

APPENDIX 3B: Precision and Accuracy of CD_4 and Measurement

3B.1 Tracer Injection¹

Since CD_4 had not been previously injected into coal fired power plant plumes, there was some concern over whether the tracer was conserved during its passage through the stack environment. There was also a need to address the problem of injection of CD_4 into the stack in such a way that CD_4 was uniformly mixed across the stack diameter.

Two experiments were planned to address the issues of tracer mixing and conservation. The first experiment was to determine whether the tracer would be completely mixed with the stack gases before exiting the stack. The experimental approach was to inject SF_6 into the stack at the location planned for the CD_4 release and measure the cross-sectional concentration profile of SF_6 in the stack emissions at a point downstream of the SF_6 injection port. The second issue, whether CD_4 is conserved in the stack, was addressed by injecting a known mixture of CD_4 and SF_6 and measuring the CD_4/SF_6 ratio in samples collected at the downstream sampling port.

For these initial tests, as well as for the tracer release during the entire WHITEX experimental period, the tracers were introduced into the stack gases through a stainless steel tube that extended about 1 ft into a plenum that joined the stack at about 100 ft above the ground. A mixture of 3% SF_6 in nitrogen was injected into the stack to assess mixing.

To assess the conservation of CD_4 in the stack, a mixture of SF_6 in CD_4 was injected into the stack. This tracer was prepared by mixing 10.3 ± 0.2 grams of SF_6 with 52.9 ± 0.2 grams of CD_4 . The mixture had a CD_4/SF_6 volumetric mixing ratio of 37.5 ± 0.7 .

Stack gas samples were collected at sampling ports located approximately 365 feet up the 755 foot stack. For assessing the cross-sectional uniformity of the tracer distribution within the stack, samples were collected at each of the twelve locations indicated in Figure 3B.1. A metal bellows pump pulled stack gases through a conventional stack sampling probe followed by a drying tube filled with P_2O_5 . The stack gases were then pumped through a sample loop of a portable gas chromatograph equipped with an electron capture detector. Three determinations of SF_6 were made at each of the twelve positions. For determining the CD_4/SF_6 ratio, four samples of stack gases were compressed by the same metal bellows pump into evacuated steel gas bottles. These bottles were returned to Los Alamos National Laboratory for determination of SF_6 and CD_4 concentrations.

The results of the experiment to assess tracer mixing are also presented in Figure 3B.1. There is no apparent bias in the cross-sectional distribution of the tracer. The mean concentration of SF_6 in the stack was 217 ± 10 ppt. The maximum departures of the mean concentration at any location from the mean concentration of all locations within the stack are +8% and -6%. Table 3B.1 gives

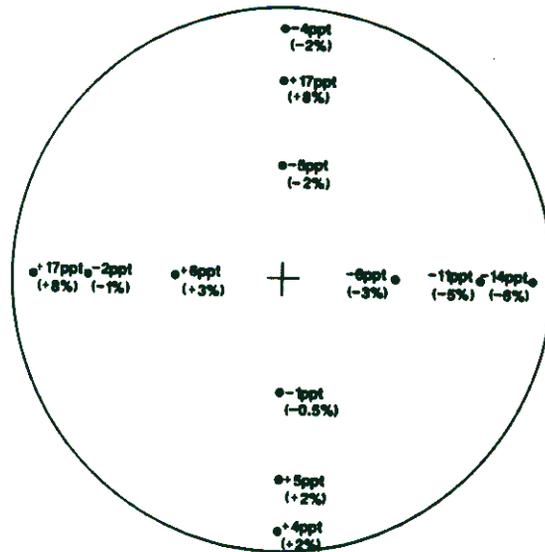


Figure 3B.1: Departures [ppt(%)] from the mean concentration of SF_6 (217 ± 10 ppt) in the stack of the Navajo Generating Station.

the CD_4/SF_6 ratios of the four samples collected from the stack relative to the value of the tracer mixture. The samples are within 10% of the prepared value, indicating that CD_4 is conserved in the stack.

Table 3B.1: Ratios of CD_4/SF_6 relative to the prepared tracer mixture.

Sample	$(CD_4/SF_6)_{\text{Sample}} / (CD_4/SF_6)_{\text{Expected}}$
1	0.99
2	1.03
3	0.89
4	1.09
Mean $\pm \sigma$	1.00 \pm 0.08

During the WHITEX experimental period, the tracer release system was located in a small shed at the base of one of the three stacks. Figure 3B.2 shows a block diagram of the release apparatus. The tracer flow could be introduced into any of the three stacks by a means of manifold and valve arrangement. The pressure in the manifold was monitored and used as an indication of the integrity of the polyethylene tubing used to carry the tracer to the injection ports on the stacks. The pressure in the manifold downstream of the flow controller reflected the static pressure in the stack. Under normal operating conditions, the stack static pressure was less than atmospheric pressure so there shouldn't have been tracer leaking into the atmosphere before reaching the injection port on the selected stack. Grab samples of the stack gases were taken daily to provide a check on the tracer concentration in the stack gases.

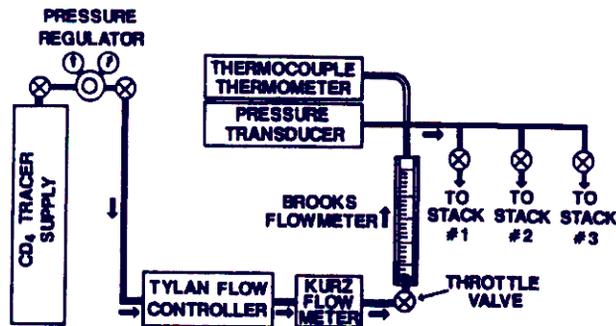


Figure 3B.2: Block diagram of the release apparatus for CD_4 .

The fittings on the release apparatus were checked several times daily for tracer leaks using a portable flammable gas detector. No leaks were detected using this detector, but samples of air taken from within the shed containing the tracer release apparatus were found to contain small concentrations (about 1 ppb (v)) of the tracer. This indicates that there was a small leak in the system that was undetectable by the portable leak detector. We estimate the leak rate to be <0.1 ml/minute which is small compared to the nominal release rate of about 100 ml/minute.

Integrating the output signal of the mass flow meter during the experimental period indicated that a total of 4.93 kg of CD_4 went to the stacks. The precision of the flow rates measured by the mass flow meter is estimated to be $\pm 0.5\%$. An independent audit of the mass flow meter using a soap-bubble flow meter revealed that the mass flow meter was indicating a flow rate that was 2% higher than the true flow rate. Applying this correction to the integrated total of 4.93 kg CD_4 brings the value to 4.83 kg CD_4 , which is in agreement with the measured mass change of the tracer bottle of 4.825 kg CD_4 .

During the experimental period, the tracer flow was adjusted to match the changing electrical output of the plant, according to the schedule given in Table 3B.2. Figure 3B.3 presents the temporal record of the mass of CD_4 released normalized to the electrical output of the plant. For about the first half of the WHITEX period, the ratio of tracer released to the amount of power produced was held between 2.0 and 2.5 mg CD_4 /Mw. On Julian day 30 the flow rate was increased because tracer consumption up to that time was below the projection based on anticipated plant electrical output. Between Julian day 37 and 41, the ratio rose from about 3.6 mg CD_4 /Mw to nearly 5 mg CD_4 /Mw because an unanticipated outage of one of the two remaining operating units reduced plant electrical output by half (from about 1500 Mw/hr to 750 Mw/hr), while the tracer flow was reduced from 112 ml/min to 75 ml/min. The ratio dropped back to about 2.5 mg CD_4 /Mw on Julian day 44 because the overhauled third unit was brought back on line earlier than anticipated.

Ambient measurements of CD_4 at receptor sites were achieved by pumping 60 liters of air into large mylar/polyethylene bags at six hour intervals and then concentrated under pressure into steel pressurized containers. The containers were shipped to Los Alamos National Laboratory for mass spectrometer analysis.

Table 3B.2: Tracer release schedule for WHITEX.

Plant Load (Mw/hr)	CD_4 (STP ml/min)
(From 7 to 30 January 1987)	
>2200	112
1800-2200	93
1400-1800	75
1000-1400	56
<1000	37
(After 30 January 1987)	
>1200	112
800-1200	93
<800	75

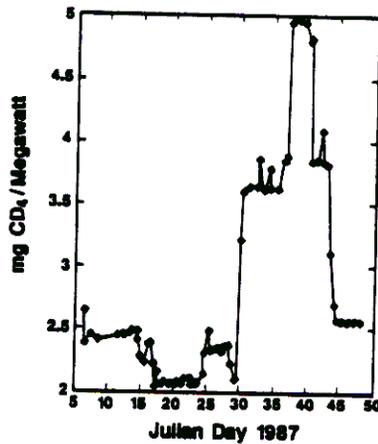


Figure 3B.3: Time plot of CD_4 mass concentration (milligrams) released normalized to Navajo Generating Station (NGS) electrical power generation (megawatts). Also indicated are the NGS units out of which CD_4 was released.

3B.2 CD_4 Measurement²

Precision

The measurement process, discussed in Appendix 3A.10, involves spiking the sample with normal methane and measuring the concentration of all methane with a flame ionization detector, isolating the methane, and measuring the ratio of CD_4/CH_4 by mass spectrometry. The concentration of CD_4 is the product of the concentration of methane in the spiked sample and the measurement of the ratio of CD_4/CH_4 . The measurement of the ratio involved measurements of the currents of both normal and deuterated methane ions.

The precision of the concentration of methane in the spiked sample was estimated from replicate analyses of each sample. The precision obtained was approximately 0.2%.

The precision of the measurement of the current of the normal methane ions was approximately 1%.

The precision of the measurement of the current of the deuterated methane ions was the dominant source of precision of the final result. The precision was associated with the counting statistics of the CD_4 ions. The statistical precisions ranged from approximately 3% for cases with a large concentration of CD_4 , to approximately 50% for cases at the minimum detectable limit of the analysis. The precision was calculated for each measurement and included in each entry in the data base.

Accuracy

The accuracy in estimating the concentration of total methane in the sample was determined from analysis of NBS Standard Reference Material for methane in air. The accuracy value here was $\pm 2\%$.

The accuracy of the prepared standards used to calibrate the mass spectrometer was estimated to be $+6\pm 3\%$. This was the largest source of possible bias.

References

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