United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S4-81-025 Sept. 1981

EPA

Project Summary

National Performance Audit Program: 1979 Proficiency Surveys for Sulfur Dioxide, Nitrogen Dioxide, Carbon Monoxide, Sulfate, Nitrate, Lead and High Volume Flow

B. I. Bennett, R. L. Lampe, and J. C. Puzak

The Quality Assurance Division of the Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, administers semiannual Surveys of Analytical Proficiency for sulfur dioxide, nitrogen dioxide, carbon monoxide, sulfate, nitrate, and lead. Sample materials which simulate ambient air pollution samples as closely as possible are furnished to participating laboratories. Surveys of high volume sample flow rates are conducted annually using a modified orifice.

The Quality Assurance Division assures that samples are stable, of uniform composition, and are representative of pollutant concentration levels encountered under field sampling conditions and that all materials conform to prescribed standards of accuracy. Sample materials are required to be similar enough to true air pollution matrices not to introduce unrealistic conditions of sample preparation or impose handling techniques that are not a part of the normal monitoring and analytical activity. A major survey objective is to assess routine analytical performance. An individual report is promptly returned to each participant after results are evaluated by the Quality Assurance Division.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The 1979 Proficiency Surveys continue the regular surveys by the Environmental Monitoring Systems Laboratory (EMSL) of agencies which routinely collect and analyze ambient air samples. Sample materials which are furnished for this purpose are designed to simulate as closely as possible several types of collected air pollution samples. The samples furnished by the EPA are used to test only the analytical portion of the total air monitoring capability, and do not deal with errors from sample collection, flow rate error, transportation, handling, storage, and data processing. Rankings in the surveys, except as may occasionally be due to unpropitious circumstances, reflect the effectiveness of internal quality assurance programs.

The Proficiency Surveys allow EPA to assess the quality of air pollution analyses in general and permit the participants to compare their own work with that of their peers.

Participants in the surveys are solicited by the Regional Quality Control Coordinator in each of the ten Regions. Once a laboratory enrolls in a survey for a particular pollutant, it is automatically notified of subsequent surveys for the pollutant. The surveys are conducted by the Quality Assurance Division (QAD)/ EMSL, Environmental Research Center, Research Triangle Park, North Carolina, 27711, with the assistance and cooperation of the EPA Regional Offices. Inquiries and applications to participate should be directed to that address. Included in the surveys were representatives of federal, state, local, industrial and foreign facilities.

Soon after a roster is established, instructional information and unknown sample materials are mailed. Surveys are presently conducted twice a year for carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), lead (Pb) on filter strips, sulfate ($SO_4^=$) and nitrate (NO_3^-) on filter strips and once a year for hi-vol flow. A report is issued to each laboratory indicating the reported value and an historical frequency distribution of test results. A comprehensive report is prepared yearly summarizing the survey results of that year.

Before 1979, the surveys provided target and sample ranges that defined the sphere of all creditable results. Under that system, results falling within the sample range indicated a fine analytical job and results within the wider target range were respectably good. This format enjoyed wide favor due to the clear, explicit and uncontestable tableau it presented for scoring any single test result.

Beginning with the 1979 survey year, in an effort to enable comparison of individual results with those of peer laboratories, format was modified by presenting cumulative frequency distributions of the results of earlier surveys.

In any survey, some of the results are far removed from the rest of the reported measurements and this small body of egregious data may be safely excluded. After the obviously inconsistent data are removed, objective judgments need to be made about values that are questionable. The standard chosen for the 1979 surveys was the Chauvenet's Criterion.

This criterion is based on the normal distribution and advises rejection of an extreme observation if the probability of occurrence of such deviation from the mean of the n measurements is less than 1/2n. The rationale for this criterion is that inclusion of spurious data vitiates test results by biasing both the survey mean and precision, whereas removal of good measurements merely excludes some of the data.

The sulfur dioxide sample material was composed of freeze-dried mixtures of sodium sulfite and potassium tetrachloromercurate (TCM) contained in 5-ml glass ampoules. Sample sets consisted of five ampoules containing 4 to 64 micrograms (μg) of SO_2 equivalent per container. The sample material was stored at -20°C to sustain the integrity of the SO_2 activity, which was confirmed by periodic retesting. Analyses were performed by the reference method for the determination of SO_2 in the atmosphere (pararosaniline method). The sample, when solubilized in 0.04N TCM forms a dichlorosulfitomercurate complex. This complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline sulfonic acid.

The nitrogen dioxide samples consisted of 5 mL of aqueous sodium nitrite contained in glass ampoules where a set consisted of five ampoules. When mixed with caustic absorbing reagent, the samples simulated ambient samples ranging in concentration from 0.17 to 1.00 μg/mL.

Samples of carbon monoxide were offered as compressed gas mixtures of CO and artificial air. Also contained in each sample was 2 ppm of methane (CH_4) and approximately 365 ppm of carbon dioxide (CO_2). Aluminum cylinders were used in the surveys. Sample concentrations ranged from 3 to 44 ppm of CO. Each participant received a set of three cylinders, one from each of three concentration levels.

Sulfate-nitrate samples consisted of 1.9 x 20 cm (0.75 x 8 in.) glass fiber filter strips with depositions of potassium sulfate (K_2SO_4) and lead nitrate ($Pb[NO_3]_2$). Filter strips samples included concentrations of various SO_4 and NO_3 concentrations. Each strip was contained in a sealed plastic envelope. The concentrations of suifate ranged from approximately 1.5 to 29 $\mu g/m^3$. Nitrate levels spanned between 1.5 and 12 $\mu g/m^3$. Concentrations were determined using the requisite filter dimensions of 20 x 25.4 cm (8 x 10 in.) and a collected air volume of 2000 m^3. It can be shown that the process of gravimetric preparation and transfer of a well-characterized homogeneous solution of chemical constituents can be accomplished with more precision and accuracy than would be obtained from the chemical analysis of spiked filter strips. Therefore, the reted) values were obtained theoretically from the deduced mass of inorganic salts deposited on the filters. Verification analyses assured that the accuracy and precision of the samples were within prescribed limits.

Lead samples were composed of 1.9 x 29 cm (0.75 x 8 in.) glass fiber filter strips with depositions of lead nitrate ($Pb[NO_3]_2$). Filter strip sample sets contained combinations of different lead concentrations, each in a sealed plastic envelope. The lead content ranged in concentration from 1.5 to 12.9 $\mu g/m^3$. Concentrations were calculated presuming that the samples were collected on the prescribed 20 x 25.4 cm (8 x 10 in.) hi-vol filter with a total air volume of 2000 m^3.

To evaluate hi-vol flow, a single reference flow device (ReF) was supplied to each participating agency. Organizations were instructed to check as many hi-vol sampling units as feasible within the allotted time. The unit received by each laboratory consisted of a modified orifice, wind deflector, manometer, and resistance plates designed to alter flow rates.

During measurement of the air flow of a hi-vol sampler, the ReF was mounted on top of the sampler replacing the filter face plate. A wind deflector was necessary to prevent fluctuation in the readings due to wind blowing across the orifice. The resistance plates, when inserted into the ReF, simulated various filter loading conditions.

Conclusions

Sulfur Dioxide

Proficiency Surveys for SO_2 were conducted in April and October 1979. Approximately 100 participants completed each of the surveys. The pararosaniline method predominated with 80 percent of the laboratories using that procedure. No systematic discrepancies or substantial bias existed in the SO_2 surveys. Comparison by the t test showed that differences in the means of the preponderant methods were not statistically significant. Within the purview of the semiannual proficiency surveys, the two methods do not differ with regard to variability, according to the F test.

Participation in the April 1979 SO_2 survey decreased by 12 percent from

the previous year; the October 1979 survey continuing at about the same level. The reduction was largely accounted for by decreased use of the pararosaniline method by state agencies. The number of users of the pararosaniline method stabilized at around 100.

Survey results are summarized in Table 1, with all methods included.

Nitrogen Dioxide

Proficiency Surveys for NO_2 were conducted in June and December 1979. Approximately 90 participants completed the first survey, and close to 80 the second.

The predominant analytical method was the manual sodium arsenite colorimetric procedure; 72.7 percent of the 0679 respondents used it. Slightly fewer reported using the manual method in the 1279 survey. Around 21 percent of respondents used the automated sodium arsenite method. The manual and automated Saltzman and TGS-ANSA manual methods made up the balance of the test methods. No systematic discrepancies or substantial bias was apparent in the NO_2 surveys.

Survey results are summarized in Table 2, with all methods included.

Carbon Monoxide

Proficiency Surveys for CO were conducted in March and September 1979. Operational assessment of approximately 300 instruments were included in each of the two semiannual surveys. The NDIR method was employed by approximately 90 percent of the survey respondents. No systematic discrepancies or substantial bias was identified in the CO surveys.

Of the test methods listed on the survey information forms, the NDIR method dominated, with 91 percent of the laboratories using that method in the 0379 survey and 87 percent in the 0979 test. Facilities using the GC method increased from 6 to 12 percent during the biannual testing period. Other methods were reported being used by approximately 2 percent of the respondents. The 1979 and previous survey results lead to the conclusion that the precision of the GC method is subordinate to that of the NDIR method. This conclusion is verified by application of the statistical F test to the data obtained.

Survey results are listed in Table 3, with all methods included.

Table 1. *Summary of Sulfur Dioxide Proficiency Surveys*

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0479 (April 1979)					
1	100	13.9	14.15	4.85	2.17- 25.76
3	105	93.3	92.56	7.97	70.74-109.10
4	103	148.3	154.30	10.45	126.51-175.68
5	105	212.7	214.48	15.03	170.80-256.99
Survey 1079 (October 1979)					
1	101	13.5	12.63	5.00	1.08- 33.30
2	103	38.5	35.80	6.57	10.13- 54.10
3	102	80.0	77.26	8.14	48.14-108.40
4	103	125.	125.24	11.31	88.00-166.50
5	104	165.	165.62	14.16	104.22-206.97

**With outliers removed.*

Table 2. *Summary of Nitrogen Dioxide Proficiency Surveys*

Sample no.	Respondents*	Expected value $\mu g/mL$	Survey mean $\mu g/mL$	Survey std. dev. $\mu g/mL$	Survey interval $\mu g/mL$
Survey 0679 (June 1979)					
1	88	0.259	0.26	0.02	0.21-0.30
2	88	0.405	0.40	0.02	0.34-0.45
3	88	0.514	0.51	0.03	0.39-0.62
4	87	0.700	0.71	0.03	0.62-0.78
5	86	0.935	0.95	0.04	0.83-1.07
Survey 1279 (December 1979)					
1	76	0.172	0.18	0.04	0.09-0.44
2	78	0.342	0.35	0.05	0.14-0.55
3	76	0.595	0.59	0.07	0.22-0.73
4	77	0.746	0.74	0.09	0.18-0.90
5	76	1.000	0.97	0.12	0.34-1.16

**With outliers removed.*

Table 3. *Summary of Carbon Monoxide Proficiency Surveys*

Sample no.	Respondents*	Expected value ppm	Survey mean ppm	Survey std. dev. ppm	Survey interval ppm
Survey 0379 (March 1979)					
1	291	6.53	6.39	0.53	4.92- 8.50
2	295	19.8	20.08	0.89	17.30-23.00
3	294	43.7	44.14	1.51	38.23-49.70
Survey 0979 (September 1979)					
1	290	2.98	2.73	0.48	1.25- 4.75
2	268	14.8	14.75	0.75	12.24-17.30
3	297	33.8	34.14	1.37	29.50-39.00

**With outliers removed.*

Sulfate

Proficiency Surveys for $SO_4^=$ were conducted in February and August 1979. Approximately 60 participants completed each survey. State and local agencies composed 70 percent of the roster of participating laboratories. Six test methods were employed with methylthymol blue and the manual barium chloride procedures dominating. Other major methods used were the Sulfa-Ver© and ion chromatography. No systematic discrepancies occurred. The barium chloride procedures exhibited the greatest variability of the test methods.

Survey results are listed in Table 4, with all methods included.

Nitrate

Proficiency Surveys for NO_3^- were conducted in February and August 1979. Approximately 45 participants completed each of the surveys. Over half the respondents used the automated cadmium reduction procedure. In all, nine analytical methods were reported in use. Others were ion chromatography, phenoldisulfonic acid, brucine, specific ion electrode, Szechrome© and ultraviolet spectrophotometric procedures. The averages of all methods were compared by an extension of the analysis of variance at the 5 percent significance level. No single method was particularly bad and no systematic discrepancies existed.

Survey results are given in Table 5, including all analytical methods.

Lead

Proficiency Surveys for Pb were conducted in January and July 1979, with approximately 80 facilities participating. The atomic absorption method of analysis was virtually the only method used. No systematic discrepancies or bias was observed in the Pb surveys.

Table 6 contains the results of the lead surveys.

Hi-Vol Flow Rate

The Proficiency Survey for hi-vol flow was conducted in May 1979 with approximately 1300 sites being tested. Six measurement methods were listed by survey participants. The pressure transducer and rotameter dominated with 72.6 percent using those methods.

Table 4. Summary of Sulfate Proficiency Surveys

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0279 (February 1979)					
0	65	10.50	10.61	2.21	6.65-21.60
1	65	19.50	18.96	1.73	14.10-23.64
2	65	1.50	1.96	1.17	0.30- 5.60
3	65	15.00	14.74	1.34	11.70-18.03
4	65	24.00	23.80	2.22	16.48-31.80
5	65	6.00	5.75	1.13	3.06- 9.15
Survey 0879 (August 1979)					
0	59	9.10	8.38	1.25	3.00-11.11
2	58	28.80	27.42	2.57	20.00-33.60
3	60	23.70	22.90	2.58	14.00-30.11
4	58	13.10	12.16	1.58	6.45-15.90
5	59	7.20	6.77	1.18	3.50-10.13

*With outliers removed.

Table 5. Summary of Nitrate Summary Proficiency Surveys

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0279 (February 1979)					
0	50	1.50	1.58	0.41	0.35- 3.39
1	50	3.60	3.52	0.38	2.53- 4.60
2	50	5.70	5.52	0.52	4.39- 7.29
3	50	12.00	11.54	1.32	7.83-14.79
4	50	7.80	7.60	0.77	5.04- 9.16
5	50	9.90	9.68	0.98	7.32-13.74
Survey 0879 (August 1979)					
0	40	3.40	3.44	0.44	2.37- 4.40
2	39	6.00	5.90	0.51	4.22- 6.88
3	40	10.20	9.97	0.95	7.12-11.57
4	40	8.30	7.94	0.84	4.99- 9.20
5	40	1.20	1.21	0.27	0.36- 1.82

*With outliers removed.

Table 6. Summary of Lead Survey Proficiency Surveys

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0179 (January 1979)					
3	76	1.46	1.45	0.16	0.93- 1.95
4	76	3.52	3.46	0.28	2.84- 4.32
5	76	5.39	5.39	0.57	2.88- 6.63
6	76	11.45	11.31	1.15	7.74-14.10
7	76	7.48	7.61	1.10	4.80-12.00
8	76	9.51	9.38	0.96	6.18-11.57
Survey 0779 (July 1979)					
0	81	3.53	3.53	0.29	2.34- 4.20
1	81	12.86	12.85	0.87	10.59-15.30
2	79	5.85	5.90	0.34	4.77- 6.97
3	81	10.39	10.42	0.91	7.50-13.80
4	80	7.93	7.99	0.48	6.81- 9.97
5	81	1.18	1.17	0.12	0.84- 1.50

*With outliers removed.

Other minor methods, as noted on the survey cards, were flow gauge, manometer, orifice manometer, and magnehelic gauge.

The sample ReF's furnished could not be all the same. Each ReF unit was calibrated individually and is distinct from all other units, because flow rates could not be duplicated precisely enough among the test devices to establish flow values that were applicable to all units. Rather than comparing collective measurements against a common standard, results from each ReF were compared to a calibration which was unique for that unit. The calibrated flow values, or expected values, developed for each of five flow constrictor plates, were compared to the values recorded on the survey forms.

Frequency distributions of the percent differences between the reported and expected values for each measurement pair are shown in Table 7.

Table 7. Percent Difference from Expected Flow Rates

Number of measurements	Percent of measurements					
	10%	20%	30%	50%	70%	90%
5902	-9.2	-4.8	-2.6	0.3	3.0	7.4

Recommendations

Since the EPA began administering the voluntary proficiency surveys in 1973, the program has progressed both in scope and participation, with approximately 300 laboratories now receiving CO survey samples and 1300 sites taking part in the hi-vol tests. Prompt return of survey reports by the QAD signal possible analytical/measurement problems or confirms the excellence of ongoing monitoring activities. Timely notification is considered one of the essential elements of the survey program.

Continuance of the surveys will render valued assistance to existing internal quality assurance programs by making accessible a variety of air pollution standard samples, furnished free of charge by the U.S. EPA, to a diverse clientele within the arena of air pollution monitoring.

☆ U S GOVERNMENT PRINTING OFFICE, 1981 — 757-012/7345

*The EPA authors **B. I. Bennett** (also the EPA Project Officer, see below), **R. L. Lampe**, and **J. C. Puzak** are with the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.*

The complete report, entitled "National Performance Audit Program: 1979 Proficiency Surveys for Sulfur Dioxide, Nitrogen Dioxide, Carbon Monoxide, Sulfate, Nitrate, Lead and High Volume Flow," (Order No. PB 81-239 402; Cost: $8.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
ERA 335

Official Business
Penalty for Private Use $300

PS 0000329
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604