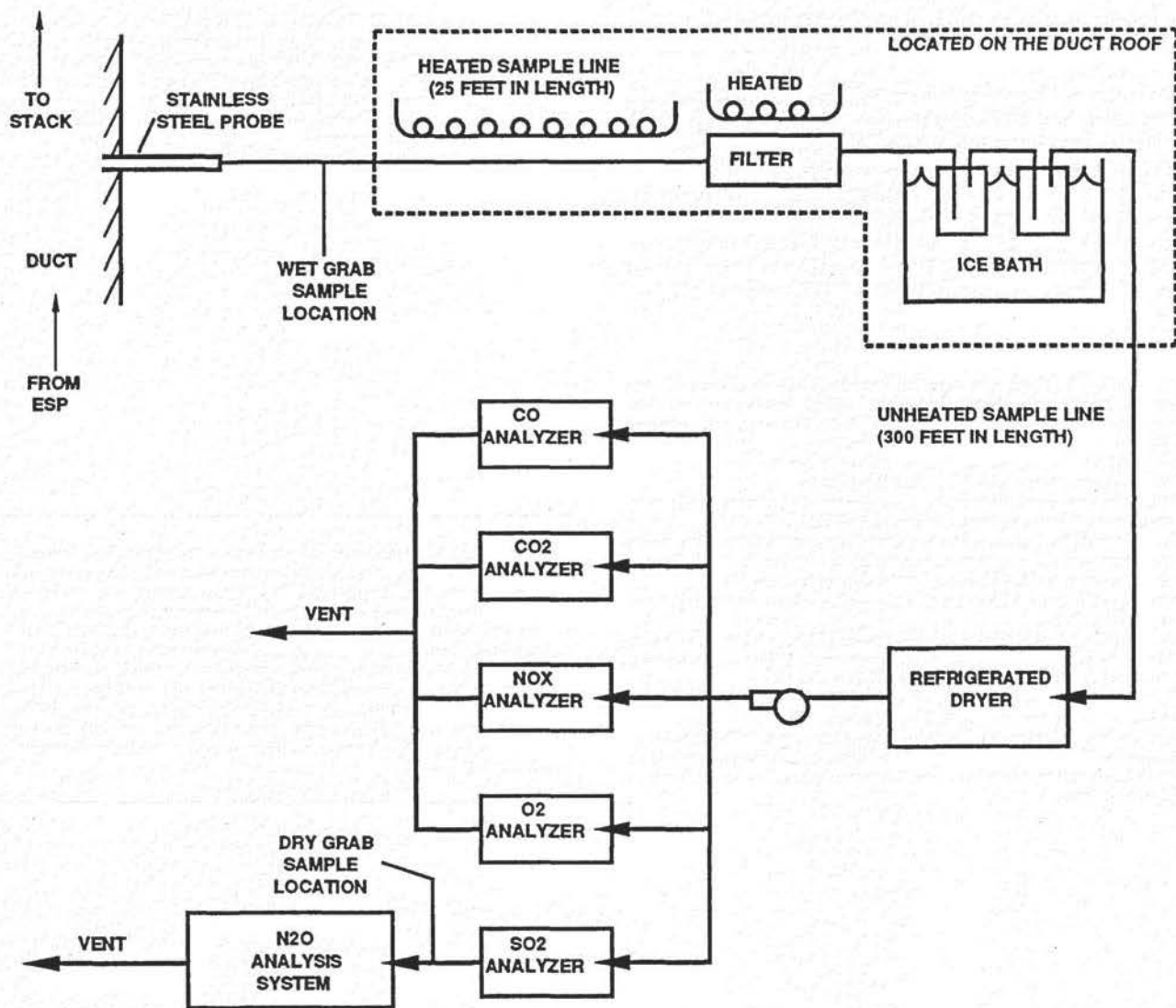


Figure 6. Field sampling system schematic.

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.^{8,9} The "standard" sampling technique simply captures flue gas in a clean, dry glass sample flask. The method suggested by Muzio and Kramlich⁸ and Muzio et al.⁹ 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.,⁹ 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	N ₂ O (ppm) ^a		Continuous
	Sample flask		
	NaOH (10N)	no NaOH	
stack	<2 ^b	26	<1
CEM	<2 ^b	—	<1

^a Corrected to 3% O₂.

^b 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_x 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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