EPA-600/7-81-010
Revised November 1989

A PROCEDURE FOR ESTABLISHING TRACEABILITY OF GAS MIXTURES TO CERTAIN NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY* SRM'S

by

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Contract No. EPA-IAG-D8-E684
EPA-IAG-DW-13932911

Project Officer
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NBSIR 81-2227

*Formerly, National Bureau of Standards

U.S. DEPARTMENT OF COMMERCE
Robert A. Mosbacher, Secretary

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ABSTRACT

A procedure is described by which the concentration of commercially produced gas mixtures may be related to certain gas Standard Reference Materials (SRM's) currently offered by the National Institute of Standards and Technology. The concentration of the gas mixture as a Certified Reference Material (CRM), must, by definition, lie within one percent relative of the concentration of a particular SRM to reduce the error involved in the comparative analysis. Statistical treatment of the traceability process is given by an example, as is the process by which a body requiring traceability can evaluate the quality of the CRM. Procedures also are included for recertification of CRM's, and for initiating the certification period from the date of sale rather than from the date of CRM approval by NIST. Appendices are included for the preparation of CRM's related to carbon monoxide, nitric oxide, sulfur dioxide, propane, oxygen, and carbon dioxide SRM's.

DISCLAIMER

This revised report has been reviewed by the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflects the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

One important role of the National Institute of Standards and Technology (NIST) is to provide those services necessary to assure data quality in measurements being made by Federal, state, local, and industrial laboratories participating in environmental measurement programs. The work at NIST is conducted in appropriate disciplinary Centers (the Center for Analytical Chemistry, the Center for Radiation Research, and the Center for Chemical Technology). NIST activities address data quality assurance needs of air and water monitoring programs. NIST efforts in support of data quality assurance include:

- Studies of the feasibility of production of Standard Reference Materials (SRM's) which could be used for the verification of performance audit samples for quality control programs or used for the calibration of field and laboratory instruments.
- The development and demonstration of new or improved measurement methods, particularly when needed for the certification of SRM's.
- The evaluation and dissemination of data on the physical and chemical properties of effluents, products and raw materials of environmental significance in energy production.
- The provision of reference materials for the evaluation and validation of monitoring methods.

This document was initially issued in May 1981, as one of the Interagency Energy/Environmental Research and Development Series Reports prepared to provide detailed information on the development of a NIST measurement standard or method. The document provides a procedure by which commercial specialty gas companies could produce gas mixtures as Certified Reference Materials (CRM's) that would be directly traceable to certain NIST gas SRM's. These CRM's would be accepted by the U.S. Environmental Protection Agency (EPA) as reliable substitutes for SRM's in environmental monitoring programs required by EPA regulations. EPA published an announcement in the Federal Register that such CRM's could be used in place of SRM's. The traceability procedure described in the May 1981 issue of this document was jointly reviewed and approved by NIST, EPA, and the U.S. Compressed Gas Association.

The original issue of this document in May 1981 contained appendices for the production of four types of gaseous mixtures, covering 43 different NIST SRM's: CO in N_2 or air (Appendix C); NO in N_2 (Appendix D); SO_2 in N_2 (Appendix E); and propane in N_2 (Appendix F). This revision to the document contains appendices for two additional types of gaseous mixtures, covering 18 additional NIST SRM's: O_2 in N_2 (Appendix H); and CO_2 in N_2 (Appendix I). In addition, this revised document includes a procedure (Appendix G) for extending the certification period for existing CRM's and a mechanism by which a CRM producer can certify a CRM from the date of sale, rather (as required in the May 1981 document) from the date of NIST approval of sale. The advantage of the procedure for extending this certification period is that an approved CRM can be recertified for additional incremental periods (each period usually being two years), indefinitely, as long as the certified concentration of original gas mixture in the cylinder has not changed, supported by reanalysis data developed for each additional certification period. The advantage of the mechanism for date of sale certification is that a producer of an approved CRM can certify the concentration of the mixture for the full certification period authorized for the CRM, at the time of its sale to a customer. This mechanism eliminates the problem in selling a two-year certified CRM a year after its approval with only a one-year certification period, as required in the May 1981 document. The three additional appendices included in this revised document (Appendices G, H, and I) have been reviewed and approved by NIST, EPA, and representatives of the U.S. specialty gas industry. Questions relating to this revised document and its procedures and specifications, including the new appendices, should be addressed to Walter L. Zielinski, Jr., William D. Dorko, or George C. Rhoderick at NIST, or to Darryl J. von. Lehmden at EPA.

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CONTENTS

1. INTRODUCTION

2. CERTIFIED REFERENCE MATERIALS

    2.1 Description
    2.2 Preparation
    2.3 Analysis

3. SUGGESTED ANALYTICAL PROCEDURE

    3.1 Description
    3.2 First Analysis
    3.3 Second Analysis

        3.3.1 Stability and Homogeneity
        3.3.2 Estimation of the Uncertainty of the CRM

4. AUDIT OF THE CRM

    4.1 Introduction
    4.2 Environmental Protection Agency Audit Progress

        4.2.1 Selection of Samples
        4.2.2 Analysis
        4.2.3 Report of Results

    4.3 Examination of Results
    4.4 Certification

ACKNOWLEDGEMENTS

APPENDICES

Appendix A. Statistical Analysis of Data
Appendix B. Report Forms
Appendix C. Carbon Monoxide
Appendix D. Nitric Oxide in Nitrogen
Appendix E. Sulfur Dioxide in Nitrogen
Appendix F. Propane
Appendix G. Extension of Certification (Recertification) and Date-of-Sale Certification

    a. Introduction
    b. Procedures to Extend the Certification of a CRM
    c. Analytical Procedures for Date-of-Sale Certification
    d. Converting from Fixed Period Certification to Date-of-Sale Certification

Appendix H. Oxygen in Nitrogen
Appendix I. Carbon Dioxide in Nitrogen

1. INTRODUCTION

This procedure is intended to increase the availability of accurate gas standards by the creation of a series of secondary standards, to be referred to herein as "Certified Reference Materials" (CRM's). The CRM's prepared according to this procedure will be related, within known limits of uncertainty, to specific gaseous Standard Reference Materials (SRM's) offered by the National Institute of Standards and Technology (NIST). The CRM's are intended to supplement the supply of existing SRM's, and are not intended to offer traceability for gas mixtures at concentrations other than those of the complementary SRM's, nor for components of such mixtures that are not certified in the SRM's.

The procedures described are based on experience at NIST relative to the production and certification of gaseous SRM's, and are intended to assure the development of reliable CRM's with reasonable effort, but are not intended to reduce the effort to a minimum. The acceptance of the CRM's by regulatory agencies, by industry, and by other users, will depend on the reliability of the CRM's. The CRM's, in turn, will depend on the integrity of the gas supplier relative to the methods, conditions, and limitations of the procedure described here and on the reliability and extent of any complementary audit program.

2. CERTIFIED REFERENCE MATERIALS

2.1 Description

The CRM's will consist of compressed gas samples in cylinders prepared in lots of ten or more of identical concentration. The average concentration for any lot must lie within 1.0 percent relative to the concentration of a specific SRM, but preferably the concentration should be as close as technically possible to the SRM to reduce to a minimum any errors that might arise in subsequent analyses of the CRM's. The concentration for a specific CRM will be determined by analysis with a specific SRM and the uncertainty assigned to the concentration of the CRM will consist of the uncertainty of the SRM and the added uncertainty resulting from the intercomparison of the CRM to the SRM. The period of time during which the concentration of the CRM is certified, and the presence of any impurities of consequence will be reported by the supplier.

2.2 Preparation

Each CRM will be prepared as a homogeneous lot containing at least ten (10) cylinders, all filled from a bulk mixture prepared in a single container or in several containers ganged together in such a manner that delivery occurs simultaneously from the several containers, or by use of a dynamic blending system. The reagent gases with which the bulk mixture is prepared must be analyzed for the major component(s) and for minor constituents of interest. The concentration of the component of interest in the bulk mixture must lie within 1 percent relative to the particular SRM which is being duplicated. The cylinders into which the bulk mixture is transferred and which will become the CRM's must be clean, of known compatibility and history, and must be treated to assure stability of the mixtures which will be contained. The cylinders will be equipped with valves of appropriate material which conform to Compressed Gas Association (CGA) recommendations for the particular gas mixture.

After filling, an "incubation" period must be allowed before final analysis. This period will vary depending on the nature of the gas mixture and is described in the appendices of this document.

2.3 Analysis

The analysis consists of a comparison of each CRM to the appropriate SRM. The requirement that the CRM have a concentration within 1 percent relative of the SRM reduces the error arising from the intercomparison and simplifies the calibration procedure for the analytical instruments. In most cases, the characteristics of the analyzer are such that the response of the instrument over a small concentration range (1 percent relative or less) can be described by the linear equation

$$y = mx + b$$

where y is the signal, m is the instrument sensitivity in signal units per unit of concentration, x is the concentration, and b is a constant in signal units. Consequently, it is only necessary to determine that the sensitivity does not change significantly over the interval between the concentration of the CRM and the SRM to compare the two signals directly. It follows then that the closer in concentration that the CRM is to the SRM, the less possibility for error exists in assigning a value to the CRM.

The general characteristics of the analyzer response relative to concentration is determined by constructing a calibration curve using the SRM against which the CRM is to be compared as one calibration point, and at least two other gas mixtures for a minimum of three calibration points. These additional calibration gases should be SRM's, one higher in concentration and one lower in concentration, as compared to the SRM which is being used to analyze the CRM. Obviously, this is not possible when the CRM is being compared to either the highest or lowest concentration SRM in a particular series. In this case, the CRM should preferably have a concentration slightly lower than the SRM, if it is the highest SRM in a series, or slightly higher if the SRM is the lowest in a series. If the SRM is the lowest in a series, the use of a "zero" gas may be feasible. However, either the use of a zero gas or extrapolation beyond the calibration curve established with SRM's is not recommended without technical justification.

The ideal case where the instrument response over a wide range is directly proportional to concentration can be readily recognized by measuring the signal generated by each of the three SRM calibrating gases and dividing each by its certified concentration to obtain the sensitivity (m) at the three concentrations. If the response is linear and if the calibration line passes through the origin, the value for m will be essentially the same at all three concentrations, and the equation reduces to $y = mx$. If m is constant over a wide range of concentrations, then it should follow that it will be constant over a smaller range. In this case, the concentration of the CRM is simply

$$C_{CRM} = \frac{I_{CRM}}{I_{SRM}} C_{SRM} \quad \text{or} \quad C_{CRM} = \frac{I_{CRM}}{m} \quad \text{since} \quad m = \frac{I_{SRM}}{C_{SRM}}$$

where I is the signal generated by either the SRM or the CRM and C is concentration.

In the somewhat less ideal case where the response is linear but does not pass through the origin, the value of the signal divided by the concentration will not be equal at the three concentrations but a straight line of slope m and intercept b can be fitted to the data. It again follows that if m is constant over a wide range of concentrations, it should be constant over a small interval, and the concentration of the CRM is expressed as:

$$C_{CRM} = \frac{I_{CRM}-b}{I_{SRM}-b} C_{SRM} \quad \text{or} \quad C_{CRM} = \frac{I_{CRM}-b}{m} \quad \text{since} \quad m = \frac{I_{SRM}-b}{C_{SRM}}$$

A third case is that of an analytical instrument having a slight non-linear response. In this situation, a calibration curve is constructed using three or more (preferably, five) SRM's, and the concentrations are determined using the derived equation for the curve. However, in most cases, the component in a CRM that is being analyzed will be measured with an instrument which is essentially linear over small ranges of concentration. In other words, the sensitivity of the instrument - the response in signal units per unit of concentration - will not change within the limits of the precision of the instrument over short intervals of concentration. If the sensitivity is found to be essentially constant over the internal of 1 percent of the concentration of the SRM that is to be reproduced by the CRM, then the sensitivity measured for the SRM can be used to calculate the concentration of the CRM. In this case, the closer the CRM is in concentration to the SRM, the smaller will be the error introduced by assuming short range linearity.

It is essential in analyzing the CRM's that the analyses be made with the highest of degree of precision possible so that the uncertainty of the concentration of the CRM not be appreciably larger than the total uncertainty of the concentration of the SRM with which it is compared.

The principal elements that contribute to the imprecision of this comparison include instrument sensitivity and instability. The sensitivity of the instrument should be high enough so that differences of concentration of 0.1 percent relative easily can be measured. Instruments are available that are capable of measuring all current SRM's with this sensitivity. However, most instruments exhibit drift to one degree or another. The drift has two components, short term drift (or noise), and a long term drift characterized by a slowly changing signal under constant operating conditions. The effect of short term drift can be minimized by a number of techniques including the multiple analyses of each sample, and signal averaging. The effect of long term drift can be minimized by frequent calibration of the instrument. The characteristics of each analytical system should be considered individually to determine the optimum frequency of calibration and the approach to compensation or control of the effect of noise. However, it should be noted that the effort expended in minimizing these effects will be reflected in the precision of the analyses relating the CRM to the SRM. In general, if duplicate analyses of single samples consistently agree within 0.1 percent relative, then the effect of noise is at an acceptable level, and if repeated analysis of the same sample performed at intervals during the analysis of a lot agree within the same limits, then the long term drift is at an acceptable level.

3. SUGGESTED ANALYTICAL PROCEDURE

3.1 Description

The analytical procedure recommended here is considered to be the minimum effort necessary to adequately reduce the possibility of accepting an unstable CRM. All CRM's must be stable, and each batch should be homogeneous. An unstable batch must be rejected, while an inhomogeneous batch may be acceptable, providing that the reason for the inhomogeneity is known and further providing that the cause of the inhomogeneity will not result in a future change in concentration not revealed by the test for stability.

The object of the analysis is to compare a lot of at least ten samples of presumably identical concentration to an SRM and to express the concentration of each sample in the lot with error limits defined by the uncertainty of the SRM and the uncertainty added by the analytical procedure. Obviously, the simplest procedure would involve direct analysis of the CRM with the SRM, but with most analytical methods this approach would be unduly extravagant in terms of SRM consumption. Consequently, it is recommended that the concentration be determined on a relative basis by comparing one sample from the lot of all others in the lot. Thus, only the one sample is compared to the SRM and the concentration of all others in the lot can then be determined from the measured ratio of each to the one sample. An additional uncertainty is introduced in this procedure but the size of this uncertainty can be reasonably small, and the final uncertainty in the CRM will not be increased significantly.

The sample from the lot with which the rest of the lot is to be compared, the lot "internal standard", is selected at random from the lot. The signal generated by the internal standard is compared to the signal generated by each sample. The internal standard is repeated throughout the sequence of analysis so that any long term instrument drift can be compensated for, if necessary.

The resulting data can be expressed as the ratio of the signal generated by individual CRM's to that generated by the internal standard. The ratio in all cases should be very close to 1.000 if the lot is homogeneous.

3.2 First Analysis

An initial analysis of the batch of CRM's should be performed as soon as practical after the preparation of the CRM's. A sample is selected at random from the lot to serve as the lot "internal standard" to which a number of samples from the lot are compared. At least ten samples selected at random from each lot should be analyzed during this first analysis. However, if the lot is small (<20 samples) it is recommended that all samples be analyzed.

The internal standard should be analyzed against the appropriate SRM during the first analysis to confirm that its concentration lies within 1 percent relative to the SRM and to establish a reference for later analyses intended to define the stability of the lot. The internal standard should be analyzed at least ten times using SRM's to calibrate the instrument. Each of the remaining nine or more samples selected is then analyzed in duplicate, using the internal standard as a reference.

Some preliminary conclusions regarding the homogeneity and stability of the batch may be drawn from the results of this first analysis. For instance, if the batch was inhomogeneous when transferred and if no subsequent reactions have occurred randomly in the cylinders, the concentration of all samples analyzed should be the same within the limits of precision of the analytical method. The appropriate statistical treatment at this step is given in the appendices. If the statistical test shows lack of homogeneity among the samples, it is not possible at this time to determine whether such inhomogeneity is due to improper preparation or to reaction in the cylinders. If the test shows reasonable closeness among the results for all samples, then there is some assurance that the batch is homogeneous.

If the analyses at this point indicate that no serious problem exists, the entire batch is set aside for the required "incubation" period. If, however, the batch appears to be somewhat inhomogeneous the analyses should be continued to include all samples in the batch. An analysis of each sample at this time may become critical later in differentiating inhomogeneity resulting from preparation and inhomogeneity arising from instability.

3.3 Second Analysis

After the requiring incubation period has passed, all samples in the lot are analyzed, including those analyzed during the first analysis. The first analysis served to define the concentration of the CRM and to test the stability and homogeneity of the lot on a qualitative basis. Final decisions regarding these factors depend on the second and more extensive analysis. Sufficient time will have elapsed so that reactions in individual cylinders, which were of too low a rate to be recognized by the distribution of concentrations obtained in the first analysis, will be revealed by this subsequent analysis. Decisions regarding homogeneity, which may have been based on analysis of a portion of the batch, will now be based on results obtained on the entire batch.

3.3.1 Stability and Homogeneity

The stability of the lot is assumed if the concentration in each CRM cylinder included in the first analysis has not changed appreciably at the time of its second analysis (see appendix A). An inspection of the data of the first and second analyses may reveal gross instability, and, if such is found, the lot should be discarded and remade.

In a lot consisting of cylinders prepared by transfer of a single bulk mixture to a number of smaller containers, the composition of the gas in all the smaller cylinders should be identical. Differences observed among cylinders should reflect only the random error in the analytical process. Differences greater than this random error arise from two sources. First, there are the differences that result from faulty mixing or from dilution by residual gases left in the cylinder prior to transfer of the bulk mixture. The second and more critical source arises from reactions, chemical or physical, that occur in the cylinder after transfer. Because these reactions are largely due to wall effects and because no two cylinder walls are alike, the reactions generally proceed at different rates in different cylinders. The two effects may be differentiated by sets of measurements made over a period of time sufficiently long so that the extent of reaction is greater than the error in the analysis. For instance, if a lot is analyzed immediately after preparation and individual samples are found to have concentrations that vary more than can be accounted for statistically by the analytical imprecision, then the mixture is either inhomogeneous or some or all samples in the lot are unstable. If the lot is reanalyzed after some time and each sample has retained essentially its previous value, then the samples are probably stable, but the lot is inhomogeneous. If the concentration of one or more of the samples has changed significantly, then it is plausible to conclude that the lot is unstable.

An inhomogeneous lot need not necessarily be discarded, but an unstable lot <u>must</u> be discarded. An inhomogeneous but stable lot in which the range of values does not exceed 1 percent of the value of the SRM with which it is to be compared may be used, providing that the reason for the inhomogeneity is determined and that the cause does not otherwise affect the integrity of the CRM. If the bulk container consists of several large cylinders ganged together to allow simultaneous delivery, then some inhomogeneity may arise if the concentrations in the several bulk containers differ slightly. In the special case of large scale dynamic dilution systems where two components are mixed under constant flow conditions and are then compressed into the cylinders in the lot, some inhomogeneity may result, depending on the design of the delivery system. If variations in concentration are observed in a lot prepared by this method, the variation may be related to the position of individual cylinders on the manifold, and it is therefore <u>important</u> to record the <u>manifold</u> position of each cylinder for possible future reference.

It should be reemphasized at this point that <u>all</u> samples in a batch which is not entirely homogeneous should be analyzed both during the first and second analysis. It is essential in cases where the samples are stable but not entirely identical in terms of concentration, that each sample should be certified separately.

The nature of the distribution of the concentration of samples in a lot may give significant information concerning both the inhomogeneity and stability of the lot. A lot which has concentrations that vary no more than can be accounted for by the error of the analytical method, is probably homogeneous and stable. A lot in which the range of values exceeds significantly what might be expected on the basis of analytical error and in which several samples are considerably below the average, probably is unstable. A lot in which the range of values is large but all concentrations are essentially symmetrically distributed around the average, was probably not prepared or transferred in such a way that homogeneity was assured. A lot may be found with concentrations grouped around two or more average values (bimodal or multimodal distributions). This usually results from errors in the gas blending or transfer operations. It should be noted, however, that the detection of such situations is, except for very large number of cylinders, statistically very uncertain. Occasionally, a single sample in a lot will be found with a concentration appreciably below the average for the lot. A single such sample probably represents a fault in the preparation or filling of the cylinder and may be omitted from the lot, providing the lot is otherwise stable and homogeneous. The presence of more than one outlier in a lot or the occurrence of a single outlier in several lots should be cause for concern, and, in the absence of a reasonable explanation for the multiple outliers, the lots should be remade.

All of the evidence at this point must support the assumption that the lot is stable, reasonably homogeneous, and that it meets all other requirements for a CRM. If there is any suspicion that the lot may be unstable or excessively inhomogeneous, then further analytical work should be conducted before a final decision is made.

3.3.2 Estimation of the Uncertainty of the CRM

The estimated uncertainty of the CRM is composed of at least three components: (1) the uncertainty of the SRM with which the CRM is analyzed; (2) the imprecision of analysis of the internal standard with the SRM; and (3) the imprecision of analysis of the CRM's with the internal standard. A discussion of the statistical procedure for estimating and combining these three sources of error will be found in the appendices. Here we merely mention that the second component is evaluated on the basis of ten or more measurements of the concentration of the internal standard, and that the third component is evaluated from the variability of the results of all samples in the lot. From the combined variability of these three sources, an upper limit for the uncertainty of the concentration can be calculated for each individual CRM sample, for use in the certificate accompanying the CRM.

4. AUDIT OF THE CRM

4.1 Introduction

At this point the producer should have sufficient evidence to make a decision as to whether or not the batch will qualify as a CRM. This decision must be based on the measured stability and homogeneity and on the fact that the measured concentration of any sample in the batch lies within 1 percent relative to the complementary SRM. The evidence for compliance with the requirements for a CRM may be so overwhelming that a visual examination of the data may convince the producer that all is well. However, the final decision must await the results of an independent examination of the data and of an independent analysis of at least some of the samples. This independent analysis will be referred to as the "audit program". Upon its completion, the data of the CRM producer and those resulting from the audit will be intercompared, using appropriate statistical procedures of data analysis which are described in the appendices.

4.2 Environmental Protection Agency Audit Program

The purpose of the Audit Program is to determine whether or not the CRM's in a particular lot are of the concentration claimed by the producer. This will be determined by an analysis of two or more samples from the lot. The analysis will be performed by a laboratory chosen by the Environmental Protection Agency (EPA). Analytical results obtained by the auditor and the CRM producer will be submitted to NIST for evaluation. If the results of the analysis by the auditor confirm the analysis claimed by the producer, the EPA will be so informed by NIST. If the results do not agree, either the auditor or the producer (or perhaps both), will be asked to repeat the analysis. If the additional analysis demonstrates the validity of the producer's value, the EPA will be so informed by NIST. If, however, there is still disagreement, the samples used in the audit will be submitted to NIST for analysis. The auditor may be required to analyze the CRM's for substances other than that for which they are certified, depending on the requirements specified in the appendix concerning the particular substance.

4.2.1 Selection of Samples

The producer will submit a list of samples identified by sample number and cylinder number to the auditor. The auditor will select two samples at random which the producer will then send to the auditor. The producer will inform the auditor of the particular SRM which the CRM is intended to duplicate. This SRM will be identified by SRM number, sample number, cylinder number and date of purchase.

4.2.2 Analysis

The analysis of the CRM will be performed with an instrument whose response characteristics are known at the concentration of the CRM. The auditor will calibrate the instrument using SRM's, one of which must be of the same nominal concentration as the CRM. The number of other SRM's used in the calibration will depend on the characteristics of the instrument but should include at least two others. The auditor must be able to demonstrate the validity of the calibration of the instrument in the concentration range between the SRM and CRM.

Each sample will be analyzed ten times with the calibrated instrument. The procedure and sequence of analyses will be planned by the auditor and should be such that a high degree of precision is obtained.

The average concentration for each sample and the standard deviation are to be reported. In general, the precision of the methods used in the analysis of gas mixtures of a type represented by the CRM should yield standard deviations which do not exceed 0.5 percent relative. If this value is exceeded, then the procedure should be carefully examined for sources of imprecision and the analyses should be repeated. In calculating the average and the standard deviation of the ten measurements for each sample, it is not permissible to omit or change any values (possible "outliers") except where experimental conditions were known to be inappropriate during the measuring process.

4.2.3 Report of Results

Both the producer and the auditor will submit a comprehensive report of their respective analyses to NIST. Each individual analysis result for each of the samples analyzed should be reported. The producer will also report the SRM's, identified by SRM number, sample number, cylinder number, concentration, and purchase date, which were used in the calibration of the instrument. A brief description of the method, the calibration procedure and the measured instrument sensitivities at the calibration points will also be submitted.

The auditor will submit the individual result of each analysis on each of the two samples, with information concerning the SRM's used, the instrument employed, the calibration procedure, and any other analytical results obtained as may be required for the particular mixture.

The report may be made on the forms shown in the appendices, or by a letter containing the same information.

4.3 Examination of Results

The analytical data submitted by the producer will be examined by NIST to assess the homogeneity and stability of the batch. The results reported by the auditor will be used to confirm or reject the concentration claimed by the producer. It is assumed that an unstable lot would be readily evident to the producer and would not have been retained for processing as CRM's. It is further assumed that an inhomogeneous lot would be recognized and would not be retained except in the very special case where the reason for the inhomogeneity was known and where the stability was unequivocally demonstrated. Such batches will be individually considered and further analyses may be requested of the producer.

4.4 Certification

If the particular batch of CRM's is reasonably homogeneous and definitely stable, and if there is no significant difference between the concentration claimed by the producer and that found by the auditor, both the EPA and the producer will be notified by NIST. The producer may then certify the samples in that particular batch as having met the requirements of a Certified Reference Material that has traceability to the respective SRM.

To assure the purchaser of a CRM that it has been prepared according to the procedures described herein, and that the results of the EPA audit and the NIST analysis of the analytical data confirm the producer's concentration within acceptable limits, the producer will supply the purchaser with the following:

1. A copy of the letter from NIST to EPA and to the producer stating the particular lot meets the requirements for CRM's. The NIST letter will list each cylinder in the lot, identified by cylinder and sample

number, and will show the producer's value for the concentration of each sample in the lot. In addition, the letter will identify the samples audited by EPA and will give the concentration determined by the audit.

2. A producer's "Certificate of Analysis" will include, as a minimum, the cylinder and the sample number, the concentration for the particular sample, and the uncertainty assigned to that concentration. In addition, the period of certification and the date of the beginning of the period will be given.* Finally, the certificate will identify the SRM used by the producer to establish traceability of the CRM to that NIST SRM.

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*The date of the beginning of the period of certification normally is the date of the NIST letter to EPA and to the producer. However, the producer may elect to follow the procedure given in appendix G for date-of-sale certification. If appendix G is strictly followed, the date of the beginning of the period of certification is the date of sale of the CRM by the producer to a purchaser of the CRM.

ACKNOWLEDGMENTS

Special acknowledgment is made to Ernest E. Hughes, the principal scientist responsible for the development of the NIST gas SRM program, who led the development and approval of the May 1981 document, and who recently passed away. It is to his outstanding technical efforts that this revised document is dedicated.

Appreciation is given to Robert Wright of Research Triangle Institute and to Darryl J. von Lehmden of EPA for their thorough review of this revised document.

Acknowledgment also is made to Robert Wright who has conducted the analytical audits for EPA for the certification of CRM's since the initiation of the CRM traceability program in 1981.

APPENDIX A

Statistical Analysis of Data

I. Introduction

The data submitted to NIST by the producer and the auditor will be examined in detail to determine that the candidate lot of CRM's is of the concentration claimed and that the lot is stable and homogenous. The statistical treatment is illustrated in this appendix by means of an example based, for the most part, on real experimental data. However, it was necessary to synthesize some data, particularly in describing the auditor results, to produce an example illustrative of the whole process. It should be noted that this example does not define the degree of measurement precision required of a CRM, and, in many cases, the precision shown may not necessarily be attainable, due to such factors as instrument sensitivity and the chemical and physical properties of the gases involved.

II. Illustrative Example and Statistical Analysis

1. Producer's Calibration Data:

The producer provided the following data on the calibration of his instrument:

Table 1

SRM No.	Concentration*	Signal or Sensitivity
1677	9.67 ± .09 ppm	11.51 mV (signal)
1678	44.9 ± .5 ppm	54.10 mV (signal)
1679	97.1 ± .9 ppm	114.86 mV (signal)

*The ± values are the total uncertainties given in the SRM certificates.

A linear regression of signal vs. concentration provides the equation:

$$\text{signal} = .464 + 1.181\ (\text{concentration})$$

The fit to the straight line is good, and is only minimally affected by making the intercept zero. This leads to the modified equation:

$$\text{signal} = 1.187\ (\text{concentration})$$

The fit provided by this equation is shown in the following table where the fitted values in the last column should be compared with the observed values of signal:

Table 2

Signal	
Observed	Fitted
11.51	11.48
54.10	53.30
114.86	115.26

We conclude that the instrument gives essentially a linear response and is in good state of calibration. However, since the samples to be analyzed have a concentration close to that of SRM 1678 (about 45 ppm), a sensitivity value can be adopted that is based on a calibration line going through the origin and through the point whose abscissa is the certified value of SRM 1678 and whose ordinate is the measured value for this SRM. This gives the calibration equation which will be used for all further analyses:

$$\text{signal} = 1.205\ (\text{concentration})$$

2. Analysis of Internal Reference Standard

One of the cylinders was randomly selected as the lot "Internal Reference Standard." The measurements,* in mV are shown in the second column of Table 3. The third column shows the concentration values, in ppm, obtained by using the sensitivity 1.205 mV/ppm for the conversion.

The average concentration for the Internal Reference Standard is:

$$\bar{x} = 44.6139 \text{ ppm}$$

with a standard deviation among single replicate measurements of

$$s_x = 0.018 \text{ ppm}$$

The standard error of the average value for this cylinder is:

$$s_{\bar{x}} = \frac{0.018}{\sqrt{10}} = 0.0057 \text{ ppm}$$

Table 3

Measurement No.	Signal (mV)	Concentration (ppm)	Measurement No.	Signal (mV)	Concentration (ppm)
1	53.7623	44.616	6	53.7683	44.621
2	53.7382	44.596	7	53.7454	44.602
3	53.7454	44.602	8	53.7237	44.584
4	53.7948	44.643	9	53.7707	44.623
5	53.7719	44.627	10	53.7767	44.628

*Note: It is not required that either producer or auditor provide the actual measured value of the signal. However, the value of the concentration calculated from the signal should be expressed with sufficient digits to reflect the magnitude of the signal. In other words, don't round off the calculated concentration when submitting the data for evaluation.

3. Analysis of All Samples

The Internal Reference Standard is now used by the producer to analyze all the cylinders in the lot. This is generally accomplished by measuring the ratio of the signal for the sample to that for the internal standard. Table 4 shows the signal ratios, denoted as R, and the corresponding calculated concentrations, denoted as C, using the value 44.6139 ppm for the internal standard. Thus, each concentration is obtained by the equation:

$$C = R\ (44.6139)$$

where

$$R = \frac{\text{signal for sample}}{\text{signal for internal standard}}$$

The last column of Table 4 is used for two purposes: a) to obtain an additional estimate of the standard deviation among replicates, and b) to test whether a significant systematic shift has occurred between the two sets ("first analysis" and "second analysis"). The estimate of the standard deviation, converted to a single measurement basis is 0.021 and is consistent with that obtained previously (s = 0.018) [see section 2, preceding]. As to a possible shift, there is no evidence for such an occurrence. A test of significance can be carried out as follows:

$$t = \frac{-0.0048}{0.030/\sqrt{10}} = -.50$$

This value is not significant, when compared with the critical value of Student's t, for 10-1 = 9 degrees of freedom.

The standard deviations, 0.021 and 0.022, for the two sets of values in Table 4 are mutually consistent. Moreover, since they are of the same order of magnitude as the measurement error (as derived from replicate measurements on the same sample), it may be concluded that no measurable heterogeneity exists between the cylinders of this lot.

Table 4

	First Analysis		Second Analysis		Calculated Concentration Difference Between Duplicates
Sample	R	C	R	C	
5	1.000177	44.622	0.999601	44.596	0.026
6			1.000592	44.592	
11			1.000592	44.640	
13	1.000102	44.618	1.000406	44.632	-0.014
15			1.000392	44.631	
21			0.999482	44.591	
23	1.000904	44.654	0.999807	44.605	0.049
29			1.000438	44.633	
30			1.000368	44.630	
31	0.999906	44.610	1.000353	44.630	-0.020
33	0.999350	44.585	1.000307	44.628	-0.043
34	0.999520	44.592	1.000050	44.616	-0.024
35			1.000480	44.635	
39	0.999563	44.594	1.000210	44.623	-0.029
45	0.999514	44.592	1.000050	44.616	-0.024
46			0.999415	44.588	
48			0.999168	44.577	
49			0.999800	44.605	
50	0.999881	44.609	0.999304	44.583	0.026
51			0.999060	44.572	
52	0.999452	44.589	0.999321	44.584	0.005
Average		44.6065		44.6099	-0.0048
Std. dev.		0.021		0.022	0.030*

*Since the numbers in this column are differences of two measurements, the standard deviation found for this column is $\sqrt{2}$ times that for single measurements. Consequently, the standard deviation for single measurements derived from the differences is $(0.030)/\sqrt{2} = 0.021$. This values does not include possible variability between samples.

The best average value for the concentration of the lot is:

$$\frac{(44.6065 \times 10) + (44.6099 \times 21)}{10 + 21} = 44.6088$$

The standard error of this overall average is:

$$\frac{0.022}{\sqrt{31}} = 0.0040$$

This standard error does not include calibration error, or errors in the value of the SRM and in the value of internal reference standard.

4. Auditor's Calibration Data

Table 5 shows the auditor's calibration results.

Table 5

SRM No.	Concentration*	Signal (counts)
1677	9.79 ± .09	19,688
1678	45.3 ± .5	91,642
1679	97.1 ± .8	197,990
1680	476. ± .4	979,130

*The ± values are the total uncertainties given in the SRM certificates.

The sensitivities (signal/concentration) are successively:

2011, 2023, 2039, and 2057 counts/ppm.

These values indicate a trend due, either to the presence of a blank or to curvature, or to both.

A regression analysis shows a slight amount of curvature, but otherwise the calibration data appear satisfactory. Since the samples are of the order of magnitude of SRM 1678, the latter will be used for conversion of signal to concentration, through the equation:

signal = 2023 (concentration).

5. Auditor's Sample Measurements

The auditor made 10 replicate analysis on each of two cylinders, no. 48 and no. 29. The results are shown in Table 6.

Table 6

Cylinder 48		Cylinder 29	
Signal	Concentration	Signal	Concentration
89866	44.422	89781	44.380
90044	44.510	90121	44.548
89495	44.239	89874	44.426
89570	44.276	90050	44.270
90024	44.500	89558	44.270
89997	44.487	89874	44.426
89568	44.275	90226	44.600
89708	44.344	89888	44.433
89742	44.361	89987	44.482
89852	44.415	89655	44.318
Average	44.3829		44.4396
Std. dev.	0.099		0.101

6. Evaluation of Uncertainties and Intercomparison of Results

a. Internal Comparison of Auditor's Results

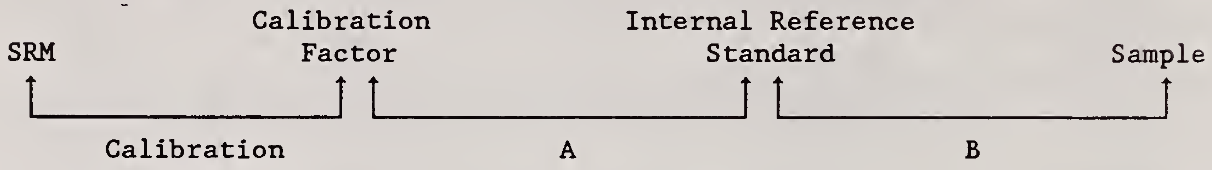
The standard deviation of a single measurement made by the auditor is 0.10. The results for cylinders 48 and 29 may be compared by Student's *t*-test:

$$t = \frac{44.3829 - 44.4396}{0.100\sqrt{\frac{1}{10} + \frac{1}{10}}} = -1.27$$

The t-value is not significant. There is, therefore, no evidence of heterogeneity between the two cylinders.

b. Total Uncertainty of Producer's Values

The value of each sample obtained by the producer is obtained by a procedure represented by the following diagram:



The total error in the sample value is composed of four parts:

1) the uncertainty in the SRM value
2) the uncertainty in the calibration experiment
3) the uncertainty due to comparison A
4) the uncertainty due to comparison B

We use the rule (derived from the law of propagation of errors) that the square of the relative error of the final value is equal to the sum of the squares of the relative errors of the components.

More specifically, if $\hat{c}_i$ is the final concentration value obtained for a particular sample (denoted by the subscript i) in the lot, we have (from step B):

$$\hat{c}_i = R_i \, C_{Ref} \tag{1}$$

where R_i is the ratio of signals for sample i to the reference sample, and C_{Ref} is the concentration attached to the reference sample. But C_{Ref} is obtained in step A by averaging ten values obtained each as

$$\frac{\text{Signal}}{k} \tag{2}$$

where k is the calibration value derived from the calibration experiment. In our case, $k = 1.205$. The average of the ten measurements may be described by

$$C_{Ref} = \frac{\overline{S}}{k} \tag{3}$$

where $\overline{S}$ is the average of ten replicate signal values. Combining (1) and (3) gives

$$\hat{c}_i = R_i \frac{\bar{S}}{k} \tag{4}$$

The value of k is obtained experimentally from a single signal value divided by the concentration of the SRM. Thus we may write:

$$k = \frac{S_o}{C_o} \tag{5}$$

where C_o is the concentration attached to the SRM by the SRM certificate and S_o is the signal corresponding to it.

Combining (4) and (5), we obtain finally:

$$\hat{c}_i = R_i \bar{S} \frac{C_o}{S_o} \tag{6}$$

The law of propagation of errors gives:

$$\left(\frac{{}^{\sigma}\hat{c}_i}{\hat{c}_i}\right)^2 = \left(\frac{{}^{\sigma}R_i}{R_i}\right)^2 + \left(\frac{{}^{\sigma}\bar{S}}{\bar{S}}\right)^2 + \left(\frac{\sigma S_o}{S_o}\right)^2 + \left(\frac{{}^{\sigma}C_o}{C_o}\right)^2 \tag{7}$$

The first term of the <u>right</u> side represents step B; the second term, step A; and the third term the uncertainty of the calibration experiment itself. The last term represents the uncertainty of the SRM used for calibration.

We now estimate these four components.

1) $\frac{{}^{\sigma}R_i}{R_i}$ (step B) is obtained from the last column of Table 4:

$$\frac{{}^{\sigma}R_i}{R_i} = \frac{0.021}{44.61} = 4.71 \times 10^{-4} \tag{8}$$

2) $\frac{\sigma_{\bar{S}}}{\bar{S}}$ (step A) is obtained from the calculations derived from Table 3:

$$\frac{\sigma_{\bar{S}}}{\bar{S}} = \frac{0.0057}{44.62} = 1.28 \times 10^{-4} \tag{9}$$

3) $\frac{\sigma S_o}{S_o}$ (calibration experiment) has not been measured, but we can assume the same precision as in step A for a single measurement:

$$\frac{\sigma S_o}{S_o} = \frac{0.018}{44.62} = 4.03 \times 10^{-4} \qquad (10)$$

4) $\frac{\sigma C_o}{C_o}$ (uncertainty of SRM) is derived from the uncertainty stated in the SRM certificate. This stated uncertainty is equal to two standard deviations. Thus:

$$\frac{\sigma C_o}{C_o} = \frac{1}{2}\,\frac{0.5}{44.9} = 55.68 \times 10^{-4} \qquad (11)$$

Adding the squares we have:

$$\left(\frac{\sigma \hat{c}_i}{\hat{c}_i}\right)^2 = \left[\ (4.71)^2 + (1.28)^2 + (4.03)^2 + (55.68)^2\ \right] \times 10^{-8}$$

$$= 3140 \times 10^{-8}$$

Hence:

$$\sigma \hat{c}_i/\hat{c}_i = \pm 56 \times 10^{-4}$$

Since all $\hat{c}_i$ values are approximately the same and equal to

$\hat{c}_i$ = 44.62 ppm, we obtain

$$\sigma \hat{c}_i = 56 \times 10^{-4} \times 44.62 = \pm 0.25 \text{ ppm} \qquad (12)$$

We see that the predominant component of uncertainty, in this case, is that of the SRM.

c. Comparison of Producer's and Auditor's Values

By a calculation similar to that above, we obtain, for the auditor's value for a particular cylinder, say c_i^*:

$$\left(\frac{\sigma c_i^*}{c_i^*}\right)^2 = \left(\frac{\sigma_{\overline{ct}}}{\overline{ct}}\right)^2 + \left(\frac{\sigma_{ct}}{ct}\right)^2 + \left(\frac{\sigma C_o^*}{C_o^*}\right)^2 \qquad (13)$$

Step A is not present for the auditor's data. The symbol ct represents a count, and ct an average of ten counts; C_o^* represents the value given by the certificate for the SRM used in the calculation of the calibration factor. We have:

$$\left(\frac{{}^{\sigma}c_i^*}{c_i^*}\right)^2 = \left(\frac{0.10/\sqrt{10}}{44.4}\right)^2 + \left(\frac{0.10}{44.4}\right)^2 + \left(\frac{0.25}{45.3}\right)^2$$

$$= (7.12\text{x}10^{-4})^2 + (22.52\text{x}10^{-4})^2 + (55.19\text{x}10^{-4})^2$$

$$= 3604\text{x}10^{-8} = (60\text{x}10^{-4})^2 .$$

Since c_i^* = 44.4 ppm for both samples analyzed by the auditor, we have:

$$^{\sigma}c_i^* = 60\text{x}10^{-4}\text{x}44.4 = \pm 0.27 \text{ ppm}$$

We now obtain the following summary results (Table 7):

Table 7*

	Sample 48	Sample 29
Producer	44.58 ± .25	44.63 ± .25
Auditor	44.38 ± .27	44.44 ± .27

*The ± values represent standard errors in this table.

It is apparent that the result obtained by the auditor for each sample is not significantly different from that of the producer for the same sample. Thus, the auditor's values in this case, substantiate those provided by the producer.

In general, it may be assumed that there is no significant difference between the concentration claimed by the producer and that found by the auditor if the following expression is satisfied:

$$\left| c_i - c_i^* \right| \leq 2 \sqrt{{}^{\sigma}c_i^2 + {}^{\sigma}c_i^{*2}}$$

APPENDIX B

Report Forms

The following forms, A and B, are suggested report forms which will be made available to both the producer and the auditor.

FORM A. Report of Analysis of Certified Reference Materials

(Producer)

Prepared by: (Company name & address)

(Individual preparing report
& date)

Description:

Composition:

Corresponding SRM No.:

Date Blended:

Date Transferred:

Analysis

SRM's Used as Calibrants:

	No.	Sample No.	Cylinder No.	Concentration	Purchase Date
1.					
2.					
3.					
4.					
5.					

FORM A (Continued)

Brief Description of Methods:

Brief Description of Calibration Procedure:

Calibration Data:

	SRM No.	Signal or Sensitivity (Identify)
1.		
2.		
3.		
4.		
5.		

Results

Analysis of Internal Standard (if used)

Sample No. Cylinder No.

	Concentration	Date of Analysis
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		

Average ________ s.d. ______________

FORM A (Continued)

Analysis of CRM's

Sample No.	Cylinder No.	Concentration on Date Shown

Average ________ Std. Dev. ______________

FORM B. Report of Analysis of Certified Reference Materials

(Auditor)

Prepared by:

Description:

Analysis:

SRM's Used as Calibrants:

	No.	Sample No.	Cylinder No.	Concentration	Purchase Date
1.					
2.					
3.					
4.					
5.					

Brief Description of Method:

Brief Description of Calibration Procedure:

Calibration Data:

	SRM No.	Signal or Sensitivity (Identify)
1.		
2.		
3.		
4.		
5.		

FORM B (Continued)

Analysis of CRM

Sample No. Cylinder No.	Concentration	Sample No. Cylinder No.	Concentration
	Average ________		Average ________
	Std. Dev. ________		Std. Dev. ________

APPENDIX C

Carbon Monoxide

a. The Available SRM's are as Follows:

CO in N_2

SRM No.	Nominal Concentration
1677	10 ppm
2635	25 ppm
1678	50 ppm
1679	100 ppm
2636	250 ppm
1680	500 ppm
1681	1000 ppm
2637	2500 ppm
2638	5000 ppm
2639	1 %
2640	2 %
2641	4 %
2642	8 %

CO in Air

SRM No.	Nominal Concentration
2612	10 ppm
2613	18 ppm
2616	42 ppm

The concentrations shown are in parts per million (ppm) by mole and in mole percent. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of the CRM.

The maximum permissible levels of impurities in the CRM are as follows:

Water Vapor	10 ppm	
Methane	1 ppm	(CO in N_2)
Methane	5 ppm	(CO in air)
Carbon Dioxide	5 ppm	(CO in N_2)
Carbon Dioxide	400 ppm	(CO in air)

b. Cylinders

CRM's must be packaged in new aluminum cylinders or in used aluminum cylinders that have been used exclusively for mixtures containing carbon monoxide in nitrogen or air. The history of any cylinder to be reused must be known and confirmation must be obtained by analysis that the contents have not been diluted or contaminated. Cylinders to be reused must contain sufficient gas from the last filling to allow an analysis. The concentration must lie within ±1 percent relative of the original analysis. The cylinder must be evacuated before refilling and the concentration of the CRM to be added must lie within 2 orders of magnitude (±100% relative) of the concentration of the CRM previously contained.

c. Preparation of Analysis

Prepare a lot of at least 10 cylinders all at identical concentration. The concentration of carbon monoxide must lie within ±1 percent relative of the certified concentration of the specific SRM cylinder with which the lot is to be compared. Analyze a representative number of cylinders by direct comparison to the SRM or by comparing cylinders in the lot to a single sample selected at random from the lot (internal standard from the lot). Analyze each sample at least two times. Calculate the average of all results for all samples and calculate the standard deviation of the average.

The lot should be put aside to "incubate" for at least one month after which time all samples in the lot are analyzed. The results for the first and second analyses should be statistically identical. If the two analyses are the same, then it may be assumed that the lot is homogeneous and stable. If the analyses were performed by direct comparison to the SRM, then the analytical value for the sample will be the certified value. If the analyses were performed by comparison to an internal standard for the lot, then it will be necessary to determine the concentration of the internal standard. This is done by repeated comparison of the internal standard to the SRM. The concentration measured for the internal standard is then multiplied by the measured ratio of each sample.

The uncertainty of the CRM is composed of the uncertainty of the SRM and any random errors introduced by the analysis of the CRM. The error of the SRM, E_{SRM}, is given on the certificate for the particular SRM cylinder and is defined as the estimated upper limit of the total uncertainty. The estimated upper limit of the uncertainty for the CRM should be calculated as follows:

$$E_2 \text{ (Total Error)} = 2 \sqrt{\left(\frac{E_{SRM}}{2}\right)^2 + a^2 + b^2 + c^2}$$

where E_2 is the uncertainty of the CRM; a is the imprecision of intercomparison of the internal standard with the lot; b is the imprecision of intercomparison of the internal standard and the SRM; and c is the error of the calibration experiment if applicable (see appendix A).

The following table lists the methods of analysis that are applicable to the analysis of CRM's of carbon monoxide in nitrogen or air. The method chosen is not necessarily limited to those shown providing that the method chosen is of adequate sensitivity, precision and linearity. The precision and sensitivity are evaluated during the analysis described earlier and are reflected directly in the imprecision of intercomparison. The linearity must be defined in the concentration range between the CRM and the SRM.

Table 1. Methods for the Intercomparison of CRM's and SRM's of Carbon Monoxide in Air or Nitrogen

Method	Concentration of CO
Gas Chromatography - TC Detector	8% - 0.5%
Gas Chromatography - Ultrasonic Detector	1% - 0.05%
Gas Chromatography Followed by Catalytic Reduction to Methane with Flame Ionization Detection	1% - 10 ppm
Non-dispersive Infrared	8% - 10 ppm

d. Period of Certification

Experience at NIST indicates that carbon monoxide mixture contained in aluminum cylinders are stable for periods of three years or more. If no change in concentration of the CRM's is indicated by the results of the producer's first and second analysis, then stability for a period of at least two years from the date of the second analysis is assured with a high degree of probability.

e. Recertification (see appendix G for further details)

CRM's of carbon monoxide in nitrogen or air that have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 MPa).

2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.

3. The concentration of the internal standard, determined by comparison to the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.

4. The concentration of the SRM must be known either by comparison with a new SRM or the original SRM must have been recently recertified by NIST.

5. If either the original SRM or the internal standard no longer exists, then no recertification can be made.

6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.

APPENDIX D

Nitric Oxide in Nitrogen

a. The Available SRM's are as Follows:

SRM Number	Nominal Concentration of NO ppm (molar)
2627	5
2678	10
2629	20
1683	50
1684	100
1685	250
1686	500
1687	1000
2630	1500
2631	3000

The concentrations shown are in parts per million (ppm) by mole. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of the CRM.

The maximum permissible levels of impurities in the CRM are as follows:

Water vapor	5 ppm
Nitrogen dioxide	<1% of the NO concentration

b. Cylinders

Nitric oxide mixtures will remain stable in aluminum cylinders which have been treated to assure stability. The treatment must be such that the sample remains stable with regard to adsorption, absorption, and desorption. Because many methods are available to achieve stability, the choice of method is left to the producer of the CRM, and confirmation that stability has been achieved will be based on the observed homogeneity of the batch and on the stability analysis.

Aluminum cylinders that previously contained mixtures of nitric oxide in nitrogen, either CRM's or other mixtures, may be reused. It is recommended that if such cylinders are reused, the concentration of the new mixtures be within one order of magnitude of the previously contained mixture (within 0.1 to 10 times). The history of any reused cylinder must be known, and cylinders in which mixtures of nitric oxide were observed not to be stable must not be used for CRM's. Cylinders to be reused must have a residual pressure greater than one atmosphere of the mixture of nitric oxide in nitrogen before preparation for use with a CRM's.

c. Preparation and Analysis*

Prepare a lot of at least 10 cylinders of identical concentration. The concentration of nitric oxide must lie within ±1 percent relative of the concentration of the specific SRM with which the lot is to be compared. Analyze at least 10 samples from the batch if the batch contains more than 20 samples. All samples should be analyzed in batches of 20 or less. Analyze the internal standard from the lot by comparison to the appropriate SRM's. Analyze each sample at least two times. Calculate the average for the samples analyzed and calculate the standard deviation of the average using,

$$\bar{s}_1 = \sqrt{\frac{\Sigma d^2}{N_1 - 1}}$$

where d is the difference between a sample and the mean, and N_1 is the number of measurements, or the number of samples times the number of measurements per sample.

The lot should be put aside to "incubate" for at least two months (60 days) after which time all samples in the lot are analyzed. The internal standard should be reanalyzed at this time using the same SRM's for comparison as were used in the first analysis. The results for the first and second analyses should be statistically identical (see appendix A). If the two analyses are the same, then it may be assumed that the lot is homogeneous and stable. If the analyses were performed by direct comparison to the SRM, then the analytical value for the sample will be the certified value. If the analyses were performed by comparison to an internal standard from the lot then it will be necessary to determine the concentration of the internal standard. This is done by repeated comparison of the internal standard to the SRM. The concentration measured for the internal standard is then multiplied by the measured ratio of each sample to the internal standard to obtain the concentration of each sample.

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*The reader should be familiar with the procedures of analysis given in the body of this document, particularly Section 3, "Suggested Analytical Procedure" and appendix A, "Statistical Analysis of Data".

The uncertainty of an individual CRM must include the error of the SRM and the added uncertainty due to the imprecision of the intercomparison.

The error of the SRM, E_{SRM}, is given on the certificate for the particular SRM cylinder and is defined as the estimated upper limit of the total uncertainty. The estimated upper limit of the uncertainty for the CRM should be calculated as follows:

$$E_2 \text{(Total Error)} = 2 \sqrt{\left(\frac{E_{SRM}}{2}\right)^2 + a^2 + b^2 + c^2}$$

where E_2 is the total uncertainty of the CRM; a is the imprecision of the intercomparison of the internal standard with the lot; b is the imprecision of the intercomparison of the internal standard and the SRM; and c is the calibration error.

The recommended method of analysis for nitric oxide in nitrogen is chemiluminescence. The instrument used must have adequate sensitivity and precision in the concentration range represented by the SRM which the CRM is duplicating and as many other SRM's at other concentrations which are necessary to define the response curve of the instrument. A zero gas may be used as one calibration point when the lower concentration SRM's (2627 and 2628) are being prepared.

Some general considerations concerning calibration are given in the main body of this document. These considerations apply to the calibration of most gas analysis instruments and may be directly applicable to the calibration of instruments for the analysis of nitric oxide. In any case, it will be the responsibility of the producers of CRM's to assess and document the linearity, stability, and precision of their instruments.

d. Special Considerations

Certain peculiar effects may be observed when analyzing batches of CRM's consisting of nitric oxide in nitrogen by the procedure outlined in the main body of this document. If a number of samples are analyzed by comparison to an internal standard from the batch, the ratio of each sample to the internal standard may be consistently less than 1.00. This effect has been observed for nitric oxide mixtures and for certain other reactive gases. It is probably related to the following: greater amounts of sample are removed from the cylinder chosen as the internal standard than from each other sample in the lot because the internal standard is used at frequent intervals throughout the analysis of the samples. The phenomenon probably results from slight adsorption on the surface of the valve exposed to the sample inside the cylinder. A very slight depletion of the nitric oxide probably occurs in the gas phase in the vicinity of the valve and, because of the small quantity of gas removed during analysis, the observed concentration will be slightly lower than that of the bulk of the mixture remaining in the cylinder.

If such a difference exists it may be obscured by the imprecision of the results, in which case it is compensated for in the final assigned uncertainty. However, if the degree of precision of the intercomparison of the samples with the internal standard is high, the difference may be readily observable. In this case, and if the difference is small (0.1 percent relative or less) compared to an estimated total uncertainty of greater than 1 percent relative, a slight correction should be applied. This can be done simply by multiplying the final concentration of each sample by the reciprocal of the average of the measured ratios for all samples. For instance, if the average of the measured ratios is 0.9995, multiply the concentration of each sample by 1.0005.

If the precision of measurement of the ratios in high and the average of all ratios is significantly less than 1.000, some further work will be necessary to fully evaluate the problem. A simple approach is to reanalyze a large number of samples choosing a different sample from the batch as the internal standard. If the large difference is no longer observed then the problem may have been with the first internal standard. If, however, the difference is still evident then it is likely that the valves or perhaps the cylinders are not compatible with the particular gas mixture and the mixture should be remade using more appropriate containers.

e. Impurities

The impurity of greatest concern in nitric oxide mixtures is nitrogen dioxide. Careful preparation of the mixture from analyzed reagents and the exclusion of all oxygen from the system is necessary to maintain the nitrogen dioxide at the low level required (<1 percent relative to the NO content of the sample). This quantity of nitrogen dioxide can be measured with most chemiluminescent analyzers designed to measure, NO, NO_2, or NO_x. The calibration of such instruments to measure 1 percent relative or less of NO_2 in a mixture of NO and nitrogen may be somewhat difficult. In general, however, if the three components, NO, NO_2, and NO_x are measured and if the sum of NO and NO_2 is equal to the NO_x then the instrument is probably functioning adequately. If this is not the case, then the instrument should be serviced and reevaluated.

It is possible to measure nitrogen dioxide in the presence of nitric oxide by chemical means, but the details of such a procedure are complicated and lengthy and will not be included here.

The nitrogen dioxide should be measured during both the first and second analyses to be certain that no positive changes are occurring. Decreases in nitrogen dioxide with time are expected and do not adversely affect the samples. Increase in nitrogen dioxide, however, can only occur if there is a substantial amount of oxygen in the sample, and such a case would be cause for discarding the batch.

It is not necessary to measure the nitrogen dioxide in all samples. If the concentrations of all samples in the batch lie within the required limits and the nitrogen dioxide is found to be less than 1 percent relative to the nitric oxide in ten percent or more of the samples, then it can be assumed that the batch concentration of nitrogen dioxide is within limits.

If a careful measurement is made of the nitrogen dioxide and if it is initially found to be at a low relative concentration, then the probability that any significant amount of oxygen is in the samples is quite low. If the nitrogen dioxide then remains low or disappears the assumption that no oxygen is present is probably valid.

The water content of the diluent nitrogen should be measured before preparing the mixture, and several samples should be analyzed for water content during the initial analysis. If the concentration is the same in the diluent and the samples, it may be assumed that the sample cylinders and the transfer systems were adequately dried before use.

The methods used and the results of analysis for impurities should be reported along with the other required information for each lot of CRM's.

f. Period of Certification

Experience at NIST indicates that nitric oxide mixtures contained in aluminum cylinders generally remain stable for periods of time greater than two years. If no significant changes in the concentration of nitric oxide occurs during the incubation period and if the batch is reasonably homogeneous to begin with, there is a high probability that samples will remain stable for at least two years.

g. Recertification (see appendix G for further details)

CRM's of nitric oxide in nitrogen that have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 MPa).

2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.

3. The concentration of the internal standard, determined by comparison to the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.
4. The concentration of the original SRM must be known either by comparison with a new SRM, or the original SRM must have been recently recertified by NIST.

5. If either the original SRM or the internal standard no longer exists, then no recertification can be made.

6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.

APPENDIX E

Sulfur Dioxide in Nitrogen

a. The Available SRM's are as Follows:

SRM Number	Nominal Concentration of SO_2 ppm (molar)
1693	50
1694	100
1661	500
1662	1000
1663	1500
1664	2500
1696	3500

The concentrations shown are in parts per million (ppm) by mole. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of the CRM.

The maximum permissible levels of impurities in the CRM are as follows:

Water vapor	5 ppm
Sulfur compounds other than SO_2	0.1 ppm

b. Cylinders

Sulfur dioxide mixtures will remain stable in aluminum cylinders that are dry and which have been treated to assure stability. The treatment must be such that the mixture remain stable with regard to adsorption, absorption, and desorption. Because many methods are available to achieve stability, the choice of method is left to the producer of the CRM and confirmation that stability has been achieved will be based on the observed homogeneity of the batch and on the stability.

Aluminum cylinders which previously contained mixtures of sulfur dioxide in nitrogen, either CRM's or other mixtures, may be reused. It is recommended that if reused, the concentration of the new mixtures be within one order of magnitude of the previously contained mixture (within 0.1 to 10 times.) The history of any reused cylinder must be known and cylinders in which mixtures of sulfur dioxide were previously observed not to be stable must not be used for CRM's. Cylinders to be reused must have a residual pressure greater than one atmosphere of the mixture containing sulfur dioxide before preparation for use with a CRM.

c. Analysis-General

Several methods of analysis are applicable to the analysis of mixtures of sulfur dioxide in nitrogen. These include gas chromatography non-dispersive infrared, electrochemical titration, pulse, fluorescence, and flame photometry. Most of these are relative methods requiring calibrating gases. Another method, the "peroxide" method, is an absolute technique requiring no calibrating gases.

Some general considerations concerning calibration are given in the main body of this document. These considerations apply to the calibration of most gas analysis instruments and are directly applicable to the calibration of instruments for the analysis of sulfur dioxide.

The alternative to the relative instrumental methods, the peroxide method, is a wet chemical method. It involves collection of the sulfur dioxide from a mea-sured volume of the sample, in a solution of hydrogen peroxide. The sulfur dioxide is oxidized to sulfuric acid which is subsequently titrated with standard sodium hydroxide solution. The method as described in the literature* is not directly applicable to the analysis of SRM's or CRM's in the concentration range from 50 to 3500 ppm. Consequently, we will describe the method in some detail as adapted for the analysis of SRM's. (See section G, below).

d. Preparation and Analysis of the CRM's

Prepare a lot of at least 10 cylinders of identical concentrations of sulfur dioxide in nitrogen. The concentration must lie within ±1 percent relative of the concentration of the SRM with which the lot is to be compared. Analyze at least 10 samples from the lot if the lot contains more than 20 samples. If the lot contains 20 or fewer samples, it is advisable to analyze all samples. The lot should then be set aside to "incubate" for at least two months (60 days), after which all samples in the lot are analyzed.

If an instrumental method of analysis is used, it will be necessary to analyze the internal standard for the batch using the appropriate SRM's. This analysis should be performed at the time of the first analysis and again at the time of the second analysis. The analysis must confirm that no change in concentration of the internal standard has occurred during this time and the difference between the two values should be no greater than would be predicted from the precision of the method. In such cases, the concentration assigned to the internal standard is the average of the two separate sets of measurements.

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*See for instance the description in "The Analytical Chemistry of Poisons, Hazards, and Solvents", by Morris B. Jacobs, Interscience, 1941, p. 250.

If the peroxide method is used for the analysis, the "true" value will have been directly obtained for each CRM sample. However, it will be necessary to confirm the analyses by also analyzing the appropriate SRM using the peroxide method. The value obtained by analysis using the peroxide method should agree with the value given on the certificate for the SRM. If the difference between these two values is small and is consistent with the expected errors of the analysis, then a correction to the CRM values may be made to align the CRM value with the certified value for the SRM. This assumes that the difference between the two values results from an accumulation of small random errors. If the difference is large, then the source of error must be identified and corrected.

At this point, the producer of the CRM will have completed two analyses and will have assigned a concentration to the CRM's. These data will allow decisions to be made regarding stability and homogeneity, and will indicate whether there is compliance with the concentration requirements for a CRM. Details of the procedures of analysis are to be found in the main body of this document, particularly in section 3, "Suggested Analytical Procedure" and in appendix A, "Statistical Analysis of Data". In addition, the total error of the CRM may be calculated from the various errors generated during the analysis of the CRM. Details of the calculation of the error where instrumental methods are used will be found in appendix A. In the special case of the peroxide method, the error will be calculated as described in section G, paragraph 5 of this Appendix.

e. Period of Certification

Experience at NIST indicates that sulfur dioxide mixtures contained in aluminum cylinders generally remain stable for periods of greater than two years. If no significant changes in the concentration of sulfur dioxide occurs during the incubation period and if the batch is reasonably homogeneous to begin with, there is a high probability that samples will remain stable for at least two years.

f. Recertification (see appendix G for further details)

CRM's of sulfur dioxide in nitrogen which have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 MPa).

2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.

3. The concentration of the internal standard, determined by comparison to the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.

4. The concentration of the SRM must be known either by comparison with a new SRM or the original SRM must have been recently recertified by NIST.

5. If either the original SRM or the internal standard no longer exists, then no recertification can be made.

6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.

7. The concentration determined by the peroxide method must agree with the original value to within the combined limits of uncertainty of the two measurements. The validity of the peroxide method must be confirmed by analysis of the SRM.

g. Analysis - Hydrogen Peroxide Method

The sample is passed through an absorption train as shown in the accompanying figure.

The sample cylinder is equipped with a metering valve, and a three-way valve allows the flow to be set at the appropriate rate using the rotameter before beginning the analysis. The midget impingers contain a hydrogen peroxide solution. The wet-test meter measures the total volume of gas passed through the train.

1. Reagents

   a. Hydrogen Peroxide Solution

   Prepare a 1.5 percent peroxide solution by diluting 50 mL of 30 percent H_2O_2 to 1 liter with distilled water. Using a pH meter, adjust to a pH of 5.5 by adding dropwise 0.1N nitric acid. This reagent is stable at room temperature for one month.

   b. Standard Sulfuric Acid (0.06N)

   Carefully add 5.0 mL of concentrated reagent grade sulfuric acid to 3 liters of distilled water. Standardize against approximately 0.310 g portions of THAM (tris[hydroxymethyl]aminomethane). This solution may be stored indefinitely.

   c. Standard Sodium Hydroxide (0.05N)

   Dissolve approximately 4.1 g of NaOH pellets in 2 liters of freshly boiled distilled water. Pipette 50.0 mL portions of the standardized sulfuric acid into a beaker. Add a stirring bar and, with moderate stirring, titrate with the sodium hydroxide solution to a pH of 7.0. Store this solution in a polyethylene bottle and restandardize it bimonthly.

2. Apparatus

a. Absorbers

Two standard midget impingers are connected in series with short lengths of Teflon tubing.

b. Burettes

Several calibrated burettes will be needed depending on the concentration of the sulfuric dioxide and the volume of the sample. Minimum graduation should be 0.2 percent of the volume titrated.

c. Wet-Test Meter

A 1 liter per revolution wet-test meter is used to measure the volume of sample. The meter must be calibrated with a maximum inaccuracy of 0.25 percent relative. Details of a procedure by which this accuracy may be accomplished will be found at the end of this appendix.

3. Procedure

a. Fill each impinger base with 10 mL of hydrogen peroxide solution.

b. Adjust flow to desired rate using rotameter.

c. Rotate 3-way valve to flush tubing and impinger head.

d. Attach second impinger followed by first impinger.

e. Stop flow when desired volume has passed through train.

f. Quantitatively transfer contents of both impingers to a 100 mL beaker rinsing impinger tube and body with distilled water. Fill beaker to 50 mL level.

g. Titrate solution with standard base to pH 5.5.

h. Determine a reagent blank using 20 mL of peroxide solution.

4. Calculation

At the temperature, pressure, and concentration of the components of the mixture the following may be assumed to be correct.

$$\frac{V_{SO_2}}{V_{SO_2} + V_{N_2}} = \frac{M_{SO_2}}{M_{SO_2} + M_{N_2}}$$

where V is volume and M is moles.

The volumes of both species, SO_2 and N_2, must be expressed at the same conditions of temperature and pressure. The volume of nitrogen measured with the wet test meter, for instance, is corrected to 25 °C and one atmosphere (760 mm or 101.3 KPa). The volume of sulfur dioxide is expressed at the same conditions using the relationship:

$$1 \text{ milliequivalent NaOH} = 12.235\ \mu L\ SO_2$$
$$\text{Volume NaOH (mL)} \times N_{NaOH} \times 12{,}235 = \mu L\ SO_2$$

and

$$\frac{\mu L\ SO_2}{\dfrac{\mu L\ SO_2}{10^6} + L_{N_2}} = \text{conc. in ppm}$$

The following table is included to give some guidance for the selection of sample size, burette size and reagent concentration needed to analyze samples of various concentration. Factors such as the concentration of the alkali and the sample size may be adjusted to accommodate the skill of the operator or the size of burettes available.

Table 1

Concentration of Sulfur Dioxide	Volume of Sample	mL of 0.05N NaOH	Burette Volume (mL)
50 ppm	15 L	1	5
100 ppm	12 L	2	5
500 ppm	15 L	11	50
1000 ppm	6 L	10	50
1500 ppm	3 L	7	50
2500 ppm	3 L	12	50
3500 ppm	3 L	17	50

5. Errors

The peroxide method is essentially an absolute method and the total error should be definable by the random errors of the various elements of the procedure. These sources of random error are as follows:

1. Calibration of wet-test meter.

2. Calibration of burettes.

3. Imprecision of preparation of reagent solutions.

4. Imprecision of titration.

5. Analysis of reagent purity.

In addition to these sources of random error there may be biases, but these biases most likely will be small relative to the random error.

In the absence of blunders, the major sources of error will be the uncertainty of measurement of the sample volume with the wet-test meter and the imprecision of the titration of the absorbed sulfur dioxide. Both of these errors will be combined into the uncertainty of the measured value of the concentration and will be represented by the uncertainty of the average of replicate measurements of single samples. Reliable reagents carefully used to prepare standard solutions and careful standardization will result in very small errors in the chemistry preceding the titration of the absorbed sulfur dioxide.

The magnitude of the random error and the possible existence of biases in the system are evaluated by analysis of an SRM of appropriate sulfur dioxide concentration. The SRM must be analyzed in triplicate, and the average of the results should agree within experimental limits with the value appearing on the certificate for the SRM. The following relationship should be satisfied if the analysis of the SRM by the procedure has been done correctly:

$$|A - B| \leq 2\sqrt{\left[\frac{a}{2}\right]^2 + b^2}$$

where A is the certified value of the SRM with the associated uncertainty, a, (as given on the SRM certificate) and B is the average of the producer's replicate analysis of the SRM with the associated standard deviation, b, of the average of its determination.

If this relationship is not satisfied and the value of b is reasonably small (<0.5 percent relative), then further work will be necessary to discover the source of error. Consultation with the appropriate group at NIST is the logical first step in resolving any conflict at this point.

If the NIST value and the producer's values agree, then it can be assumed that no significant bias exists between the two values and the error of the producer's value can be calculated from the observed random errors of the measurement.

Stepwise, these include the following:

a. The imprecision of standardization of the sulfuric acid based on titration of at least three weighed portions of THAM. This error, represented by the relative standard deviation of the average measured normality of the acid includes both the weighing error and the titration error.

b. The imprecision of standardization of the hydroxide solution represented by the standard deviation of the average of replicate titrations of the base with the acid.

c. The imprecision of measurement of the sulfur dioxide represented by the standard deviation of the replicate measurements of the sample. This uncertainty includes both the titration error and the error associated with the repeatability of the volume measurement.

d. The error in the measured volume represented by the uncertainty in calibration of the wet-test meter.

These errors may be summed as follows:

$$E = \sqrt{a^2 + b^2 + c^2 + d^2}$$

In general, the first two factors, a and b, associated with standardization of solutions should not exceed 0.1 percent relative. The third factor, c, which is the imprecision of measurement of the sulfur dioxide, will depend somewhat on the concentration but should not exceed 0.25 percent relative. The errors in calibration of the wet test meter should be less than 0.25 percent relative. Thus, the total error should be in the vicinity of ±0.5 percent relative, or 1 percent at the 2σ level.

h. Calibration of Wet Test Meter

Minimum uncertainty in a volume measurement using a wet-test meter is obtained when the conditions of the calibration duplicate the conditions of use as nearly as possible. The procedure described here is intended to satisfy that requirement. The method is basically very simple - a weighed quantity of gas is passed through the wet-test meter and the volume indicated by the meter is related to the measured weight of gas. The gas is contained in a cylinder which is weighed. Gas from the cylinder is then passed through the meter and the cylinder is once again weighed. The weight loss of the cylinder represents the mass of gas passed through the meter. This mass can be expressed as a volume if temperature and pressure are known. The only equipment needed other than the wet-test meter is a high-capacity balance capable of weighing to ±0.1 g and a small cylinder equipped with a regulator. The weight of the cylinder filled with gas and equipped with the regulator should not exceed the capacity of the balance.

The cylinder is filled with air and nitrogen to a pressure that will allow the release of at least 200 liters of gas at N.T.P. (normal temperature [25 °C] and pressure [1 atm.]). The regulator is attached and the cylinder is connected to the wet-test meter. The outlet control valve on the regulator is adjusted for the flow rate to be used in the analysis, and the cylinder valve is then shut off without changing the adjustment of either the regulator or the outlet control valve. The cylinder is then weighed and reattached to the system. The zero reading of the wet-test meter is recorded, as is the temperature and barometric pressure. The cylinder valve is opened and about 50 L of gas is allowed to flow through the meter. The cylinder valve is closed and the cylinder is reweighed. This sequence should be repeated at least three times.

Fifty liters of air or nitrogen will weigh somewhat over 50 g, and the weighing error should not exceed about ±0.2 percent relative. The observed weight loss of the cylinder represents the mass of gas passed through the meter. This mass is expressed as a volume of gas, V_g, at the measured temperature and pressure using the ideal gas relationship,

$$V_g = \frac{\frac{g}{M} RT}{P}$$

If the gas from the cylinder is dry and no saturation occurs except in the wet test meter it will be necessary to reduce the volume indicated by the meter, V_m, by a fraction representing the volume increase in the sample due to uptake of water vapor, or more simply:

$$V_g + V_{H_2O} = V_m$$

The water vapor correction (V_{H_2O}) is $V_g \cdot \frac{P_{H_2O}}{P}$, where P_{H_2O} is the saturation pressure of water at the temperature of the wet test meter and P is the barometric pressure and, thus,

$$V_m = V_g \left(1 + \frac{P_{H_2O}}{P} \right)$$

A simpler approach is to saturate the flowing gas between the cylinder and the wet-test meter. In fact, the apparatus used for collection of sulfur dioxide may be used in the calibration of the wet-test meter. The system as shown contains a rotameter to facilitate setting the flow, and the impingers can be used to saturate the gas, eliminating the need for water vapor corrections. In this case, the relationship becomes:

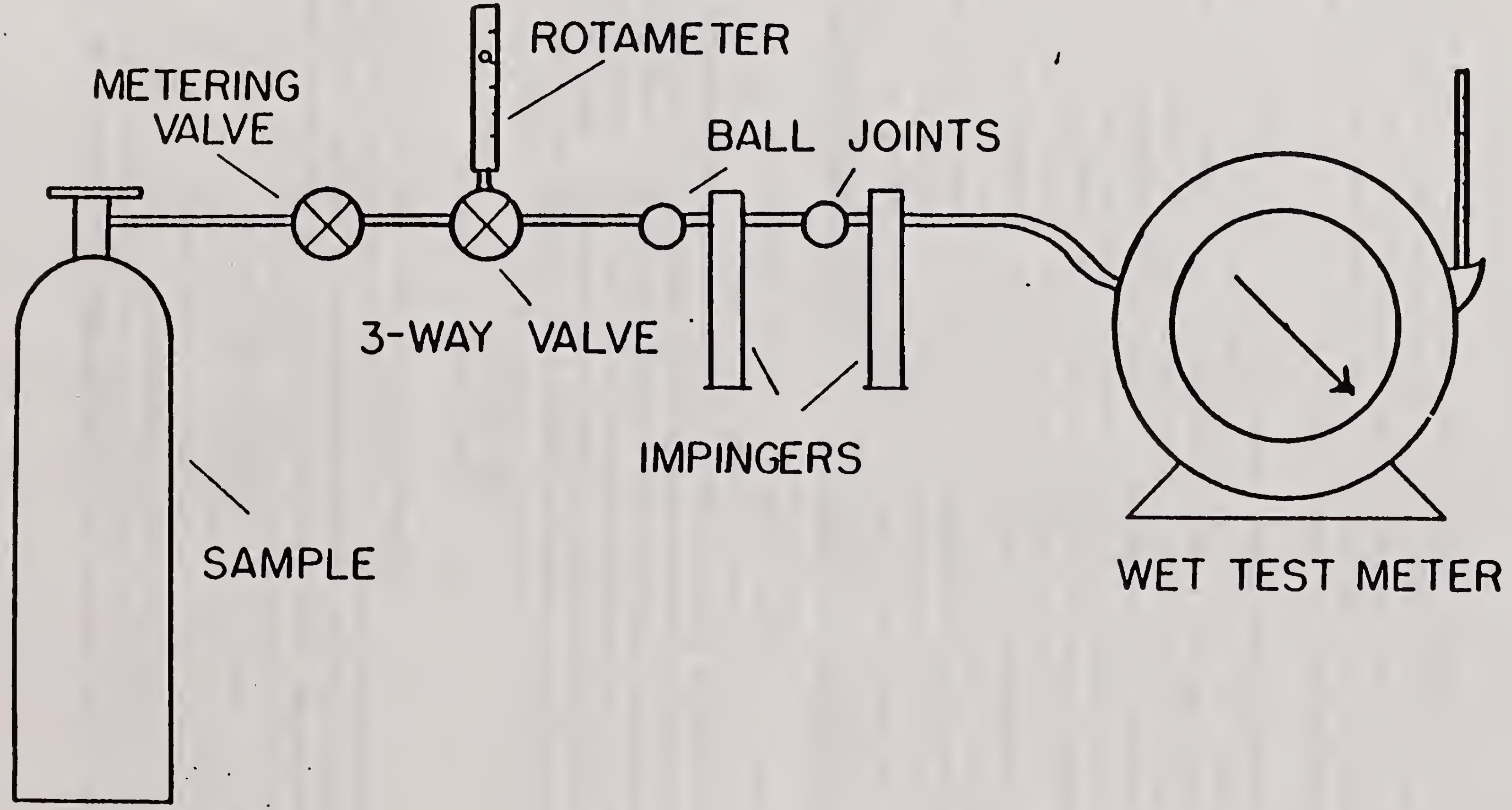
$$V_g = V_m$$

If, however, the meter does not read correctly, a factor, a, should be applied such that

$$a \cdot V_m = V_g \text{ or}$$

$$a \cdot V_m = V_g \quad 1 + \frac{P_{H_2O}}{P}$$

Using this method, and using sufficiently large quantities of gas, it is possible to calibrate a wet-test meter in place under identical conditions to those which will be used in the analysis with an absolute uncertainty not exceeding 0.25 percent relative.



SAMPLING TRAIN FOR PEROXIDE METHOD

APPENDIX F

Propane

a. Introduction

This appendix describes the preparation of Certified Reference Materials (CRM's) consisting of propane in nitrogen or propane in air. The reader should be familiar with the general description of the preparation and analysis of CRM's as described in the main body of this document.

b. Current SRM's

Following is a list of SRM's of propane in either nitrogen or air for which CRM's may be made. The concentrations shown are in parts per million (ppm) by mole and in mole percent. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value, and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of a CRM.

C_3H_8 in Air

SRM No.	Nominal Concentration
1665	3 ppm
1666	10 ppm
1667	50 ppm
1668	100 ppm
1669	500 ppm

C_3H_8 in N_2

SRM No.	Nominal Concentration
2643	100 ppm
2651	100 ppm C_3H_8; 5% O_2
2652	100 ppm C_3H_8; 10% O_2
2644	250 ppm
2645	500 ppm
2646	1000 ppm
2647	2500 ppm
2648	5000 ppm
2649	1%
2650	2%

c. Cylinders

CRM's must be packaged in new aluminum cylinders equipped with valves of appropriate material which conform to CGA recommendations for these particular mixtures. Aluminum cylinders previously used for propane CRM's or which have been used only for propane in air or in nitrogen mixtures may be used for CRM's. The history of a reused cylinder must be known, and, in the case of a CRM cylinder, an analysis must be performed of the gas mixture remaining in the cylinder to assure that the contents have not been diluted or contaminated. The concentration of the remaining gas mixture must lie within ±1 percent relative of the concentration of the original CRM, as previously certified. The cylinder must be evacuated before refilling and the concentration of the new CRM gas mixture must lie within one order of magnitude (within 0.1 to 10 times) of the concentration of the previous CRM or other propane mixtures previously contained.

d. Preparation and Analysis

Prepare a lot of at least 10 cylinders all at identical concentration. The concentration of propane must lie within ±1 percent relative of the concentration of the specific SRM with which the lot is to be compared. Analyze at least 10 samples from the lot, if the lot contains more than 20 samples. If the lot contains fewer than 20 samples, it is recommended that all samples be analyzed. Analyze the samples by direct comparison to the SRM or by comparing samples in the lot to a single sample selected at random from the lot (designated as the "internal standard" of the lot). Analyze each sample at least two times. Analyze for impurities as required in Section E, below.

After this first analysis, the lot should be put aside to "incubate" for at least two months after which time _all_ samples in the lot are analyzed and at which time the impurities are redetermined. If the two sets of analyses are the same, then it may be assumed that the lot is homogeneous and stable. If the analyses were performed by direct comparison to the SRM, then the analytical value for the sample will be the certified value. If the analyses were performed by comparison to an internal standard for the lot, then it will be necessary to determine the concentration of the internal standard. This is done by repeated comparison of the internal standard to the SRM. The concentration of the internal standard must be determined at the time of the first and second analysis by comparing it to the appropriate SRM's. The measured concentration of the internal standard should be the same for both analyses within the limits of error of the analyses. The concentration measured for the internal standard is multiplied by the measured ratio of each sample to the internal standard to obtain the concentration of each sample.

The uncertainty of the CRM includes the error of the SRM and the uncertainty due to the imprecision of the intercomparison. The error of the SRM, E_{SRM}, is given on the certificate for the particular cylinder, and is defined as the estimated upper limit of the total uncertainty. The estimated upper limit of the uncertainty for the CRM should be calculated as follows:

$$E_2 \text{ (Total Error)} = 2\sqrt{\left[\frac{E_{SRM}}{2}\right]^2 + a^2 + b^2 + c^2}$$

where E_2 is the estimated upper limit of the uncertainty of the CRM; a is the imprecision of the intercomparison of the internal standard with the lot; b is the imprecision of intercomparison of the internal standard and the SRM; and c is the error of the calibration.

e. Analytical Method

Analysis of these CRM propane mixtures may be done by gas chromatography or any other method specific for propane determination. The method chosen should have adequate sensitivity and precision, and the nature of the instrument response must be known for the concentration region bracketing the SRM and the CRM. The precision and sensitivity are evaluated during analysis, and are reflected directly in the "imprecision of intercomparison." The instrument response characteristic is evaluated over the small concentration range between the SRM and CRM by observing the response over a wider range using SRM's as calibration standards.

f. Impurities

The major impurities in SRM's of propane in air or propane in nitrogen are other organic compounds. The propane content of an SRM is certified, while the concentrations of other hydrocarbons are given for information only. If a method of analysis is used that is specific for propane (gas chromatography, for example), then the presence of other hydrocarbons will not affect the measurement of propane. However, if a non-specific method (such as using a total hydrocarbon analyzer) is used, then it is essential that the type and concentration of each other organic compound be known. Furthermore, the source of the other organics must be known to assure future assessments of the stability of the samples.

There are three major sources of organic contamination of SRM's or CRM's. These include trace hydrocarbons, usually methane, present in the diluent air or nitrogen, other aliphatic hydrocarbons that are present in the reagent propane, and solvents, usually chlorinated compounds, which are used to clean cylinders and valves and which are not always completely removed before assembly of the cylinder. The first two sources generally do not create analytical problems, provided that the total concentration of the hydrocarbon is low and further provided that the specific hydrocarbons are identified. The last source may cause serious problems if the concentration is high and if the concentration increases with time as the material desorbs inside the container.

The aliphatic hydrocarbons in the CRM's can be measured by gas chromatography, and their concentration and identity should be consistent with the impurities in the reagent propane and in the diluent nitrogen or air (which should have been analyzed before the preparation of the CRM's). The presence of other organic material may be determined by exhaustive analyses utilizing any number of trace analytical techniques, but if reasonable precautions were used in excluding organic impurities from the preparatory process, a simple test will suffice to assure that the only impurities are those originating in the reagents. This involves comparing the hydrocarbons measured with a total hydrocarbon analyzer, with the sum of the aliphatic hydrocarbons individually measured by gas chromatography. If the two values are the same or similar, there is a high degree of assurance that the other organics in the sample are aliphatic hydrocarbons originating from the reagent gases. If the value obtained by total hydrocarbon analysis is significantly higher than the sum of the compounds measured chromatographically, then a serious problem exists, and either the batch of CRM's must be discarded or the source of the other organics must be identified. Further, it must be determined that these organic impurities will not create future analytical problems.

In general, the following requirements must be met in regard to impurities:

1. The hydrocarbon impurities* must be less than one percent of the propane.

2. Organic impurities other than aliphatic hydrocarbons must be less than 0.25 percent of the propane.

3. Neither the aliphatic hydrocarbons nor the other organics should increase between the first and second analysis.

Compliance with these requirements can be confirmed by use of the following procedure. This procedure is the minimum effort that should be expended to characterize the impurities, and it is not intended to discourage more strenuous efforts to identify the exact nature of the impurities:

1. Select at least five samples from the batch for analysis of total other hydrocarbon [TOH] and total organics [TO]. This analysis must be performed within 10 days after preparation of the batch, and again sixty days after the first analysis.

2. Analyze the selected samples for total organics using a flame ionization total hydrocarbon analyzer. Calibrate the analyzer with SRM's of propane in air or propane in nitrogen, whichever are appropriate. (The total concentration of hydrocarbon in the SRM, $[TH]_{SRM}$, is the sum of the propane and of the reported other hydrocarbon, expressed as propane, whereas the total organics [TO] is the sum of the propane, the total other hydrocarbon [TOH], and any other organic compounds, such as chlorinated hydrocarbons.)

3. Calculate the total organics [TO] in the CRM using the following relationship:

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*The concentration of each impurity is expressed as the equivalent concentration of propane. When measured with a total hydrocarbon analyzer calibrated with propane, the measured concentration of the impurities is equivalent to propane. If the individual compounds are measured by chromatography, the concentration of each is multiplied by $\frac{n}{3}$ where n is the number of carbon atoms in the particular molecule.

$$[TO]_{CRM} = [TH]_{SRM} \frac{i_{CRM}}{i_{SRM}}$$

where i is the signal generated by the CRM or the SRM. The total other hydrocarbon (TOH) in the CRM is simply the total hydrocarbon expressed as propane minus the propane. ([TH] = [TOH] + Propane).

4. Analyze the CRM's for aliphatic hydrocarbons using gas chromatography. The analysis must be such that hydrocarbons from C_1 through C_7 can be quantitatively determined. Several different analyses may be required to accomplish this.

5. Calculate the total hydrocarbon [TH] in the CRM by summing the individual hydrocarbons after expressing each as the equivalent propane concentration. This is done as follows:

$$[TH]_{CRM} = 1/3[CH_4] + 2/3[C_2H_6] + \ldots . \frac{n}{3} [C_nH_{2n+2}]$$

6. Compare the value for total organics measured with the hydrocarbon analyzer to the total hydrocarbon measured by chromatography after first subtracting the propane concentration from each. The concentration of other organics is at an acceptable level if the other organics ($[TO] - [C_3H_8]$) do not exceed the total other hydrocarbons ($[TH] - [C_3H_8]$) by more than 25 percent or

$$([TO] - [C_3H_8]) \le 1.25\ ([TH] - [C_3H_8]).$$

Furthermore, the total organics must not exceed 1 percent of the propane, or

$$[TO] \le 1.01\ [C_3H_8]$$

Finally, the value for total organics must not differ between the first and second analysis in excess of what would be calculated from the uncertainty of the two analyses.

In addition to the limit for the concentration of organic impurities, the water vapor content must not exceed 5 ppm by mole.

g. Reporting Results

A complete report concerning the concentration of impurities will be required in addition to the information concerning the concentration of propane and the stability of the propane concentration. The report on impurities should summarize the results obtained in steps 2 through 6 of the previous section on impurities.

h. Period of Certification

Experience at NIST indicates that propane mixtures contained in aluminum cylinders are stable for periods of more than two years. If no change in concentration of the CRM's is indicated by the results of the producer's first and second analysis, then stability for a period of two years from the date of the second analysis is assured with a high degree of probability.

i. Recertification (see appendix G for further details)

CRM's of propane in air or in nitrogen that have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 MPa).
2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.
3. The concentration of the internal standard, determined by comparison the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.
4. The concentration of the SRM must be known either by comparison with a new SRM or the original SRM must have been recently recertified by NIST.
5. If either the original SRM or the internal standard no longer exists, then no recertification can be made.
6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.

APPENDIX G

Extension of Certification (Recertification) and Date-of-Sale Certification

a. Introduction

In Appendices C through F and Appendices H and I of this document, the period of certification for a Certified Reference Material (CRM) has been limited to two years from the date of the second analysis of its CRM lot by its producer. This limitation is necessary in the absence of confirmatory measurements proving long-term stability (>2 years). Short-term stability (up to 2 years) of CRM's must be established before they can be certified, but long-term stability can only be proven by periodic reanalyses after certification. Guidelines for establishing short-term stability are given in the main body of this document (see section 3.3.1). Changes which might not affect the certified concentration over a two-year period may become evident after more than two years.

The purpose of this appendix is to provide CRM producers with procedures for extending the certification of CRM samples that either are unsold or are still in use at the end of the original period of certification.

Two approaches may be taken to achieve this: (1) the first approach is to extend the certification of all unsold (or sold samples, if returned to the CRM producer for recertification) in a batch for a specified period following reanalysis of these samples (see section b, below); and (2) the second approach is to certify individual samples in a lot for a specified period, beginning at the time of sale of each sample to a purchaser (see "date-of-sale" certification; section c, below). The procedures to be followed to demonstrate long-term stability are slightly different in each of these two approaches. Simply stated, date-of-sale certification (section c) requires that the CRM producer retain the samples for a longer period of time and perform a third analysis, six months after preparation, before submitting data for approval of the lot as CRM's, and, subsequently, perform additional reanalyses at 18 and 30 months on samples of the lot remaining unsold.

This appendix also contains a procedure for converting existing lots of CRM's (that had originally been limited to two years from the date of the second analysis of the lot by the CRM producer) to date-of-sale certification (see section d, below).

b. Procedures to Extend the Certification of a CRM

The certification period for a CRM may be extended if it can be demonstrated that the concentration, on reanalysis, has not changed from that of its initial certification. The period of recertification will begin at the time of completion of the reanalysis and will continue for an additional period of time not to exceed two years. A CRM may be recertified more than one time, as long as the concentration, on reanalysis, has not changed from that of its initial certification. This section is written to describe the first recertification of a CRM, which represents its third analysis (the first two analyses being performed during the original certification of the CRM). Hence, in the discussion given below, for subsequent recertifications of the same CRM sample, the new recertification analysis is compared to the most recent previous recertification analysis. The recertified CRM may be one or more of the samples remaining unsold in a particular lot, or may be a sample that has been returned by a purchaser for recertification.

The analyses performed during recertification must be sufficient to show that the concentration of the sample has not changed within the limits of the combined error of the original two analyses and the recertification analysis. For CRM samples that are recertified more than once, the analyses performed during any subsequent recertification must be sufficient to show that the concentration of the sample has not changed within the limits of the combined error of the original two analyses and all subsequent recertification analyses.

Any recertification analysis is performed in an identical manner to the second analysis of the original certification (see section 3.3 in the main body of this document), except that a smaller number of samples may be involved. The statistical test to demonstrate that the concentration has not changed between the second and the third analyses is the same as that which was used to show that no change had occurred between the first and the second analyses.

The third analysis must be performed with reference standards that are traceable to the same source as was used for the first and second analyses. These standards must include one of the following combinations:

1. The original SRM and the original internal standard of the lot;

2. A new SRM and the original internal standard of the lot; or

3. The original SRM and a new internal standard of the lot.

Any SRM used in the recertification of a CRM must either be within the original period of its certification by NIST or must have been recertified by NIST and still be within the period of its recertification.

The linearity and precision attained with the instrument used for the third analysis must be similar to that attained with the instrument used in the first and second analyses. The linearity in the concentration region between the CRM and the SRM must be confirmed by the method outlined in section 2.3 of the main body of this document and as illustrated in section II of appendix A. The imprecision of the measurement method is evaluated by ten (10) replicate measurements of the internal standard of the lot (e.g., see section II in appendix A). The value of the imprecision thus obtained should be the same as or smaller than that obtained during the first and second analyses.

The analyst should be aware of the effect of precision on the decision concerning the stability of the samples being analyzed. Ultimately, a decision must be made as to whether an observed difference between the second and third analyses is real, or, if no difference is observed, whether the third analysis was sufficiently precise to reveal a difference. Thus, if the imprecision of the third analysis is the same as or smaller than that of the first or second analyses, it will be possible to recognize small real differences in concentration that have occurred during the interval between the second and third analyses. However, if the imprecision of the third analysis is large (i.e., two or more times that of the second analysis), then larger differences in sample concentration values would need to be observed to conclude that a group of samples was unstable (i.e., it would not be possible to state with confidence that samples in a lot are stable and, hence, acceptable for recertification, if the imprecision of the third analysis is large).

The analyst should not proceed with the analysis of the samples in the lot if the imprecision of the analysis (evaluated by replicate measurements of the internal standard, as stated above) or if the concentration of the internal standard is questionable. The concentration of the internal standard should be the same as measured during the second analysis. This can be determined by observation if agreement is close and the imprecision is small, or, more rigorously, by application of a simple "t" test of the form:

$$t = (C_2 - C_3)/S_p(1/n_2 + 1/n_3)^{0.5}$$

where $(C_2 - C_3)$ is the difference between the average concentration of the internal standard for the second and third analyses, the pooled standard deviation, S_p is the average of the standard deviations for the second and third analyses of the internal standard, and the value for n (the number of measurements) is ten (10) for both of these analyses. If the value of t lies in the interval from +2.2 to -2.2., there is no significant difference between the concentrations measured during the second and third analyses. Practically speaking, if the difference between the two averages is equal to or less than the larger of the two standard deviations, then it can be confidently assumed that no change has occurred in the concentration of the internal standard.

Once it has been shown that the concentration of the internal standard has not changed and that the imprecision and linearity are within acceptable limits, then analysis of the samples to be recertified should be performed. This analysis is intended to reveal whether or not a change in the concentration of any sample has occurred during the time internal following the second analysis. Because this time interval is much greater than that between the first and second analysis, it will be easier to recognize any samples in which slow changes in concentration have been occurring. Individual samples that have changed significantly should be evident by visual inspection of the results. An entire batch that has changed in concentration will be evidenced by a significant change in the average concentration of all samples, or by the sign of the difference between the second and third analyzed concentration values being the same for all samples. However, in some cases, the change may be small and may not be easily recognized. In these cases, the paired results of the second and third analyses are treated in the same manner as the paired results of the first and second analyses (see appendix A, section II, part 3).

There are three situations which might result from a comparison of the second and third analyses. These are:

1. An obvious and unquestionable change in the concentration of some or all samples in the batch has occurred.

2. No significant difference is found between the second and third analyses.

3. A small but real change in concentration is revealed on application of statistical tests for differences.

In the first situation, an obvious problem exists which requires further action, probably of a drastic nature. In the second case, all is well and the certification period may be safely extended. In the third case, we are faced with deciding whether or not a difference is significant. That is, will a statistically significant difference translate into an analytically significant difference, considering the total uncertainty of the certified concentration and the length of the period of certification. For example, suppose that the second and third analyses have been executed properly and that the imprecision of the measurement of the difference between the two sets is less than 0.1 percent relative. In principle, it should be possible to detect real differences of 0.1 percent relative between the second and third analyses. Because of the nature of the changes which take place in compressed gases contained in cylinders, a change of 0.1 percent relative over one year can be extrapolated to a change of no more than 0.3 percent relative over three years. Therefore, a 0.1 percent relative change will not compromise the analytical utility of the sample, and may be safely ignored. Changes greater than 0.1 percent relative per year, however, may or may not be acceptable with respect to extending the certification period. A final decision may have to be based on factors in addition to the results of the third analysis. Factors which might be considered are: (i) the results of the first and second analyses as compared to the third; (ii) the relative contributions of random errors and systematic errors to the total error of the CRM; and/or (iii) the sign and nature of the observed change.

Evaluation of the Data

The producer must submit to the NIST the results of the analysis of the internal standard, the imprecision and linearity data, and the individual results obtained for each sample for which extension of the period of certification is sought. NIST will examine these data and will decide whether or not the results justify an extension of the period of certification. The producer will be notified of NIST's decision in writing. If the decision is negative, the producer will be supplied with the reason and a summary of all statistical treatments of the data. In either regard, EPA will be notified of the decision in writing and will be informed of any further action to be taken either by the producer or by NIST.

Consequence of the Third Analysis

If the evaluation of the data of the third analysis concludes that the batch is stable or that observed changes will not become analytically significant during the period of the recertification, then all samples analyzed as part of the third analysis may be certified for two years or more. If changes have occurred that can be extrapolated to become significant changes by the end of the requested period of recertification, the samples cannot be recertified and will remain in certification only through the original period of certification. If the analysis reveals changes that are substantial and are considered significant even during the original period of certification, then all samples still within the certification must be recalled from the purchasers. However, before a "recall" decision is made, NIST and the CRM producer will make every effort to determine whether or not the change is real or if it is the result of an analytical error committed at the time of the second or third analyses. Since a recall could occur, a CRM producer should maintain records of the names and addresses of all purchasers of CRM's.

c. Analytical Procedures for Date-of-Sale Certification

This section describes procedures that allow a CRM producer to certify an individual CRM for a two-year period starting from the date of its sale to a customer. These procedures differ slightly from those for regular CRM certification. The principal difference is that all samples in the lot must be analyzed three times rather than twice before approval as a date-of-sale certified CRM. An initial analysis of the lot should be performed as soon as practical after its preparation, followed by reanalyses at 3 and 6 months after its preparation. After the third analysis, the CRM producer should submit a comprehensive report of the three analyses to NIST for review and approval. The CRM producer should at this time also send two samples, randomly selected by EPA from the lot, for an EPA Performance Audit. If the review of the producer's and auditor's analytical results by NIST indicates that the batch has satisfied the requirements of a CRM, NIST will notify EPA and the producer by letter that the lot may be certified for sale. If reservations concerning the stability or homogeneity of the lot arise as a result of the review of the analytical results by NIST, an additional analysis may be required or, alternately, the lot may be rejected.

The period of certification for each CRM sample in an approved lot will be two years from the date of sale to a customer for those sales that occur within two years after preparation of the lot. Individual CRM's may continue to be sold after this two-year period with a two-year certification from date of sale if additional analyses are performed at 18 and at 30 months. For these analyses, only 20 percent of the lot (or at least 4 cylinders) need to be reanalyzed. The results of the reanalysis should be submitted to NIST for review.

During each analysis of the lot, ten (10) replicate measurements must be performed on an internal standard from the lot. Each analysis must be performed with reference standards, all of which are traceable to the same source. This traceability can be established with:

1. The original SRM and the original internal standard of the lot;

2. A new SRM and the original internal standard of the lot; or

3. The original SRM and a new internal standard of the lot.

Any SRM used as a reference standard must be within the period of original certification or within the period of some subsequent recertification by NIST. It should again be emphasized that the analyst should never proceed with the analysis of the lot if the imprecision of the analysis or the concentration of the internal standard is questionable.

The CRM producer's report to NIST should contain information concerning the imprecision and linearity of the analytical method, the stability of the internal standard, and the stability and homogeneity of the lot. The statistical tests to determine the stability and homogeneity of a lot before its certification are described in appendix A of this document. After certification, the stability of the reanalyzed cylinders should be determined as described in section B of this appendix (appendix G).

The CRM producer shall provide a "Certificate of Analysis" and a copy of the certification authorization letter from NIST to EPA, to any purchaser of a CRM that is certified from date of sale. The certificate shall include, as a minimum, the sample number, the cylinder number, the certified concentration of the CRM, the uncertainty assigned to the certified concentration, the date of sale, and the period of certification. The certificate also must identify the SRM used by the producer to establish the traceability of the CRM.

d. Converting from Fixed Period Certification to Date-of-Sale Certification

It should be apparent from the preceding narratives in this appendix that there is little difference between the analytical requirements for a fixed period certification (or extension of a certification through recertification) and a date-of-sale certification. In fact, there is no reason why a lot originally certified for a fixed period cannot be converted to date-of-sale certification if the additional necessary analyses are performed and the resulting data are made available for NIST review. These data must support the conclusion that all samples in the lot are stable and can be expected to remain stable for at least 4 years if no changes are observed during the first six months. If the initial six-month observation period was extended to two years, for instance, and no changes were observed, then the assumption that the lot was stable and could subsequently be certified from date of sale would be equally valid.

Thus, unsold samples remaining from a lot originally certified for a two-year certification could be certified for subsequent date-of-sale certification if all samples are analyzed and found to be stable (as specified in section C, preceding). The results of this analysis would be treated in the same manner as the third analysis of the date-of-sale certification described in section C of this appendix. Samples from the lots old before this analysis could not be retroactively recertified unless they are reanalyzed at the same time as the remainder of the lot.

A CRM producer who wishes to convert from fixed period certification to date-of-sale certification should proceed as follows:

1. Analyze all remaining samples in the lot, being certain that either the original analytical standards (SRM or internal standard) or acceptable replacements are available.

2. Forward all data to NIST, together with a letter requesting conversion of the remaining samples in the lot to date-of-sale certification.

NIST will examine the data for the reanalysis as well as for any previous analyses, and will advise both the CRM producer and EPA as to whether or not the request should be granted. If the data indicate that the request is justified, NIST will inform the CRM producer and EPA by letter of its approval. If deemed necessary, NIST may require either an additional analysis by the producer, or that another pair of samples be submitted for an EPA Performance Audit.

APPENDIX H

Oxygen in Nitrogen

a. Introduction

This appendix describes the preparation of Certified Reference Materials (CRM's) consisting of oxygen in nitrogen. The reader should be familiar with the general description of the preparation and analysis of CRM's given in the document, and the material in Appendix G for extending the certification of CRM's and for date-of-sale certification of CRM's.

b. Current SRM's

Following is a list of SRM's of oxygen in nitrogen for which CRM's may be made. The concentrations shown are in mole percent. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of a CRM.

SRM No.	Nominal Concentration
2651	5.0 mole percent*
2652	10.0 mole percent*
2657	2 mole percent
2658	10 mole percent
2659	21 mole percent

c. Cylinders

The CRM's must be packaged in new aluminum cylinders equipped with valves of appropriate material that conform to CGA recommendations for these particular mixtures; alternatively, aluminum cylinders previously used for oxygen in nitrogen CRM's or which have been used only for oxygen in nitrogen mixtures may be used for these CRM's, provided that the history of a reused cylinder is well known, and, in case of a CRM cylinder, an analysis must be performed of the remaining gases to assure that the contents have not been diluted or contaminated. Note: The concentration of the remaining gas mixture must lie within plus or minus one percent relative of the concentration of the original CRM, as certified. In the case of reused cylinders, the cylinder must be evacuated before refilling, and the concentration of the new CRM gas mixture must lie within one order of magnitude (within 0.1 to 10 times) of the concentration of the previous CRM or other oxygen mixtures previously contained.

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*SRM Nos. 2651 and 2652 also contain 0.01 mole percent propane.

d. Preparation and Analysis

Prepare a lot of at least 10 cylinders all at identical concentration. The concentration of oxygen must lie within ±1 percent relative of the concentration of the specific SRM with which the lot is to be compared. Analyze at least 10 samples from the lot, if the lot contains more than 20 samples. If the lot containing fewer than 20 samples, it is recommended that all samples be analyzed. Analyze the samples by direct comparison to the SRM or by comparing samples in the lot to a single sample selected at random from the lot (internal standard from the lot). Analyze each sample at least two times. Analyze for impurities as required in Section F.

After the first analysis, the lot should be put aside to "incubate" for at least one month after which time all samples in the lot are analyzed and at which time the impurities are redetermined. If the two sets of analyses are the same, then it may be assumed that the lot is homogeneous and stable. If the analyses were performed by direct comparison to the SRM, then the analytical value for the sample will be the certified value. If the analyses were performed by comparison to an internal standard for the lot, then it will be necessary to determine the concentration of the internal standard. This is done by repeated comparison of the internal standard to the SRM. The concentration of the internal standard must be determined at the time of the first and second analysis by comparing it to the appropriate SRMs. The measured concentration of the internal standard should be the same for both analyses within the limits of error of the analyses. The concentration measured for the internal standard is multiplied by measured ratio of each sample to the internal standard to obtain the concentration of each sample.

The uncertainty of the CRM includes the error of the SRM and the uncertainty due to the imprecision of the intercomparison. The error of the SRM, E_{SRM}, is given on the certificate for the particular cylinder and is defined as the estimated upper limit of the total uncertainty. The estimated upper limit of the uncertainty for the CRM should be calculated as follows:

$$E_2\,(\text{Total Error}) = 2\sqrt{\left(\frac{E_{SRM}}{2}\right)^2 + a^2 + b^2 + c^2}$$

where E_2 is the estimated upper limit of the uncertainty of the CRM; a is the imprecision of the intercomparison of the internal standard with the lot; b is the imprecision of the intercomparison of the internal standard and the SRM; and c is the error of the calibration.

e. Analytical Method

Analysis of these CRM oxygen mixtures may be done by gas chromatography, paramagnetic analyzers, or any other method specified for oxygen determination. The method chosen should have adequate sensitivity and precision, and the nature of the instrument response must be known for the region between the SRM and the CRM. The precision and sensitivity are evaluated during analysis and are reflected directly in the "imprecision of intercomparion." The instrument response characteristic is evaluated over the small range between the SRM and CRM by observing the response over a wide range using SRMs as calibration standards.

f. Impurities

The major impurity in SRMs of oxygen in nitrogen is argon. The oxygen content of an SRM is certified while the concentration of argon is given for information only. If a method of analysis is used that is specific for oxygen (paramagnetic analysis for example) then the presence of argon will not affect the measurement of oxygen. However, if a non-specific method is used, then it is essential that the concentration of argon be known.

There are several sources of argon contamination in SRMs or CRM's. First, contamination may be present in oxygen or the diluent nitrogen. In addition, atmospheric leakage through cylinder valves or transfer system connections and valves can contribute to argon contamination. The atmospheric concentration of argon is approximately 0.93 mole percent. The argon in the oxygen, nitrogen, and CRM's can be measured by gas chromatography. The argon concentration in the CRM should be consistent with the impurities in the reagent oxygen and the diluent nitrogen that were analyzed prior to the compounding of the CRM's. If the concentration of argon in the CRM is consistent with the pure gases, it may be assumed that the sample cylinders and the transfer systems were adequate.

The maximum concentration of impurities shall not exceed the following:

Hydrocarbons as methane	3 ppm
Water vapor	5 ppm
Total other impurities except argon	15 ppm
Argon in 2% O_2/N_2	30 ppm
Argon in 5% O_2/N_2	40 ppm
Argon in 10% O_2/N_2	50 ppm
Argon in 21% O_2/N_2	100 ppm

g. Period of Certification

Experience at NIST indicates that oxygen mixtures contained in aluminum cylinders are stable for periods of more than two years. If no change in concentration of the CRM's is indicated by the results of the producer's first and second analysis, then stability for a period of two years from the date of the second analysis is assured with a high degree of probability.

h. Recertification (see Appendix G for further details)

CRM's of oxygen in nitrogen that have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 MPa).
2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.
3. The concentration of the internal standard, determined by comparison to the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.
4. The concentration of the original SRM must be known either by comparison with a new SRM, or the original SRM must have been recently recertified by NIST.
5. If either the original SRM or the internal standard no longer exists, then recertification can only be made using a new SRM.
6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.

APPENDIX I

Carbon Dioxide in Nitrogen

a. Introduction

This appendix describes the preparation of Certified Reference Materials (CRM's) consisting of carbon dioxide in nitrogen. The reader should be familiar with the general description of the preparation and analysis of CRM's given in the main text of this document and the material in Appendix G which provides procedures for extending the certification of CRM's and for date-of-sale certification of CRM's.

b. Current SRM's

Following is a list of SRM's of carbon dioxide in nitrogen for which CRM's may be made. The concentrations shown are in mole percent. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of a CRM. The eight SRM's covering 2619a through 2626a listed below were originally developed for use in calibrating combustion efficiency measurements; the remaining originally developed for use in calibrating mobile source emission measurements.

SRM Number	Nominal Concentration of CO_2
1674b	7.0 mole percent
1675b	14.0 mole percent
2619a	0.5 mole percent
2620a	1.0 mole percent
2621a	1.5 mole percent
2622a	2.0 mole percent
2623a	2.5 mole percent
2624a	3.0 mole percent
2625a	3.5 mole percent
2626a	4.0 mole percent
2632	300 ppm
2633	400 ppm
2634	800 ppm

The preparer of carbon dioxide in nitrogen CRM's should note that the CO_2 concentrations in the eight combustion efficiency SRM's (2619a through 2626a) are certified to within 0.1 percent relative at the 95 percent confidence level; the CO_2 concentrations in the remaining five SRM's are certified to within ±1 percent relative at the 95 percent confidence level.

c. Cylinders

The CRM's must be packaged in new aluminum cylinders equipped with valves of appropriate material that conform to CGA recommendations for these particular mixtures; alternatively, aluminum cylinders previously used for carbon dioxide in nitrogen CRM's or that have been used only for carbon dioxide in nitrogen mixtures may be used for these CRM's, provided that the history of a reused cylinder is well known, and, in case of a CRM cylinder, an analysis must be performed of the remaining gases to assure that the contents have not been diluted or contaminated. Note: The concentration of the remaining gas mixture must lie within plus or minus one percent relative of the concentration of the original CRM, as certified. In the case of reused cylinders, the cylinder must be evacuated before refilling, and the concentration of the new CRM gas mixture must lie within one order of magnitude (within 0.1 to 10 times) of the concentration of the previous CRM or other carbon dioxide in nitrogen mixtures previously contained.

d. Preparation and Analysis

Prepare a lot of at least 10 cylinders all at identical concentration. The concentration of carbon dioxide must lie within ±1 percent relative of the concentration of the specific SRM with which the lot is to be compared. Analyze at least 10 samples from the lot, if the lot contains more than 20 samples. If the lot contains fewer than 20 samples, it is recommended that all samples be analyzed. Analyze the samples by direct comparison to the SRM or by comparing samples in the lot to a single sample selected at random from the lot (internal standard from the lot). Analyze each sample at least two times. Analyze for impurities as required in Section F.

After the first analysis, the lot should be put aside to "incubate" for at least one month after which time all samples in the lot are analyzed and at which time the impurities are redetermined. If the two sets of analyses are the same, then it may be assumed that the lot is homogeneous and stable. If the analysis was performed by direct comparison to the SRM, then the analytical value for the sample will be the certified value. If the analyses were performed by comparison to an internal standard for the lot, then it will be necessary to determine the concentration of the internal standard. This is done by repeated comparison of the internal standard to the SRM. The concentration of the internal standard must be determined at the time of the first and second analysis by comparing it to the appropriate SRM's. The measured concentration of the internal standard should be the same for both analyses within the limits of error of the analyses. The concentration measured for the internal standard is multiplied by measured ratio of each sample to the internal standard to obtain the concentration of each sample.

The uncertainty of the CRM includes the error of the SRM and the uncertainty due to the imprecision of the intercomparison. The error of the SRM, E_{SRM}, is given on the certificate for the particular cylinder and is defined as the estimated upper limit of the total uncertainty. The estimated upper limit of the uncertainty for the CRM should be calculated as follows:

$$E_2\text{(Total Error)} = 2\sqrt{\left(\frac{E_{SRM}}{2}\right)^2 + a^2 + b^2 + c^2}$$

where E_2 is the estimated upper limit of the uncertainty of the CRM; a is the imprecision of the intercomparison of the internal standard with the lot; b is the imprecision of the intercomparison of the internal standard with the SRM; and c is the error of the calibration.

e. Analytical Method

Analysis of these CRM carbon dioxide mixtures may be done by gas chromatography, paramagnetic analyzers, or any other methods specified for carbon dioxide determination. Analysis of SRM's 2632-2634 also employed a non-dispersive infrared technique. The method chosen should have adequate sensitivity and precision, and the nature of the instrument response must be known for the region between the SRM and the CRM. The precision and sensitivity are evaluated during analysis and are reflected directly in the "imprecision of intercomparison." The instrument response characteristic is evaluated over the small range between the SRM and CRM by observing the response over a wide range using SRM's as calibration standards.

f. Impurities

The maximum concentration of impurities shall not exceed the following:

Carbon monoxide	0.1 ppm
Nitrous oxide	0.5 ppm
Hydrocarbons as methane	1 ppm
Water vapor	5 ppm
Total other impurities	10 ppm

g. Period of Certification

Experience at NIST indicates that carbon dioxide in nitrogen mixtures contained in aluminum cylinders are stable for periods of at least two years. If no change in concentration of the CRM's is indicated by the results of the producer's first and second analysis, then stability for a period of two years from the date of the second analysis is assured with a high degree of probability. Any samples not sold within two years of the second analysis should be recertified (see section h., below) and the period of certification should be appropriately extended.

h. <u>Recertification</u> (see Appendix G for further details)

CRM's of carbon dioxide in nitrogen that have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 MPa).
2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.
3. The concentration of the internal standard, determined by comparison to the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.
4. The concentration of the original SRM must be known either by comparison with a new SRM, or the original SRM must have been recently recertified by NIST.
5. If either the original SRM or the internal standard no longer exists, then recertification can only be made using a new SRM.
6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.

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10. SUPPLEMENTARY NOTES

☐ DOCUMENT DESCRIBES A COMPUTER PROGRAM; SF-185, FIPS SOFTWARE SUMMARY, IS ATTACHED.

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

This procedure includes the specifications and requirements that must be followed by gas during the preparation of compressed cylinder gas Certified Reference Materials (CRM). A CRM is a certified gas standard prepared at a concentration that does not exceed ± 1 percent of currently available NIST Standard Reference Material (SRM) cylinder gases. The procedure includes specifications and requirements for: (1) preparation of compressed gas samples in cylinders prepared in lots of ten or more of identical concentration with the average concentration for the lot within ± 1.0 percent relative to the concentration of a specific SRM; (2) tests to verify compressed gas sample stability and within lot homogeneity; (3) simultaneous submission by the gas manufacturer of analysis results to NIST and cylinder gas numbers to USEPA (without analysis results); (4) random selection by USEPA of two cylinders per lot for a USEPA performance audit analysis; (5) submission by USEPA of audit results to NIST; and (6) an evaluation by NIST to determine whether the lot satisfies the criteria for a NIST-traceable CRM. Individual CRM procedures are described for CO in N_2 or air (Appendix C), NO in N_2 (Appendix D), SO_2 in N_2 (Appendix E), propane in N_2 or air (Appendix F) O_2 in N_2 (Appendix H), and CO_2 in N_2 (Appendix I). Procedures for CRM recertifications and for date-of-sale certification are given in Appendix G.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)
Traceability, Certified Gas Standards, National Standards, Nitric Oxide, Sulfur Dioxide, Propane, Carbon Dioxide, Carbon Monoxide, Oxygen, Quality Assurance, Air Pollution, Environmental Measurements, Data Quality

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