EPA-600/4-77-022
April 1977

Environmental Monitoring Series

SURVEY OF CONTINUOUS SOURCE EMISSION MONITORS: Survey No. 1 NO_x and SO_2

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/4-77-022
April 1977

SURVEY OF CONTINUOUS SOURCE EMISSION MONITORS: Survey No. 1 NO_x and SO_2

by

Michael C. Osborne and M. Rodney Midgett

Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CONTENTS

Tables iv
Acknowledgment v

1. Introduction 1
History 1
Purpose of This Survey 2
2. Survey Preparation 5
Industries and Pollutants 5
The Survey Reference Materials 6
Data Requirements 8
Finding Monitors for the Survey 11
Monitor Descriptions 11
3. Survey Procedures 17
Scope of Activities 17
Conducting the Field Measurements 19
4. Results 21
Monitor Performance. 21
Monitor History 25
5. Discussion of Results 31
Monitor Performance 31
Monitor History 33
6. Conclusions and Recommendations 34

References 36
Technical Report Data and Abstract 37

TABLES

Number		Page
1	SPNSS Continuous Monitoring Requirements	5
2	Monitoring System History	10
3	Continuous Emission Monitor Survey Results	22, 23, 24

ACKNOWLEDGMENTS

The authors wish to acknowledge with appreciation the assistance of Mr. Berne I. Bennett and his co-workers in the Quality Assurance Branch for their assistance in analyzing the large number of gas cylinders used in this survey. Appreciation is also extended to each of the survey participants who cooperated in every aspect of the survey. Their names cannot be mentioned here for the reasons stated in the report.

SECTION 1

INTRODUCTION

HISTORY

On September 11, 1974, the U.S. Environmental Protection Agency published in the Federal Register[1] the proposed Standards of Performance for New Stationary Sources (SPNSS) and State Implementation Plans (SIP) requirements for continuous emission monitoring. On October 16, 1974, a separate continuous emission monitoring method, Method 12,[2] was proposed for primary copper, zinc and lead smelters. A slightly revised version of the proposed SPNSS and SIP requirements for continuous emission monitoring was promulgated on October 6, 1975.[3] In January of 1976,[4] Method 12 was withdrawn, and smelters were added to the list of industries required, under SPNSS, to adhere to the monitoring specifications established on October 6, 1975. Therefore, the most significant regulatory document on continuous emission monitoring is the Federal Register[3] of October 6, 1975, which lists system performance specifications, operating procedures, data reduction, and reporting requirements.

The new, or existing, sources that have been, or are being, required to install, calibrate, maintain, and operate continuous gaseous emission monitors are, initially, from five basic industries:

- Fossil Fuel-Fired Steam Generators
- Nitric Acid Plants
- Sulfuric Acid Plants
- Petroleum Refineries

- Primary Copper, Zinc, and Lead Smelters

At present, the only one of these industries in which monitors may be used to determine compliance with the standards of performance is the smelter industry.[3]

Although federal regulations requiring continuous emission monitors are fairly new, the use of these monitors in the aforementioned industries goes back several years. Some of the monitors included in this survey were installed 6 or 7 years ago, while the majority went into operation since 1973.

Very few monitors that are on-line today have actually gone through a performance test as outlined in the October 6, 1975 Federal Register.[4] There are two basic reasons for this. The first and primary reason is that most monitors in plant operation today are on processes that are not classified as new or modified sources according to SPNSS specifications. Instruments installed prior to October 6, 1975, are required to under go the Performance Test only at the request of the administrator. The second reason is that much time, effort, and money is required to conduct one of these 168-hour performance tests. Reports from the few performance tests which have been conducted indicate that most source samplers do not clearly understand many of the details outlined in the October 6, 1975 Federal Register[4] for conducting a performance test. Therefore, few industries want to be the test case for a consultant to learn how to conduct a performance test. As more experience is obtained in performance testing and as more pressure is placed on the industries to conduct the tests, a significant number of these tests may be expected.

PURPOSE OF THIS SURVEY

In most cases, when a survey is conducted, insufficient data is the

reason for the survey. The survey of continuous source emission monitors is no exception. Although several different types of source emission monitors had been evaluated by the EPA, prior to this survey, no continuing program of emission monitor evaluation could be found within or outside the Agency. The concern within the Quality Assurance Branch (QAB) of the Environmental Monitoring and Support Laboratory (EMSL) was that the monitors that were meeting initial design specifications were possibly failing to perform satisfactorily after months of continuous in-plant usage. Some question existed as to whether continuous emission monitoring technology had progressed far enough to develop a long-term maintainable system. Complaints about monitor failure, particularly from electric utility companies, tended to lend credibility to these questions. Were the industries expected to obtain valid monitoring data from instrumentation that could not be expected to adequately perform without excessive maintenance problems?

Another area of concern was which monitors worked well over extended periods and which did not. The EPA policy on continuous source emission monitoring has been, and still is, to provide basic performance requirements for the continuous monitoring systems and leave it at that. No specific monitors will be recommended, nor will EPA recommend a particular method or mechanism over any other. Yet, the Quality Assurance Branch holds to the position that long-term operation data on specific continuous monitors can, and should, be made public knowledge. This practice will be followed without officially recommending any product or method. Also, the names of the specific industries where this information was obtained will not be mentioned. Their participation in this survey was totally voluntary and these industries should, in no way, be penalized for cooperating.

Additional and more extensive surveys will be required to obtain comprehensive answers to the questions: (1) Is emission monitoring technology sufficiently advanced to provide a long-term maintainable monitoring system for industry? and (2) How well do specific continuous emission monitors perform over an extended period of time? Therefore, this report should only be considered a preliminary investigation and should be coordinated with subsequent survey reports to provide a more complete answer to these questions.

SECTION 2

SURVEY PREPARATION

INDUSTRIES AND POLLUTANTS

The industries which were considered for in-plant continuous emission monitor evaluation are the same as those listed in the introduction as having to meet the October 6, 1975, monitoring specifications. Table 1 lists these industries and the pollutants which must be continuously monitored.

TABLE 1. SPNSS CONTINUOUS GASEOUS MONITORING REQUIREMENTS

(Industry)	(Pollutant)
Fossil Fuel-Fired Steam Generators	SO_2, NO, O_2 or CO_2
Nitric Acid Plants	NO_2
Sulfuric Acid Plants	SO_2
Petroleum Refineries	SO_2
Smelters: Primary Copper, Zinc, Lead	SO_2

After a review of the list of possible industries and pollutants which could be included in the initial survey, it was concluded that a survey involving all of these industries and all of these pollutants would be too extensive for a first effort in this subject area. There were too many unknowns with regard to possible survey tools, number of monitors available, access to the plants and the monitors, and the cost of such a survey. The problem became one of properly reducing the number of industries and pollutants so that the maximum beneficial information could be obtained without exceeding time and budgetary allotments or current technical capabilities.

In the process of making this decision about which industries and pollutants were to be included, several significant considerations became apparent: 1) A satisfactory survey tool to evaluate the performance of opacity monitors has not been adequately tested; 2) The number of available nitric acid plants with continuous emission monitors is severely limited; 3) O_2 and CO_2 emissions are only indirectly related to other pollutant emissions in contrast to SO_2 and NO_x emissions, which are primary pollutants; 4) More monitors could be readily located in power plants and sulfuric acid plants than in the other listed industries; 5) A much lower range of SO_2 survey gases is required in petroleum refineries than could be used in either power plants or sulfuric acid plants; and 6) Smelters were of special interest since, in this industry, the monitor is used to determine compliance with emission standards during the performance test.

With these considerations in mind, the decision was made to limit the initial survey to Fossil Fuel-Fired Steam Generators, Sulfuric Acid Plants, and Smelters. The pollutants to be surveyed were limited to sulfur dioxide (SO_2) and nitrogen oxides (NO_x). The other industries and pollutants were to be added in future surveys as time and resources became available, enabling them to be included.

THE SURVEY REFERENCE MATERIALS

One additional limitation on the first survey was that only extractive monitors were included. Ten to twenty percent of the SO_2 and NO_x monitors encountered when setting-up this survey were <u>in-situ</u> units. The <u>in-situ</u> units could not be checked with calibration gases like the extractive units, and calibration cells were not readily available to test the <u>in-situ</u> units.

Since the beginning of the survey, Lear Siegler, a manufacturer of in-situ monitors, has developed a way of introducing calibration gases into the probe and around the sensor so that calibration cells would not be necessary. Future surveys of SO_2 and NO_x monitors will include both extractive and in-situ monitors, using gas cylinders when possible and calibration cells on all other units.

The October 6, 1975, Federal Register clearly states that extractive monitors must be checked by zero and span gases, i.e., gas cylinders. Therefore, the logical reference material for continuous extractive emission monitors is cylinder gases. Some may think that the best reference would be EPA Test Methods No. 6 and 7. It is generally agreed that these are reference methods; however, it has been proven through collaborative testing that these methods have within-laboratory standard deviations of about 4.0 and 6.6 percent, respectively.[5] At the 95 percent confidence level, this variability would, of course, be considerably greater. On the other hand, gas cylinders are readily certified by the gas vendors to be accurate within 2 percent, and, with NBS certified or traceable calibration gases as back-up standards, the concentrations may be further verified. The practicality of using gas cylinders instead of the reference methods was another major consideration. Cylinder gases were, therefore, used as the reference.

Four cylinders of SO_2 in nitrogen, having a concentration of 100, 250, 600, and 850 ppm,* were purchased. These cylinders were then sent to the

*EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice would result in undue cost or lack of clarity, ERC/RTP is providing conversion factors for the particular nonmetric units used in the document. For this report the factors are: 1 ppm SO_2 = 0.376 mg/m^3
1 ppm NO^2 = 0.802 mg/m^3

National Bureau of Standards (NBS) for analysis at the beginning of the survey and again at the end. The cylinders were used to calibrate a continuous source SO_2 monitor, which was then used to measure SO_2 in 25 survey cylinders. In this way, the survey cylinders were traceable to the cylinders analyzed by the NBS.

Four cylinders of nitric oxide (NO) in nitrogen were purchased directly from the NBS. These were Standard Reference Materials (SRMs) at the concentrations of 100, 250, 500, and 1000 ppm. As in the above case, the SRMs were used to calibrate an NO source monitor. Seventy-five NO survey cylinders were then analyzed on the source monitor, thereby once again establishing traceability.

All of the cylinders were guaranteed stable for a period of 12 months from the date of shipment from the vendor's plant. The cylinders were made of treated aluminum, fully pressurized with 30 cubic feet of gas per cylinder and weighed less than 25 pounds per cylinder.

DATA REQUIREMENTS

The information obtained from each survey participant was in two general categories: 1) measured cylinder concentration data and 2) monitor history. The concentration data were simply the monitor reading and equivalent concentration in parts per million for each survey cylinder gas that was introduced into the monitor. At least three different pollutant concentrations were introduced into each monitor, yielding at least three different data points for each monitor.

The information classified as monitor history was considerably more extensive. Answering the question, "How well do continuous emission monitors perform over an extended period of time?" required delving into the more

involved questions of "Why do monitors fail to perform?" and "What types of problems do monitor users encounter?" To obtain answers to these questions a "Monitor System History" questionnaire (Table 2) was prepared.

On the day of the field testing, the questionnaire was filled out by the individuals in the plant who were most familiar with the monitoring equipment. Most of the questions were intended to show not only whether the monitors performed satisfactorily, but also to pinpoint why the user was or was not pleased with the operation of the monitor.

TABLE 2. MONITORING SYSTEM HISTORY

1. Monitor description, including model number.
2. Date that the monitor became operational at its present location.
3. Dates and descriptions of modifications to the monitoring system.
4. How satisfied are you with the services provided by the equipment supplier?
5. How satisfied are you with the overall operation of the monitoring system?
6. What is the normal maintenance schedule for this equipment?
7. For each time that the monitoring system was inoperative during the past 6 months, list the date, number of hours, and reasons:

Date	No. of Hrs.	Reason

8. What special maintenance problems have you had during the past six months with:
   a) the probe
   b) the delivery system
   c) the monitor
   d) the recorder
9. What was the span of the instrument on the day of the test?
10. What was the concentration range of the emissions on the day of the test?

FINDING MONITORS FOR THE SURVEY

The perfect continuous emission monitor survey would seek out a sample of X number of identical monitors from each of Y number of different monitor designs. Unfortunately, the survey covered in this report was hampered from following the perfect experimental design. The major obstacle was locating enough SO_2 or NO_x extractive continuous emission monitors to conduct a survey. An initial list of nine utilities, sulfuric acid plants, and smelters with some type or types of SO_2 or NO_x monitors was submitted by the Emission Measurement Branch of the Office of Air Quality Planning and Standards. Each of these nine plants was contacted, and the planned monitor survey was discussed. Of the nine plants on the original OAQPS-suggested list, only two finally participated in this first survey. Reasons for nonparticipation included: 1) The monitors are not operating at this time, 2) A compressed gas cannot be readily introduced into the monitor, 3) The monitor has been returned to the manufacturer for repairs, 4) The monitors have been turned off until data collected earlier may be evaluated, and 5) Plant employees are not allowed to talk with EPA representatives at this time. Since two plants were an insufficient number of participants for the survey, suggestions for additional participants were sought through correspondence with instrument suppliers, EPA Regional Offices, State air pollution control agencies, and through the industries themselves. About 20 companies were contacted to obtain the 8 different companies that were finally included in the survey. Fortunately, some of the companies that participated had several monitors among a number of plants.

MONITOR DESCRIPTIONS

A total of 19 monitors were included in this initial survey. This

included 6 NO or NO_x monitors and 13 SO_2 monitors. There were four different types of NO or NO_x monitors surveyed -- Dynascience, MSA, Envirometrics, and Thermo Electron. SO_2 monitors were also of four different types - DuPont, Leeds and Northrop, Dynascience, and Thermo Electron.

The only reasons that these monitors were selected over others were that they met the requirement of being extractive NO_x or SO_2 emission monitors and that they were in operation in the plants of the companies participating in the survey.

The following description of each monitor covered by the survey should provide an insight into the differences that existed between the monitors surveyed. Literature from the monitor venders is the primary source of this information. Some difficulty in comparing system performance specifications may be encountered because each vender reported on different specifications.

DuPont Model 400 Photometric Analyzer (SO_2)

This photometric monitor operates in the UV-visible range at a "measuring" wavelength of 302 nm and a reference wavelength of 546 nm. Changes in SO_2 concentration cause the difference in absorption between 302 nm and 546 nm to vary. The light signal is detected by the monitor and displayed as changes in SO_2 concentration. The manufacturer claims that high linearity permits the use of widely different pollutant ranges with one analyzer. Each SO_2 monitor contains an optical filter that mimics the light absorption characteristics of SO_2 and is used for daily calibration, once the filter is calibrated against a known source. DuPont offers the option of purchasing just the basic Model 400 Analyzer - or a complete custom-engineered system that includes the Model 400 and a sampling system. Some system specifications include:

- Precision: ± 1% full scale
- Accuracy: ± 2% full scale
- Zero Drift: 1% full scale in 24-hr for most applications
- Sample Temperature Range: up to 1000°F (538°C)

Leeds and Northrop 7864 Infrared Analyzer (SO_2)

Essentially, the unit is the combination of two simple infrared analyzers. One senses all of the infrared-absorbed gases in the sample; the other senses all but the gas you want to measure, i.e. SO_2. The range of the particular instrument tested was 0 to 10,000 ppm. Calibration gases can be used; however, a three-way solenoid valve for selection of sample or calibrating gas must be specified as a separate option. Similarly, sample conditioning equipment must be either ordered separately, ordered as a standard sampling system, or otherwise provided by the user. Some system specifications include:

- Accuracy: ± 1% of span or 30 ppm (whichever is greater)
- Reproducibility: ± 1.5% of span (24-hr) or 30 ppm (whichever is greater)
- Zero-drift: ± .7% of span (24-hr) or 20 ppm (whichever is greater)
- Analyzer Temperature: Maximum of 140°F (46°C), thermostated

Dynascience -PSC-01, Self Contained Dual Monitor and Sample Aquisition System for NO_x/SO_2

The Dual Monitoring Model utilizes the EPD Selectro Cells. These electrochemical transducers convert the gas concentrations into electric current outputs for simultaneous readings of the two pollutants being measured. Typical concentration ranges of the instrument go up to 2000 ppm. Calibration of the

system with compressed gases is standard with the option of automatic zero and span calibration for unattended use. A complete "turnkey" system capable of continuously acquiring, conditioning, analyzing, and recording pollutant concentrations can be provided. Some system specifications include:

- Sensitivity: ± 2% of full scale
- Repeatability: ± 2% minimum
- Zero Drift: ± 2% of full scale
- Operating Temperature Range: 40-43°C (Temperature controlled at 43°C)

Thermo Electron SO_2 Pulsed Fluorescent Analyzer - Model 40

In this analyzer, a gas sample is submitted to a source of pulsed ultraviolet illumination through a monochomatic filter. SO_2 molecules, energized by the high-intensity pulsed-light source, emit an SO_2 specific illumination, which, through a narrow band filter, impinges upon the sensitive surface of a photomultiplier tube. The emitted light is linearly proportional to the concentration of SO_2 molecules in the sample.

Five standard sensitivity ranges are available, going up to 5000 ppm. Calibration gases are used for calibration purposes, but care must be taken to note the percentage of quenchable compounds in the compressed gas cylinder. A separate sample conditioning and sample collection system is available from the manufacturer. Some system specifications include:

- Accuracy: ± 0.5%
- Reproducibility: ± 0.5%
- Zero Drift: ± 1% (7 days)
- Operating Temperature Extremes: 0-40°C

Environmetrics Series N-76 Analyzer (NO_x)

Each monitor utilizes FARISTOR cartridge sensors to monitor NO_x over various sensitivity ranges. Inside the FARISTOR is a liquid-state device, containing a chemically sensitive activating surface layer upon which pollutant molecules are strongly absorbed by catalytic action. This action results in a change of oxidation state, producing a charged surface. The magnitude of the charge is determined by the rate at which the gas molecules reach the activating surface, this rate in turn being directly proportional to the pollutant concentration. Typical operating ranges for the monitor extend upward to 10,000 ppm. The system calibrates against a gas of known concentration in a nitrogen carrier gas. Sampling and conditioning systems must be obtained separately. System specifications are said to meet or exceed existing EPA standards. This statement was made in 1972, when there were no existing EPA standards on continuous emission monitors.

Thermo Electron Series 10A NO-NO_x Chemiluminescent Analyzer

This chemiluminescent analyzer includes an NO_x-NO converter for the conversion of NO_x to NO for subsequent measurement via the chemiluminescent process. The instrument has eight different concentration ranges all the way up to 10,000 ppm. Regular calibration of the monitor requires the use of calibration gas cylinders. As with the TECO SO_2 analyzers, a separate sample conditioning and sample collection system is available from the manufacturer. Some system specifications include:

- Accuracy: $\pm$ 0.5%
- Reproducibility: $\pm$ 0.5%
- Zero Stability: $\pm$ 1 ppm (24-hrs)
- Operating Temperature Extremes: 0-40°C

MSA Lira Infrared Analyzer - Model 202 (NO)

This analyzer operates on the principal of nondispersive infrared (NDIR) detection. The NDIR analysis method is used on the hypothesis that most nitrogen oxides (NO_x) emitted from power plants are in the form of nitric oxide (NO). Typical analytical ranges are 0-2000 ppm NO. Calibration selector values for using calibration gases are built into the system. The complete sampling acquisition and conditioning system consists of a specially designed 5-micron shielded filter probe assembly for installation in the stack and a heat-traced insulated Teflon or stainless steel sample line conditioning system. Some system specifications include:

- Accuracy: 1.0%
- Repeatability: 1.0%
- Zero Drift: 1.0% (24-hr)
- Operating Temperatures: 0-48°C

SECTION 3

SURVEY PROCEDURES

SCOPE OF ACTIVITIES

In the complete picture of what is involved in conducting a survey of continuous emission monitors, the actual field measurements make up only a small part. The following is the chronological order for this first survey and should be looked upon as the cycle which each additional survey is likely to follow.

1. Identified companies with monitors

This step was described earlier, including the difficulties which were encountered.

2. Initial contact with a knowledgable employee

Few plant managers knew whether their monitors were extractive, the make of the monitor, or the operating range of the monitor. An individual who worked directly with the instrument on a day-to-day basis was contacted.

3. Sent letters requesting the participation of the company in the survey

Official permission to perform tests in a given industry almost always required a written request.

4. Initial calibration of survey cylinders

This step needed to be taken within a few weeks of the actual field measurements to minimize chances of degradation taking place.

5. Receipt of confirmation of willingness to participate

The survey was held up until this letter was received.

6. Second conversation with plant contact

At this point, information was obtained concerning the span of the instrument, an agreeable testing date, and a confirmed mailing address for the gas cylinders.

7. Shipped cylinders

Available means of shipping compressed gas cylinders was limited. While SO_2 cylinders could be sent through the U.S. Mail, NO cylinders were limited to only a few commercial trucking companies. Even then, delays were common because the cylinders could not be placed on trucks hauling clothing.

8. Mailed final notification of visit

To be certain that no misunderstandings existed between the surveyor and the industry, the plant manager or supervisor received a final confirmation of the date of the proposed visit and the extent of the planned testing. The letter was received approximately a week before the actual field testing, to ensure that it was not forgotten.

9. Determined if cylinders had arrived

The surveyor did not go into the field until he was certain that all necessary equipment was on site.

10. Conducted the field measurements

This step will be expanded upon later.

11. Returned cylinders and re-analyzed concentrations

If the cylinders' concentrations are re-analyzed quickly, there is little opportunity for the cylinders to degrade.

12. Supplied participating industries with tentative results

The courtesy of letting the industries know, without delay, how they performed has created a willingness on their part to participate in the next

survey. It was often possible to provide the industries with this information during the actual field testing. The concentrations did not change significantly between pre- and post-test laboratory evaluations.

13. Combined The results of the independent surveys and published the data

Information was compiled about both instrument accuracy, based on field measurements, and instrument maintenance problems, based on the monitor history questionnaire.

Conducting the Field Measurements

Each company has its own security procedures and it is, therefore, difficult to generalize about them. In most cases, however, it was found that the best approach was to proceed to the front gate and ask to see our principal contact. In some small plants this was the plant manager, or the local plant supervisor, but in most cases our contact was the instrument man or a plant engineer.

After a discussion of the planned testing, the next task was to locate the shipped gas cylinders. After the gas cylinders were taken to the monitor location and the proper regulators attached, a determination was then made as to where in the sampling line to introduce the gas. Ideally, the gas should be introduced immediately after the sampling probe so that the majority of the sampling and conditioning system would also be evaluated. It was observed in this survey, however, that most installations were not prepared for introducing the gas immediately after the probe, so a less suitable site, such as just prior to the monitor, was usually selected. A wide range of stainless steel fittings and flexible tubing was available to ensure a leak-free connection to the sampling line.

At least three different concentrations of reference gas were introduced at each monitor, and the instrument reading was recorded in each case. No attempt was made to calibrate or zero the instrument before introducing the gas. Care had to be taken with some monitors to prevent over-pressurizing the sample lines. After obtaining the readings from the monitor for the various gases, the concentration of the stack gases being recorded on the strip chart or other recorder was noted. After the gas line was disconnected and the cylinders were re-sealed for return shipment, the appropriate plant personnel were asked to complete the monitor history forms. Usually, there was limited information available to document items on the survey form. As a result, most interviews lasted only a few minutes.

The last task was the shipment, or arranging the shipment, of the cylinders back to the laboratory for re-analysis. Leaving this task to the plant personnel would have significantly delayed the completion of the project.

SECTION 4

RESULTS

MONITOR PERFORMANCE

Table 3 shows the survey results from introducing three or more survey gases into each continuous emission monitor. Names of participating companies have been omitted for reasons stated previously. In order to be able to identify individual sources when evaluating the data, however, a number and letter have been designated for each participating company. The letters used are P, A, and S, corresponding to power plants, sulfuric acid plants, and smelters, respectively. The number in front of the letter designates which power plant, etc. In some cases, more than one of the same type of monitor were evaluated at a given site. When this happened, the monitors were also numbered.

A comparison of actual vs. measured concentration is included as the basic evaluation criteria. This value is called the percent accuracy; i.e.,

$$\% \text{ accuracy} = \frac{\text{concentration measured} - \text{actual concentration}}{\text{actual concentration}} \times 100,$$

where the "actual concentration" is defined as the value established by the Quality Assurance Branch.

The average percent accuracy that is included in the results is the absolute average, giving no consideration to the sign of the individual values. One exception to the procedure is the results from the survey of the TECO NO_x monitor. The reason for this exception is explained in the section on "Discussion of Results."

TABLE 3.

Pollutant	Plant	Monitor	Cylinder	Concen. measured @ plant ppm	Actual concen. ppm	% Accuracy
NO_x	1P	Dynascience	FF 3152	520	471	+9.9
			FF 3264	1120	975	+14.9
			FF 3275	1640	1459	+15.7
						AVE: 13.5
NO	2P	MSA	FF 1121	240	236	+0.8
			FF 1138	400	404	-1.0
			FF 1106	420	406	+1.9
						AVE: 1.2
NO_x	3P	Envirometrics	FF 1226	215	246	-12.6
			FF 1192	350	395	-11.4
			FF 1108	370	406	+8.9
						AVE: 11.0
NO_x	3P	TECO (No. 1)	FF 1226	235	246	-4.5
			FF 1192	390	395	-1.3
			FF 1232	425	407	+4.4
						AVE: 3.4
NO_x	3P	TECO (No. 2)	FF 1226	245	246	-0.4
			FF 1192	388	395	-1.8
			FF 1232	392	407	-3.7
						AVE: 2.0
NO_x	3P	TECO (No. 3)	FF 1226	235	246	-4.5
			FF 1192	390	395	-1.3
			FF 1232	400	407	-1.7
						AVE: 2.5
SO_2	3P	DuPont	FF 1073	140	150	-6.7
			FF 1176	385	367	+4.9
			FF 1065	630	782	-19.4
						AVE: 10.3

TABLE 3.

Pollutant	Plant	Monitor	Cylinder	Concen. measured @ plant ppm	Actual concen. ppm	% Accuracy
SO_2	1A	Leeds and Northrop	FF 3234	2150	2440	-11.9
			FF 3259	4450	5180	-14.1
			FF 3248	6150	7750	-20.6
					AVE:	15.5
SO_2	1A	DuPont	FF 3234	2600	2440	+6.6
			FF 3259	5300	5180	+2.3
			FF 3248	7750	7750	0
					AVE:	3.0
SO_2	1S	DuPont (No. 1)	FF 1487	6,400	5,560	+13.3
			FF 1385	10,900	10,800	+0.9
			FF 1458	15,800	16,300	-3.1
					AVE:	5.8
SO_2	1S	DuPont (No. 2)	FF 1487	4,950	5.650	-14.4
			FF 1385	9,700	10,800	-10.2
			FF 1458	14,600	16,300	-10.4
					AVE:	11.0
SO_2	1P	Dynascience	FF 1184	130	151	-13.9
			FF 1086	330	364	-9.3
			FF 1494	727	805	-9.6
					AVE:	10.9
SO_2	2A	TECO	F 312*	108	147	-26.5
			F 126*	340	453	-24.9
					AVE.	25.7
			FF 1166	193	158	+22.2
			FF 1258	408	362	+12.7
			FF 1175	427	378	+13.0
					AVE.	16.0

TABLE 3 (continued)

TABLE 3.

Pollutant	Plant	Monitor	Cylinder	Concen. measured @ plant ppm	Actual concen. ppm	% Accuracy
SO_2	4P	DuPont (No. 1)	FF 1079	792	759	+4.3
			FF 1186	816	778	+4.9
			FF 1269	808	804	+0.5
			FF 3234	2252	2440	-7.7
					AVE:	4.3
SO_2	4P	DuPont (No. 2)	FF 1079	720	759	-5.1
			FF 1186	736	778	-5.4
			FF 1269	756	804	-6.0
			FF 3234	2188	2440	-10.3
					AVE:	6.7
SO_2	4P	DuPont (No. 3)	FF 1079	756	759	-0.4
			FF 1186	764	778	-1.8
			FF 1269	792	804	-1.5
			FF 3234	2284	2440	-6.4
					AVE:	2.5
SO_2	4P	DuPont (No. 4)	FF 1079	732	759	-3.6
			FF 1186	752	778	-3.3
			FF 1269	772	804	-4.0
			FF 3234	2192	2440	-10.2
					AVE:	5.3
SO_2	4P	DuPont (No. 5)	FF 1079	844	759	+11.2
			FF 1186	848	778	+9.0
			FF 1269	860	804	+7.0
			FF 3234	2332	2440	-4.4
					AVE:	7.9
SO_2	3A	DuPont	FF 1258	355	362	-1.9
			FF 1175	400	378	+5.8
			F 126*	485	453	+7.1
			F 314*	645	615	+4.8
			F 162*	770	760	+1.3
					AVE:	4.2

*denotes air is the carrier gas instead of nitrogen.

TABLE 3 (continued)

MONITOR HISTORY

In trying to establish the overall reliability of the monitors surveyed, investigators used the series of questions in Table 2 to develop a record of the history of the monitoring system. Some of the participating industries had not maintained enough records on their monitoring equipment to answer all of the questions. Therefore, information which would have been helpful in evaluating some of the monitors was not available. Specifically, background information on the Envirometrics (NO_2) monitor could not be obtained from the company that owned the monitor.

The following is a question-by-question summary of the information obtained by use of the monitoring-system history questionnaire:

1. Monitor description including model number. The answers to this question are in the earlier sub-section on "Monitor Descriptions".

2. Date that the monitor became operational at its present location. A summary of the years in which the monitors became operational is listed below:

Year	1970	1971	1972	1973	1974	1975
No. of Monitors	1	3	0	8	3	3

3. Dates and descriptions of modifications to the monitoring system. The dates when modifications were made to the monitoring systems were not available at most plants that were visited. Several significant modifications were made, however, and are listed below:

Monitor	Modifications
4P-DuPont No. 1-5 (SO_2)	1. Added a new design particulate filter.
	2. Shortened probe.
	3. Increased sample line from 1/4 inch to 5/8 inch

Monitor	Modifications
	4. Added a fuse to prevent shorting out in 220-volt heat traced line.
	5. Made probe of 316 stainless instead of 304.
4P-DuPont No. 1-3 (SO_2)	1. Added switch to purge system during downtime.
1S-DuPont No. 1 & 2 (SO_2)	1. Added temperature gauge at the monitor.
	2. Devised a filtering system to keep out moisture and particulates.
2P-MSA (NO)	1. Replaced sample lines.
1P-Dynasciences (NO_x & SO_2)	1. Changed from a "glued-together" sample conditioner to a "screwed-together" unit.
	2. Replaced a Teflon piece in the diaphragm pump with a rubber one.
	3. Changed blow back valves from a 10-minute cycle to a 20-minute cycle.
	4. Replaced Teflon seats with nylon seats and an O-ring.
2A-TECO (SO_2)	1. Began making their own particulate filters.
3P-TECO (NO_x) and DuPont (1) (SO_2)	1. Have added heat tracing to the sampling line.

4. How satisfied are you with the services provided by the equipment supplier? There were no complaints registered with regard to any of the equipment suppliers.

5. How satisfied are you with the overall operation of the monitoring system? Most operators were pleased with the monitoring system as a whole. However, three companies (2A-TECO, 2P-MSA, and 4P-DuPont (1-5) indicated that

there had been unreasonably poor performance of the pumps, sampling lines, and probes.

6. What is the normal maintenance schedule for this equipment? Responses to this question are listed below:

Monitor	Maintenance Schedule
1P-Dynascience (NO_x and SO_2)	1. Calibrate once per week with calibration gases. 2. Check flow and battery daily. 3. Clean SO_2 scrubbers once every two weeks to one month. 4. Rebuild pumps and compressors twice a year. 5. Valve maintenance 3-4 times per year.
2P-MSA (NO)	1. Daily calibration with calibration gases.
3P-TECO(1-3) NO_x	1. Cleaning of capillary tubes and change oil in the vacuum pump once every 3 months.
3P-DuPont (SO_2)	1. No maintenance schedule available yet.
1A-Leeds and Northrop and DuPont (SO_2)	1. Check out system once per week. 2. Calibration check once per month or sooner with optical filters (DuPont). 3. Clean lenses once per month.
1S-DuPont (2)(SO_2)	1. Calibrate each morning with optical filter. 2. Particulate filter change once per week.
2A-TECO (SO_2)	1. Daily zero and calibration check with calibration gases. If error exists, then maintain.

Monitor	Maintenance Schedule
3A-DuPont (SO_2)	1. Check it 3 times a day with optical filter.
4P-DuPont (1-5)(SO_2)	1. Observed daily. 2. Weekly check with optical filter. 3. Complete calibration monthly with calibration gases.

7. For each time that the monitoring system was inoperative during the past 6 months, list the date, number of hours, and the reason. This was the most difficult question on which to obtain answers. The purpose of this question was to determine the availability of the instrument, exclusive of plant shut-downs or other times when the instrument was not needed. A rough estimate of the amount of time each monitor was non-functional during the 6-month period prior to the survey follows:

Monitor	Approximate Time Non-Functional Over 6 Mos.
1P-Dynasciences (SO_2 & NO_x)	- less than 3 weeks
2P-MSA (NO)	- 10 days
3P-DuPont (SO_2) & TECO (1)(NO_x)	- 6 weeks
3P-TECO (2&3)(NO_x)	- functioned continuously
4P-DuPont (1-5)(SO_2)	- 2-4 weeks each
1A-DuPont & Leeds & Northrop (SO_2)	- less than 1 day each
2A-TECO (SO_2)	- 1 week
3A-DuPont (SO_2)	- less than 1 day
1S-DuPont (1)(SO_2)	- 2 days
-DuPont (2)(SO_2)	- 1 day

8. <u>What special maintenance problems have you had during the past 6-months with the probe, the delivery system, the monitor, or the recorder?</u>

Plants reporting problems with clogged probes include:

- 2P - MSA (NO)
- 4P - DuPont (1-5)(SO_2)
- 1A - DuPont (SO_2)
- 2A - TECO (SO_2)
- 3A - DuPont (SO_2)
- 1S - DuPont (1 & 2)(SO_2)

Problems with the delivery system were of three types: clogging, condensation, and leaks. Those plants reporting problems with clogging were:

- 4P DuPont (1-5)(SO_2)
- 2A TECO (SO_2)

Condensation problems were reported by:

- 2P MSA (NO)
- 3P DuPont (SO_2)
- 3P TECO (NO_x)
- IS DuPont (1 & 2)(SO_2)

The problem of leakage was reported by:

- 1P Dynasciences (NO_x & SO_2)

Problems that were reported with the monitor, itself, included:

4P DuPont (1-5)(SO_2) - 1) cracked housing on solenoid
2) dirty optics
3) defective diaphragm on vacuum breakers

1S DuPont (1 & 2)(SO_2) - 1) fluorides etch lenses

1A Leeds and Northrop (SO_2) 1) cracked lenses
2) electronic problem with power supply

2A TECO (SO_2) 1) dirty optics

3A DuPont (SO_2) 1) dirty optics

Recorders were often not a part of the purchased monitor package and were also generally not a problem.

9. and 10. What were the span of the instrument and the concentration range of the emissions on the day of the test? The purpose of these questions was to place the survey gases in perspective with the operating range of the instrument, the concentration at which it was calibrated, and the normal operating level of the instrument. The results of the questions are as follows:

Monitor	Calibration Check ppm	Full scale ppm	Concen. range ppm
1P Dynascience (NO_x)	not known	600	200-400
1P Dynascience (SO_2)	not known	1500	300-600
2P MSA (NO)	888	1000	80
3P TECO (1-3) (NO_x)	900	1000	200-400
3P DuPont (SO_2)	not known	600	0
4P DuPont (1-5) (SO_2)	3233	4000	1200-2600
1A DuPont & Leeds and Northrop (SO_2)	5000	10000	1500-2000
2A TECO (SO_2)	300	500	20-30
3A DuPont (SO_2)	2300	5000	1700
1S DuPont (1&2) (SO_2)	9800	20000	4500-9000

SECTION 5

DISCUSSION OF RESULTS

MONITOR PERFORMANCE

Before a discussion of how the monitors performed as a whole, it is necessary to clarify the results of the survey of the TECO (SO_2) monitor at plant 2A. As was noted in the section on "Monitor Descriptions", the TECO (SO_2) monitor is a pulsed fluorescence instrument which is sensitive to quenchable compounds in the survey gas. We were aware of this problem when the survey was conducted and, therefore, used both cylinders of SO_2 in nitrogen and SO_2 in normal dry air (20% O_2). The results of the survey show that the monitor consistently read the SO_2 in air cylinder concentrations low and the SO_2 in nitrogen cylinder concentrations high. An analysis of the sulfuric acid plant stack gas indicated that there was 8.3 percent oxygen present. Assuming that the amount of quenching was directly proportional to the oxygen concentration of the stack gas, an estimate of the average percent accuracy based on the survey results would indicate that the TECO monitor was reading low by only 1.7 percent. This calculation is obviously questionable since additional testing would be required to measure how much oxygen quenching really occurred. The approximation obtained by ratioing the oxygen present gives, however, a much better representation of how well the monitor was functioning than either the test performed with SO_2 in nitrogen or the test performed with SO_2 in air. Further evaluation of this type of monitor, using more representative survey gases, is anticipated during our next performance

survey.

Another point which should be considered before any gross generalizations about the findings of the survey are made, relates to the concentration level of the survey gases. In some of the installations, the monitor range encountered at the site was much higher than anticipated. Therefore, the concentration levels that were introduced were occasionally on the lower end of the monitor concentration read-out range. Since few monitors are calibrated specifically for the low end of the scale, some of the monitors in the survey may seem to perform worse than they would if we had always used survey gases which were at least mid-range. Closer attention will be paid to this point in future surveys.

In general, the monitoring systems surveyed performed better than had been expected on the basis of earlier reports from industrial monitor users. Nine of the 19 monitors surveyed had an average percent accuracy of less than 5 percent. This is exceptionally good, considering the age of most of the monitors and the limited regular maintenance which they had been given. Only six of the 19 monitors failed to come within 10 percent of the actual concentrations, and the worst one of these was out by only 15.5 percent. Therefore, there were no really poor monitor performances; only some that might be classified marginal. Without making reference to any specific monitor, the data clearly show that certain monitoring systems were out-performing others. Insufficient data are available to determine if the larger percent accuracy was caused by failure within the instrument or by problems with the cylinder gases used to calibrate the instrument. No specially good or bad performance was observed in any one of the three industrial categories. It should be noted, though, that at least one monitoring system worked exceptionally well

in each of the three industrial categories.

MONITOR HISTORY

Each individual monitoring system that was evaluated in the survey was found to have had one or more maintenance problems. The significant finding was that the probe, the delivery system, and the monitor were all consistently contributing to these maintenance problems. The most prominent problem experienced by the majority of operators was clogging of either the probe or the sample lines. The second greatest problem was related to the first, in that condensation in the sample line often is the cause of, or at least contributes to, the clogging.

Several problems were listed for some installations. This fact may, however, be more closely related to the disposition of the operator who provided this information than to the quality of the monitor.

In general, most participants were at least satisfied with the overall operation of their monitor, and, as far as could be determined, no one was displeased with the services of the equipment supplier.

Several monitoring systems experienced a significant amount of downtime during the 6 months prior to the survey. This fact was partially due to the low priority attached to keeping the monitoring system going, compared to other types of instrumentation in the plant. Since downtime was usually an estimate, it may have been over-exaggerated. Until plants start keeping a record of this information, it will be impossible to obtain good monitor availability data.

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

Most of the survey participants were pleased to learn that information on the reliability and accuracy of continuous emission monitors was being gathered for public distribution. Such information can only enhance quality control in this area of instrumentation.

The initial survey produced few surprises. Several general conclusions from the survey were, however, possible.

1) Continuous emission monitors can perform exceptionally well, and some did in this study.

2) Some types of continuous emission monitors consistently perform better than others.

3) The industrial category in which the monitor is placed has no effect on how well or how poorly the monitor performs.

4) The probe, the delivery system, and the monitor all contributed to regular maintenance problems.

5) The two most prominent maintenance problems encountered were clogging of the probe and sample lines and condensation.

Recommendations for future surveys included:

1) Expand the survey to include:

   a. more different types of monitors

   b. in-situ monitors

   c. monitors in nitric acid plants, petroleum refineries, and other

types of smelters

d. CO_2, O_2, and opacity monitors

e. monitors that have passed the 168-hour performance test

2) Repeat the survey on the same 19 monitors at regular intervals.

3) Use survey gases that are at the 50 percent and 90 percent of the full-scale concentration levels that are suggested in the October 6, 1975, Federal Register[4] for calibration purposes.

4) Conduct evaluations of the pulsed fluorescence instrument at oxygen and CO_2 levels that are equal to those in the stack gas.

5) Introduce the survey gas at the probe exit whenever possible.

REFERENCES

1. U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources. Federal Register, 39:32852-32860, September 11, 1974.

2. U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources. Federal Register, 39:37040-37049, October 16, 1974.

3. U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources. Federal Register, 40:46250-46270, October 6, 1975.

4. U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources. Federal Register, 41:2332-2341, January 15, 1976.

5. Hamil, H. F., and D. Camann. Collaborative Study of EPA Methods 5, 6, and 7 in Fossil Fuel-Fired Steam Generators: Final Report. U.S. Environmental Protection Agency Technical Report No. EPA-650/4-74-013. May 1974. (Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.)

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-77-022	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE SURVEY OF CONTINUOUS SOURCE EMISSION MONITORS: SURVEY NO. 1 - NO_x AND SO_2.		5. REPORT DATE April 1977 issuing date 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Michael C. Osborne and M. Rodney Midgett		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Quality Assurance Branch Environmental Monitoring and Support Laboratory U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711		10. PROGRAM ELEMENT NO. 1HD621 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA/600/08
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

The Quality Assurance Branch (QAB) of the Environmental Monitoring and Support Laboratory has undertaken the task of evaluating the accuracy and reliability of continuous monitors which have been on-line for six months or longer. Only extractive monitors installed in power plants, sulfuric acid plants, and smelters were included in the first survey. The program was designed so that additional industries and types of monitors could be included in later surveys.

The plan for the initial survey involved sending NBS-traceable gas cylinders of varying concentrations of SO_2 or NO to the participating industries. The gases from the cylinders were introduced into the monitoring systems and the resulting data made available to both the QAB and the industry.

Results from this survey of eight different companies, ten different plant sites, and nineteen different monitors revealed that less than half of the monitors failed to achieve a performance accuracy of $\pm$ 10 percent. The instruments which failed most often were the ones that have seen less wide-spread use. In general, the SO_2 monitors and the NO_x monitors performed equally well. However, more information was available on SO_2 monitors since they outnumbered NO_x monitors in this survey almost two to one.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Monitors Sampling Sulfur dioxide Nitrogen oxide Air pollution Chimneys or Emission	Continuous emission monitors	13B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 42
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)