AN AIR SAMPLING SYSTEM TO MEASURE POWER PLANT EFFLUENTS USING A LIGHTWEIGHT AIRCRAFT*

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ABSTRACT

An air sampling system to measure power plant effluents from a fixed-wing, light aircraft has been developed and evaluated both in the laboratory and in the field. The sampling system is easily adaptable to a Cessna 206 and provides the capability to measure oxides of sulfur, oxides of nitrogen, particulates and SF_6 tracer gas.

Evaluation of the apparatus has indicated that real-time measurements of the conversion of NO to NO_2 in the plume at distances up to twenty-five miles are feasible. The oxides of sulfur are measured by a technique employing KOH impregnated filter papers which has been proven to have very high reliability and precision.

The applicability, precision, and reliability of the entire sampling system are being evaluated in field operations in St. Louis, Missouri. Results of these tests will be the subject of upcoming papers.

Introduction

Fossil fueled power plants release a large proportion of the atmosphere's particulates, sulfur dioxide, sulfates and oxides of nitrogen. In a 1970 survey [1], the electric power generating industry was the source for approximately one-fifth the total

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particulates, one-fifth the total NO_x and one-half the total SO_2 emissions in the United States. Recent concern over this release has stimulated an interest in plume chemistry modeling and the associated improved sampling techniques [2]. One approach to plume sampling is to mount all of the sampling equipment in a lightweight, low-speed aircraft and collect air samples from the active plume itself [3, 4].

The Atmospheric Diagnostics Program at Brookhaven National Laboratory (BNL) has concentrated, over the past few years, on developing the sampling apparatus and analytical techniques necessary to accurately carry out these measurements [5]. To perform the base program tasks of accurately measuring the conversion of SO₂ to sulfate and NO to NO₂, extremely precise, real-time, quantitative measurements at varying distances from the plume source were required. The equipment needed for this work was designed, constructed, developed and evaluated, and the findings are reported in this paper.

The plume chemistry program at BNL involves the study of effluents from both oil-fired and coal-fired power plants [6, 7]. Parameters which are evaluated include meteorological conditions, background contributions, effects of particulates including metallics such as vanadium, chemistry of the fuel, and pollutant interactions. A number of sampling and analytical techniques already being employed at BNL were improved upon.

The conversion of SO₂ to SO₄⁼ and NO to NO₂ in a plume can be estimated by simultaneously measuring one or more of the following:

- 1. the concentrations of SO₂, SO₄ and NO, NO₂ directly, 1
- 2. ³²S/³⁴S ratio and ¹⁴N/¹⁵N ratio [5, 9], or
- 3. the concentration of SO_2 and NO or NO_2 referenced to a tracer gas injected into the plant duct, i.e., SF_6 .

There was difficulty in performing real-time measurements for sulfur since adequate instrumentation was not yet available. For these measurements, a high volume air sampler using KOH impregnated filter papers became the basis of development. On the other hand, real-time NO_{x} monitors were commercially available, and thus became the basis of this measurement. Although a technique for real-time measurement of SF_6 was under development, the use of cannisters (grab samples) for plume sampling and analysis of SF_6 had already been quantitatively demonstrated. The latter

¹ Note added in proof. Since the writing of this article, a real time ozone measuring instrument has been added to the package to aid in the interpretation of NO chemistry. The instrument selected (A.I.D. Model 560) has been laboratory and field tested.

technique seemed to be the most attractive method to pursue for further development [10].

Plume sampling using a lightweight aircraft has been an ongoing task at BNL since 1967 [11]. Frequent design improvements have been made over the years. The designs discussed in this paper are a result of this overall expertise. In discussing the following improvements, reference will be made to the previous designs [5, 11].

Description of Apparatus

OXIDES OF SULFUR

The oxides of sulfur sampling package, shown schematically in Figure 1, consists of four units:

- 1. air scoop assembly,
- 2. filter cassette assembly,
- 3. high-volume blower, and
- 4. instrumentation.

The air scoop assembly is fabricated from stainless steel and consists of an air intake section, a transition section and a rectangular section containing the $8'' \times 10''$ filter cassette. The diameter of the air intake section is sized to achieve isokinetic velocity when the aircraft travels at 90 miles/hour and the high-volume air sampler is operated at fifty cubic feet/minute. The air intake section is shown in Figure 2. A remotely-operated nozzle cap allows for the simultaneous opening of the air intake and the starting of the blower by means of an electrical micro-switch mounted on the nozzle cap shaft. The micro-switch also activates an elapsed-time clock, an indicator light and a solenoid valve attached to the grab-sampler (to be discussed later).

The filter cassettes are fabricated using anodized aluminum frames and stainless steel screens. The assembly contains o'ring seals throughout, as shown in Figure 3, in place of the previously-used porous flat gaskets. The assembled cassette is shown as viewed from inside the cabin in Figure 4. Early work with KOH impregnated filter papers pointed out the need for at least two papers due to the high breakthrough occurring with only one paper [8]. Thus, the cassette assembly contains three filters, one glass fiber filter² (for particulates) and two KOH impregnated papers (for SO₂).

 $^{^2}$ Type GF81 filters prepared as follows: (1) wash with ~ 2 liters water, (2) remove excess water by suction, (3) ignite in air at 475 °C for 2 hours, (4) wash with 1 liter water, (5) soak with 0.5N HCl, (6) remove excess HCl, and (7) dry at 110 °C for 1 hour.

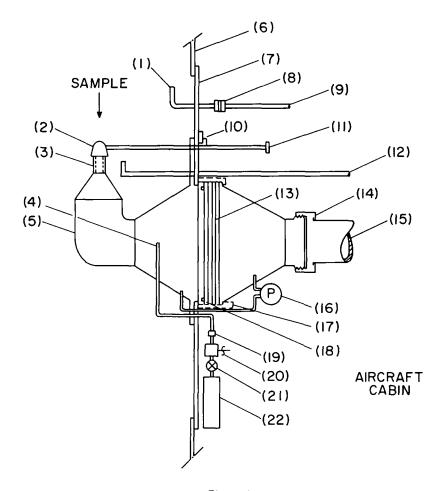


Figure 1.

- 1. Metallic particulate sampler port
- 2. Nozzle cap
- 3. Air intake section
- 4. SF₆ sampler tube (filter location)
- 5. Air scoop assembly
- 6. Aircraft shell
- 7. Lexan replacement window
- 8. 47 mm filter assembly
- 9. To vacuum pump
- 10. Microswitch
- 11. Remote operated nozzle cap shaft

- 12. To instruments
- 13. Filter cassette assembly
- 14. Flexible connector
- 15. To high volume blower
- 16. Differential pressure gauge
- 17. Typical clamp
- 18. Typical o-ring
- 19. Sapphire orifice
- 20. Solenoid valve (automatic)
- 21. Toggle valve for isolation
- 22. SF₆ sample cannister

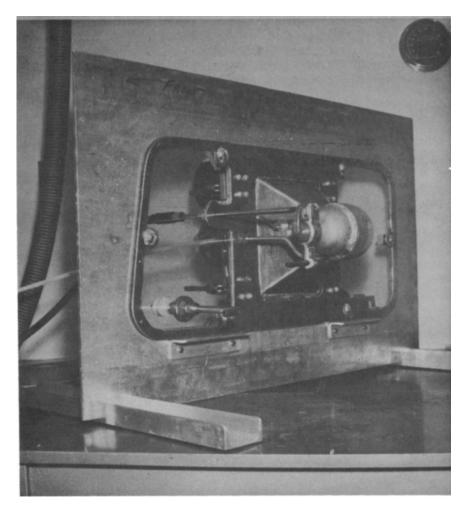


Figure 2. Air sampling system mounted on laboratory stand. View from outside of aircraft.

The air sampler contains a standard 24 volt DC Staplex blower capable of drawing ~ 50 CFM through the aforementioned filters. Flow rate is measured by a calibrated differential pressure gauge which measures the ΔP across the filter pack.

The instrumentation is variable and usually depends on the type of run to be performed. In general, the instrumentation consists of:

1. an SO₂ conductivity analyzer (Sign-X Laboratories, Essex, Conn.).

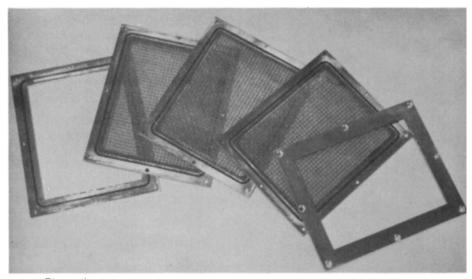


Figure 3. Screens and support frames of disassembled filter cassette.

- 2. temperature-humidity sensors,
- 3. a miniature electronic recorder or data acquisition system with a Gel-cell battery pack,
- 4. an electrically operated elapsed time clock, and
- 5. 2-12 volt batteries in series for the blower.

The SO₂ monitor is used to detect the location of the plume when it is not otherwise visible. Wind velocity and other meteorological data are normally obtained by pilot-balloon measurements or other ground level measurements. Where A.C. voltage is required, solid state D.C./A.C. inverters (Toredo Co.) are used.

A 47 mm. Gelman filter holder is also mounted on the removable window. Air can be sampled for metallic particulate content by using the appropriate filter material.

SULFUR HEXAFLUORIDE (SF₆)

The SF₆ measurements are performed by collecting finite parcels of plume air each time the aircraft traverses the plume. The apparatus used for this purpose consists of:

- 1. a filter to remove particulate matter,
- 2. a small diameter (from 1 to 10 mils) saphire orifice,
- 3. two valves and
- 4. a previously evacuated steel cannister ($\sim 700 \text{ cm}^3$).

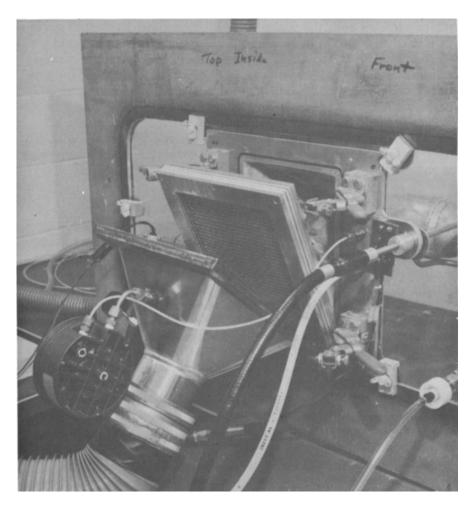


Figure 4. Air sampling system mounted on laboratory stand. View from inside of aircraft showing filter cassette assembly in place.

The combination of the evacuated cannister and the small orifice create a constant flow, critical orifice as long as the pressure in the cannister does not exceed more than 1/2 atmospheric pressure.

The present sampling system contains aluminum volumedisplacement plugs in the valve assembly in order to minimize the trapped volume upstream of the cannister. To further reduce this volume over that of the previous design, the saphire orifice is mounted in a small bore (.025"I.D. \times 1/8"O.D.) tube.

The valve assembly consists of a toggle-operated shutoff valve

which remains with the cannister at all times and a solenoid operated valve which is used only in the aircraft. The solenoid valve is electrically operated in conjunction with the high-volume sampler by means of the micro-switch mentioned earlier. This permits simultaneous sampling (sulfur oxides and SF_6) of the same parcel of air.

The filter consists of a small wad of glass wool trapped in a plastic holder mounted on the inlet end of the 1/8'' O.D. tube. The overall trapped volume upstream of the cannister in the new design is $\sim 1~{\rm cm}^3$ as compared to $\sim 20~{\rm cm}^3$ in the previous design.

OXIDES OF NITROGEN

Commercially available chemiluminescent analyzers capable of simultaneous, real-time measurements of NO and $\mathrm{NO_x}$ are presently available. At the time of this work however, two commercially available single mode $\mathrm{NO_x}$ monitors were on hand at BNL. An integrated, real-time analyzer capable of monitoring NO and $\mathrm{NO_x}$ simultaneously was created from portions of the two instruments. The final design involved using the NO measuring circuit and ozone generator of the REM monitor (REM Inc. Model 642A), and the $\mathrm{NO_x}$ measuring circuit of the TECO (TECO Model 14B) monitor together with its gas sampling and pressure stabilization system. A schematic representation of the flow sheet is shown in Figure 5.

Several modifications of the standard instruments were required. The flow capillary of the REM monitor was enlarged to match that of the TECO (0.015"), and the sample flow capillary was enlarged to accommodate the total flow required by both reaction chambers (1200 cc/min each). The RC (resistance-capacitance) bridges on the electrometer switches were matched on all of the usable ranges, and the values were chosen to give a fast electronic response time. The overall response time of the integrated instrument is about one to two seconds from start of signal rise to 90 per cent of maximum signal.

METEOROLOGICAL INSTRUMENTATION

A temperature probe is mounted outside the aircraft cabin and fastened to a wing strut. The electrical leads are run through a hole in the scoop window and attached to a temperature indicator. This temperature unit is used to obtain temperature profiles during a sampling run. The relative humidity, during a sampling run, is obtained by extending a sling psychrometer out the hole in the aircraft scoop window. The aircraft altimeter is used to obtain the

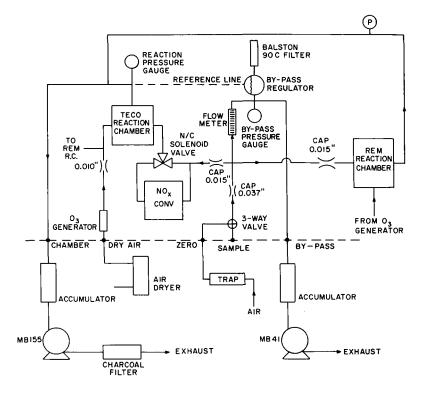


Figure 5. Schematic flow diagram of dual NO/NO_x analyzer.

height of the plume and the changing heights during a temperature profile run.

Laboratory Evaluation

Laboratory evaluation of the aircraft's sampling packages was carried out on individual instruments or samplers and in combination in several stages. First, individual samplers were calibrated using gas mixtures manufactured in the laboratory by making precise volumetric additions of SO_2 , NO or SF_6 to a previously evacuated ~ 50 liter stainless steel vessel to which pre-purified nitrogen was then added to raise the pressure to two to three atmospheres. Next, individual instruments were evaluated for response to gas transients (simulating plume traverses). Finally, combinations of instruments and sampling techniques were simultaneously evaluated for response to transients using gas mixtures containing precise ratios of the aforementioned gases.

CALIBRATED GAS MIXTURES

Volumetric additions of pollutant gases were made to stainless steel vessels described above. Two types of calibration gas mixtures were prepared in this manner for use in the evaluation:

- 1. low concentration mixes, < 1 ppm, which were flowed directly into the sampler to be calibrated, and
- 2. high concentration mixes, ~ 2000 ppm, which were diluted with air before flowing into the sampler.

Mixes containing SF_6 were also prepared but the concentrations used were lower by a factor of 10^3 . As long as subsequent testing with the gas mixture was carried out within a short period of time, the concentrations remained essentially constant.

In the case of NO gas mixtures, the calculated volumetric additions were often verified using an ozone titration technique [12]. The method consists of mixing the calibration gas with ozone generated from a previously calibrated generator, thus titrating the NO with $\rm O_3$ to form $\rm NO_2$. Starting with no ozone flow, both NO and $\rm NO_x$ are monitored until a titration curve is generated. Verification, using this technique, was usually good when some care was exercised in assuring good mixing.

SAMPLER CALIBRATION AND EVALUATION

Low concentration gas mixtures of one or more constituents were used to evaluate instrument behavior and sampling techniques with the following objectives:

- 1. Calibrate span of instrument or sampling technique by direct flow into sampling apparatus, and
- 2. determine interaction of other pollutant species on the sampling technique in the concentration range anticipated in a plume. Two or more sampling techniques or instruments were often intercompared simultaneously.

High concentration mixtures were used to simultaneously evaluate several instruments or sampling techniques with the apparatus shown in Figure 6. In the case shown, a mixture of NO, NO₂, SO₂, and SF₆ was diluted with room air ($\sim 10^6$ parts air to $\sim 10^3$ parts gas) at various constant gas flow rates. The following samplers were evaluated:

1. Simultaneous NO and NO_x gas analyzer (chemiluminescent) discussed earlier,

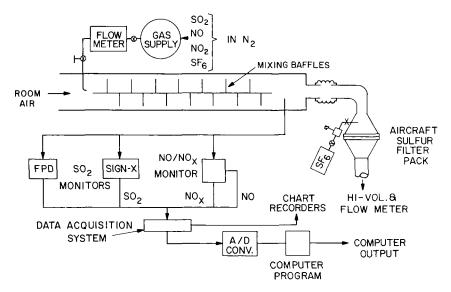


Figure 6. Evaluation of aircraft instrumentation.

- 2. SO₂ conductivity analyzer (Sign X) and flame photometric analyzer (FPD)—planned for future flights,
- 3. KOH impregnated filter papers (for SO₂), and
- 4. SF₆ grab sampler (cannisters).

In addition to intercomparing the analytical results obtained by the analyzers and analytical techniques listed above, a final comparison can be made by calculating the concentrations in the mixing tube based on the relative flow rates of the calibration gas and the air. For the tests the aircraft's sulfur filter pack and SF₆ cannister were installed in the same manner as they would be in the aircraft, i.e., on the window unit.

Results of a constant-flow type of test are given in Figure 7. Four dilutions were established for this test, simulating various distances downwind from a source. The results, which appear as a series of near parallel lines (also parallel to gas flow calculation curve), indicate a good quantitative intercomparison was achieved. The results for NO and NO_x are approximately the same, since very little NO_2 was added to the calibration gas.

For the typical run discussed above, the calibration gas flow was held constant. Another type of run used in the evaluation was one in which the gas flow rate was varied in order to simulate the concentration vs. time profile which might be encountered in a plume traverse. Such runs were used to evaluate the real-time

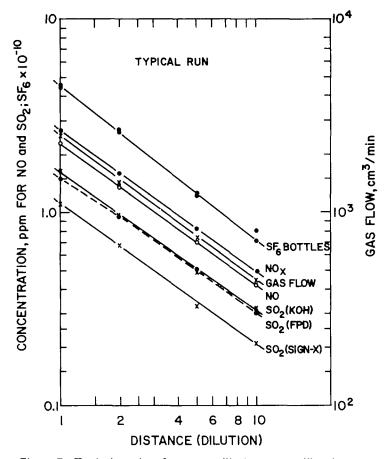


Figure 7. Typical results of constant dilution type calibration run.

behavior of the instrumentation. The apparatus shown in Figure 6 was used to perform the tests. The runs were carried out by mixing air with a known ratio $SO_2/SF_6/NO/NO_2$ source gas and reproducing plume concentration profiles by varying the gas flow rate, thus simulating airborne operation.

Laboratory evaluation of the entire integrated aircraft sampling system was carried out using this simulated plume technique. For example, a plume traverse was simulated by adding calibration gas to the mixing tube for a short time interval (\sim 10-20 sec.), and repeating as many times as required. A number of passes were thus simulated by injecting the calibration gas into the mixing tube, visually observing the response on the instrumentation, and energizing the high volume sampler and SF₆ cannister solenoid valve

Table 1. Results of Simulated Plume Runs

by tripping the micro-switch. Results of two typical simulated plume runs are given in Table 1. The two runs performed were each at about 0.2 ppm SO_2 concentration. One run was timed to collect ~ 7 mg SO_2 while the other was timed to collect ~ 2 mg SO_2 on the filter papers.

The following conclusions were drawn from the data:

- 1. It is more desirable to collect ~ 7 mg SO₂ because of the effect of the blank correction (~ 0.1 mg SO₂).
- 2. The new SF₆ cannister design appeared satisfactory as indicated by the analytical results which were consistent with SO₂ analyses.
- 3. The SO_2/SF_6 ratios measured were as follows:

Run 5.2
$$SO_2/SF_6 = 7.43 \times 10^3$$

Run 14.05 $SO_2/SF_6 = 7.67 \times 10^3$

The 3 per cent reproducibility is about as good as the flow techniques and analytical measurements would allow.

- 4. The power supply package (four 12 volt D.C. heavy-duty batteries) appears to be limited to \sim six hours of operation when sampling for NO/NO_x. Six hours of SO₂ sampling can be obtained using two 12 volt batteries.
- 5. The performance of the dual NO/NO_x analyzer was extremely encouraging however there were difficulties in the method of integration used. Subsequent improvements in this technique have improved the accuracy of the results as will be discussed later.

Field Evaluation

Since plans for airborne sampling involved using a lightweight aircraft (Cessna 206 or equivalent), sampling packages were assembled to suit the available space provided by such an aircraft.

^a Computer calculated from digitized magnetic tape output of data acquisition system.

In addition to the available aircraft power, additional required electrical power was supplied by 12 volt D.C. batteries brought aboard. A Cessna 206 is a six-passenger, single-engine, high-wing aircraft with ample space available when three or four of the passenger seats are removed.

For the preliminary field work, two sampling packages were installed and evaluated independently. These consisted of the $\rm NO/NO_x$ analyzer and its associated equipment, and the sulfur oxides filter pack and its associated equipment. The window unit and the $\rm NO/NO_x$ dual analyzer were flight tested several times at the Long Island Lighting Co.—Northport plant. Some of those results will be briefly discussed in this paper. The sampling systems were subsequently used in an extensive investigation carried out in St. Louis, Mo., between June and October, 1974 at the Union Electric Co.—Labadie plant. The data from these studies are presently being analyzed and will be presented in a forthcoming paper.

INSTALLATION OF EQUIPMENT IN AIRCRAFT

The previously described oxides of sulfur sampling equipment can be installed in either of two different aircraft since the window of a Cessna 206 is interchangeable with a Cessna 187. The Cessna 206 is preferred for our work because of its higher weight carrying capacity, which is required when using the NO_x sampling system, and the capability of a third seat being installed for an assistant unit operator when the sulfur unit is installed.

For installation of the sulfur sampling package onto a Cessna 206, the left front seat and left door window are removed. The window is replaced by the window unit containing the sulfur sampling system. The high volume blower package is installed on the floor rails that normally support the left front seat and the instrumentation package is then installed behind the right front seat, which now becomes the pilot's seat. The observer seat is on the left side of the instrument package. The NO/NO_x dual analyzer and support equipment are generally installed to the rear of the observer's seat. This equipment is also mounted to seat tracks. Individual air supply lines feed the SO₂ conductivity meter, the NO/NO_x dual analyzer and the metals particulates filter located on the window unit.

PRINCIPLE OF OPERATION

Sampling of a power plant plume is carried out by:

1. performing background measurements,

- 2. performing several traverses of the plume perpendicular to its path and repeating at several distances downwind and as far as is possible,
- 3. obtaining a sample of the fuel whenever possible,
- 4. obtaining plant operation data,
- 5. performing as many meteorological measurements as possible,
- 6. obtaining temperature profile data from the aircraft and
- 7. collecting SF₆ injection data when it is used.

Background measurements are usually taken up wind of the plume source. Plume traverses are usually made at distances of one, three and ten miles, and then out to the furthest possible distance. A nomograph is used in conjunction with the Sign-X instrument to assure that $\sim 5~\text{mg SO}_2$ is obtained at each distance. Two temperature profiles are taken, one during the background run and one at the three mile location. Temperature profiles start at five hundred feet above ground level and end at three thousand feet above sea level or five hundred feet above plume, whichever is higher.

When SF_6 tracer gas is used, it must be injected into the plant duct about two hours before the aircraft starts sampling. A flow apparatus has been designed wherein constant-flow regulating valves are employed to maintain a total flow rate of about 50 SCFH for the entire plant site. The gas is injected equally into all of the operating stacks. When SF_6 is used, it is essential to obtain plant operating data so that flue gas flow rate can be calculated.

RESULTS OF FIELD EXPERIMENTS

Much of the data obtained with the improved sampling system is presently being examined and is the subject of a forthcoming paper. However, some typical results will be given and discussed in this paper in order to demonstrate the capability of this mode of analysis.

 NO/NO_x results—Several flights were made at the LILCO power-station at Northport. All investigations were carried out during the morning hours (0600 to 0830), with stable atmospheric conditions and winds of five to ten knots. Sampling was conducted out to as great a distance as possible from the source. This was dependent upon the power supply, other air traffic in the area, plume density, and the ability to stay in the plume. Usually, six passes were made at each indicated distance from the stacks during cross-plume

sampling. On other occasions, sampling was carried out by flying longitudinally in the plume for as great a distance as possible. Periodic in-flight calibrations were performed while flying longitudinally in the plume. During this time both portions of the dual NO_{x} analyzer were placed in the NO mode of analysis. Thus both portions of the instruments analyzed only for NO in the plume and performed the analysis simultaneously. The usually more reliable TECO portion was used as the standard and the REM portion was adjusted accordingly.

A dual-pen chart recorder was employed to record NO and NO. levels. Conversion ratios were determined by comparing the integrated areas under each curve. Integration of the peaks was performed with a planimeter instead of the digitized magnetic tape method used earlier. Results are given in Table 2. The data clearly illustrate that quantitative conversion ratio measurements can be made and in fact the technique can sometimes be used out to great distances from the plant stacks. The ratios given in Table 2 were obtained from the respective areas under the curves, after correcting for background contributions, of the NO and NO_x outputs of the analyzer. Assuming the ratio is a measure of $\frac{NO}{NO + NO_2}$, a value of 1.0 indicates no conversion has occurred whereas a ratio of 0.34 (as was measured at twenty-five miles on June 13) indicates that the NO₂ content of the plume air is nearly two times the NO content. A typical plume profile is shown in Figure 8, which also provides visual corroboration of the relative response times of the two portions of the dual analyzer.

Sulfur results—On September 13, 1973, the Northport steam plant was sampled using the improved window unit. Samples were

Date of sampling	Miles from Stacks									
	0	1	2	5	10	15	20	25		
Cross Plume										
June 6	_	.96	.88	.79	.65	_				
June 12	_	.90	.60	.56	.60	_				
June 19	_	.74	.60	.48	.44	.45				
In Plume										
June 12	1.0	_	.98	.75	.45	.45				
June 13	.82	.82	.71	.79	.61	.54	.44	.34		

Table 2. Results of Northport Plume Runs Average NO/NO_x Conversion Ratios^a

^a Obtained by ratioing average integrated area under curves.

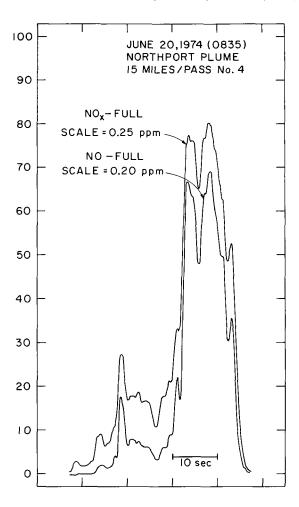


Figure 8. Typical response curves of dual NO/NO_x analyzer from Northport plume run, June 20, 1974.

taken at one, two, five and ten miles from the stack. Weather conditions were stable with winds of \sim four knots. Background samples for SO_2 and $SO_4^=$ were not taken during this run. Previous samplings have given average background values of 0.02 ppm SO_2 and $20~\mu g/m^3~SO_4^=$ which were used for correction of the data given in Table 3. The del values for SO_2 were fairly constant, indicating virtually no oxidation between sampling points. The ratio of sulfate to total sulfur declined with distance, indicating little or no conversion of SO_2 to sulfate. The decrease in

Miles from stack	SO ₂ , ppm	SO ₄ = μg/m ³	δ,ª SO ₂	δ, ^a SO ₄ *	% SO ₂ conversion, based on conc.
1	1.01	195	+4.6	+10.6	4.7
2	1.02	160	+4.7	+ 9.2	3.8
5	.58	67	+4.5	+ 8.6	2.9
10	.39	35	+5.1	+ 6.6	2.2

Table 3. Plume Run at Northport Sulfur Measurements

ratios could conceivably arise from drop-out of particulate matter with distance. Results indicate the plume at one mile (taken last in this sequence of measurements) was beginning to disperse. The precision in the last column in Table 3, % SO₂ conversion, is indicative of the sensitivity of the sampling technique. In this case, the precision was considered excellent.

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^a The isotope ratios are presented in units of del (δ) . See ref. 6 for the significance of the measurements.

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