United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
Research Triangle Park, NC 27711

Research and Development

EPA/600/S4-86/045 Apr. 1987

EPA

Project Summary

NBS/EPA Certified Reference Material Performance Audit Program: Status Report 2

Robert S. Wright, W. Cary Eaton, and Clifford E. Decker

A traceability procedure has been established that allows specialty gas producers to prepare gaseous pollutant Certified Reference Materials (CRMs). The accuracy, stability, and homogeneity of the CRMs approach those of NBS Standard Reference Materials. Part of this procedure is an independent quality assurance audit of each CRM batch by an EPA-coordinated auditor. As of October 1986, 36 candidate batches had been audited. Generally, the agreement between the producer's analytical results and the audit results is within plus or minus 0.5 percent relative. Additional data suggest that CRMs are stable during their two-year certification periods.

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 legal implications of many environmental measurements require that accurate and stable standards be used to calibrate the monitoring instrumentation. In the past, EPA regulations have required that gaseous pollutant calibration standards for ambient air quality measurements be traceable to National Bureau of Standards (NBS) Standard Reference Materials (SRMs). Similarly, calibration standards for mobile source emission measurements had to be traceable to either SRMs or other approved gas standards. The use of SRMs in these and other applications created a demand which occasionally exceeded NBS's production capacity.

In response to this demand for high accuracy standards, NBS and EPA established a traceability procedure (EPA Publication No. EPA-600/7-81-010) by which specialty gas producers can prepare standards whose accuracy approaches that of SRMs. These standards are called NBS/EPA Certified Reference Materials (CRMs). EPA regulations now allow CRMs to be used as equivalents of SRMs for ambient air quality surveillance, for continuous emission monitoring systems, for new motor vehicle certification, and for vehicle inspection and maintenance programs.

The traceability procedure contains appendices that describe the preparation and analysis of CRMs which contain carbon monoxide in nitrogen or air, nitric oxide in nitrogen, sulfur dioxide in nitrogen, and propane in nitrogen or air. The procedure also contains an appendix for recertifying CRM batches. An appendix for preparing and analyzing CRMs that contain oxygen in nitrogen is being developed.

The purchaser of a CRM is assured that its accuracy is high because of four features of the CRM program:

1. The general technical procedure for producing and analyzing CRMs has been specified by NBS;
2. CRMs are directly traceable to SRMs which are used as reference standards during the analysis of CRMs;
3. The producer's analytical results are verified by measurements which are performed by an independent auditor; and

4. Both the producer's and the auditor's analytical results must be reviewed and approved by NBS before the CRMs may be sold.

Since the CRM program's inception in November 1980, the Research Triangle Institute (RTI) has been the EPA-coordinated auditor. The Project Report summarizes the CRM program in general and the audit program specifically, including the analytical instrumentation and the procedures used in the audits. The results of the CRM audits are summarized and compared with the producers' analytical results. Additional information is presented concerning CRM stability and availability.

Procedure

CRMs must be produced in batches of at least 10 cylinders having identical concentrations. The traceability procedure specifies that the CRM producer must analyze the batch on two different occasions that are separated by at least a one-month interval. Further, an SRM must be used as the reference standard during these analyses. These analyses must demonstrate that the batch is homogeneous and stable. Following the analyses, the producer sends a report of the analytical results to NBS and a letter to the auditor stating that a CRM batch is available for audit.

The purpose of the EPA performance audit program is to provide NBS with an independent set of analytical results for each CRM batch. NBS uses these audit results to verify the producer's analytical results. The audit is conducted on two random samples from the batch. If there is good agreement between the audit results and the producer's results, NBS can conclude that the producer has accurately measured the two samples and, by inference, the remainder of the batch.

The traceability procedure has several features that help to assure that the audit results are representative, accurate, and precise. The audit is representative because the two audit samples are chosen at random by the auditor, who is unaware of the producer's results. The procedure specifies that an SRM must be used as the reference standard for the audit. In addition to assuring the accuracy of the audit, this specification allows the audit results to be validly compared with the producer's results because both analyses use SRMs as their reference standards. The precision of the audit may be quantified because the auditor must make 10 replicate measurements of the audit samples. The audit must be repeated if standard deviation of these measurements exceeds 0.5 percent relative.

The audit procedure being used by RTI is adapted from that used by NBS in its analysis of SRMs. The audit samples, the reference SRM, and a zero gas are plumbed by a solenoid valve manifold to the analytical instrumentation. The gases are not diluted for the analysis. A timer controls the solenoid valves and produces a measurement cycle of zero gas-SRM-CRM (1) - CRM (2), which is repeated at least 10 times. An instrument zero value and an instrument sensitivity are determined for each CRM measurement by interpolation between the two adjacent zero gas measurements and the two adjacent SRM measurements. These calibration values are used to calculate concentrations for the audit samples. In addition to the audit measurements, three SRMs of differing concentrations and the zero gas are measured at least three times to determine the linearity of the instrumentation.

Following the audit, a written report of the audit results is sent to NBS for review. All audit and linearity check measurements are included in the report. The report also includes information concerning the analytical instrumentation and procedures, the reference standards, and a statistical analysis of the data.

NBS reviews the two sets of results. The producer's results must demonstrate that the batch is homogeneous and stable. The audit results must be in good agreement with the producer's results. If NBS is convinced that a batch has satisfied the requirements for CRMs, both the producer and EPA will be notified that the batch may be sold as CRMs. In the event that NBS is not convinced of the stability, homogeneity, or accuracy of the batch, the producer or the auditor may be required to perform additional analyses. Alternatively, audit samples may be sent to NBS for analysis. In this manner, NBS remains the final arbiter concerning the stability, homogeneity, and accuracy of each CRM batch and ensures its credibility as a SRM substitute.

Results and Discussion

As of October 1986, audits have been performed on 36 candidate CRM batches containing carbon monoxide in nitrogen or air, nitric oxide in nitrogen, and propane in nitrogen. For all 36 batches, acceptable agreement was found between the producer's results and the audit results. Two of these batches could not be certified because of problems not associated with the audit (i.e., batch instability and the producer's analytical precision). The frequency distribution of the absolute value of the agreement between the producer's and the audit results is given in Figure 1.

In general, the absolute value of the agreement has been within 0.5 percent relative. The mean absolute value for the 72 audit samples is 0.18 percent relative, and the maximum absolute value is 0.60 percent relative. This level of agreement is within the limits set for the program and demonstrates that specialty gas producers can prepare and analyze CRMs with a high degree of accuracy.

The coefficient of variation (CV) for the 10 or more measurements in each audit can be used as an index of precision for the audit program. The CV varies with the instrument used for the audit measurements. Non-dispersive infrared analyzers were used for carbon monoxide CRM audits at concentrations of 1 percent or less. The 44 audit samples in this concentration range had a mean CV of 0.05 percent relative and a maximum CV of 0.14 percent relative. A gas chromatograph with a thermal conductivity detector was used for carbon monoxide CRM audits at concentrations of 2 percent or greater. The 10 audit samples in this concentration range had a mean CV of 0.35 percent relative and a maximum CV of 0.56 percent relative. A chemiluminescence analyzer was used for nitric oxide CRM audits. The 10 nitric oxide audit samples had a mean CV of 0.09 percent relative and a maximum CV of 0.19 percent relative. A gas chromatograph with a flame ionization detector was used for propane CRM audits. The four propane audit samples had a mean CV of 0.19 percent relative and a maximum of 0.27 percent relative. The CVs for all of the audits are within the limits specified by the NBS/EPA traceability document, although the precision for the high concentration carbon monoxide audits is not as good as is desirable.

During the development of SRMs, NBS found that the concentrations of carbon monoxide, nitric oxide, sulfur dioxide, and propane mixtures contained in aluminum cylinders were stable for periods of two or more years. Accordingly, the original traceability procedure for CRMs specified that a CRM batch may be certified for two years following the batch's second analysis. If no significant concentration changes were found between the first and second analyses, then it was highly probable that the batch would remain stable during the two-year certification period. However, a batch could not be

given an unlimited certification period. Concentration trends which would not affect the certified concentration over a two-year period may become significant after more than two years.

As CRMs were beginning to be produced, NBS and EPA decided to investigate whether the CRMs' concentrations would remain stable through their two-year certification period. As a result, an informal long-term stability study was conducted with the cooperation of the CRM producers. During the winter of 1983, nine selected audit samples were reanalyzed. The time between the original audit and the long-term stability study reanalysis ranged from 11 to 25 months. A histogram of the concentration change which was observed between these two measurements is given in Figure 2. Most of the concentration changes were statistically significant. However, the magnitude of these changes was small in comparison to the overall CRM uncertainty. The largest variation observed was 0.29 percent relative after 25 months, which is well within the total uncertainty of 1 percent relative for the sample's certified concentration. One cannot make broad statements concerning the long-term stability of all CRMs based on measurements of a few samples; nevertheless, these data are encouraging and suggest that CRMs remain stable during their certification periods.

The traceability procedure contains an appendix which describes how a producer may recertify a CRM batch after its two-year certification period has expired. Basically, the recertification involves the reanalysis of all unsold members of the batch, using the same analytical technique that was used in the original analysis. The reanalysis must demonstrate that the CRM's concentration has not changed significantly since the first analysis. A performance audit is not needed for recertifications. As of October 1986, seven CRM batches have been recertified. Among the CRMs that were reanalyzed, only one showed signs that it might be unstable.

Conclusions

This Project Summary deals with the performance audit program for CRMs. The audit results have been compared with the producer's results for each of 36 candidate CRM batches. In general, the agreement between the two sets of results has been within plus or minus 0.5 percent relative. This comparison demonstrates that specialty gas producers can prepare and analyze CRMs with an accuracy approaching that of SRMs. Limited data have been presented concerning the long-term stability of CRMs which suggests that they are stable during their certification periods.

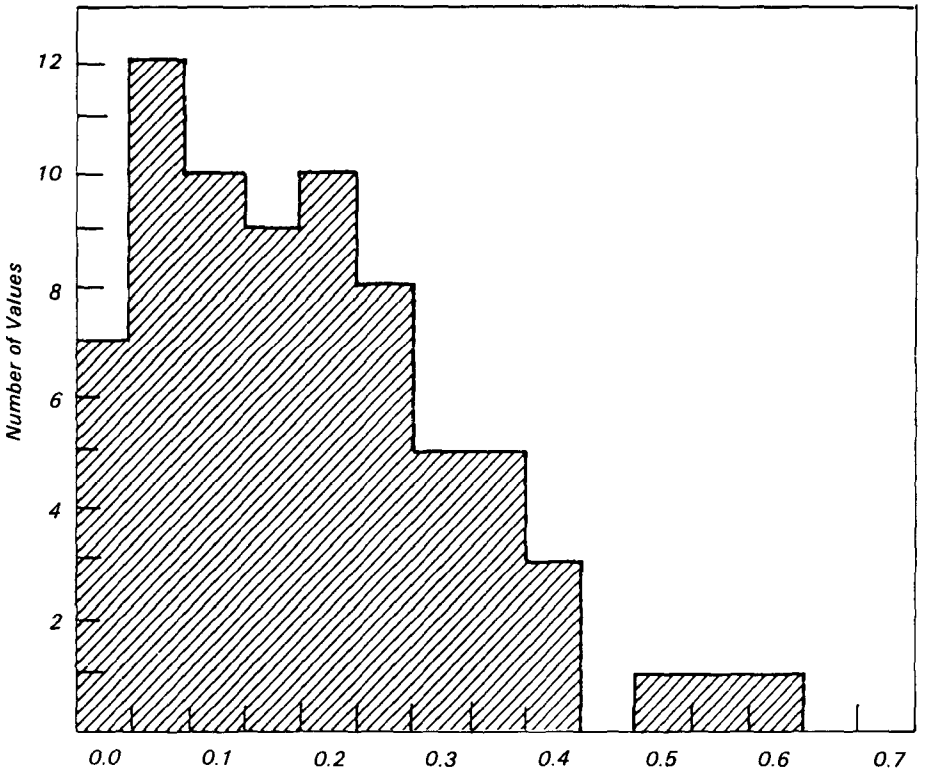

Figure 1. *Frequency distribution for the percent difference between producer and audit results for CRM audit samples*

$$\text{Percent Difference} = 100 \left[\frac{\text{(Audit Result - Producer Result)}}{\text{(Audit Result)}} \right]$$

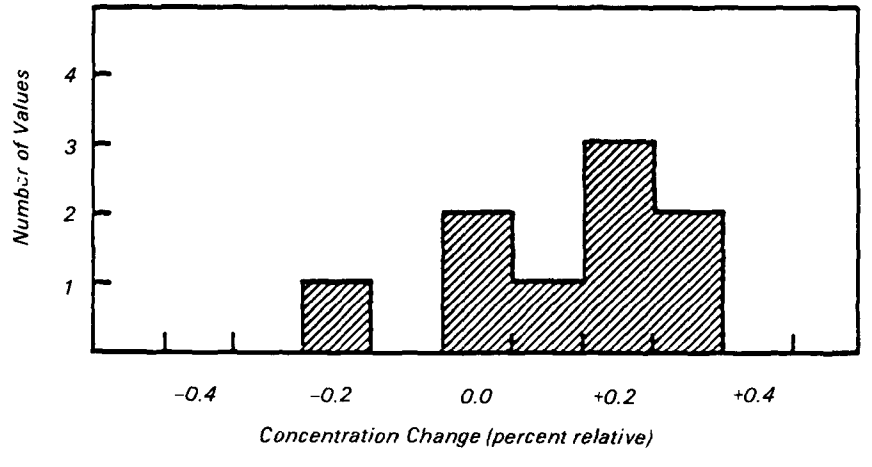

Figure 2. *Frequency distribution for the concentration change between the first and second analysis of selected CRM audit samples*

Robert S. Wright, W. Cary Eaton, and Clifford E. Decker are with Research Triangle Institute, Research Triangle Park, NC 27709.
***Darryl J. von Lehmden** is the EPA Project Officer (see below).*
The complete report, entitled "NBS/EPA Certified Reference Material Performance Audit Program: Status Report #2," (Order No. PB 87-140 463/AS; Cost: $11.95, 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

Official Business
Penalty for Private Use $300
EPA/600/S4-86/045