

REPORT

Summary of Comparisons of Gas Standards between NPL and NIST

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And M J T Milton

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Centre for Optical and Environmental Metrology

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Approved on behalf of Managing Director, NPL
by D H Nettleton, Head of Centre for Optical and Environmental Metrology

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Summary of Comparisons of Gas Standards between NPL and NIST

by

A J Davenport, P A Holland, P T Woods and M J T Milton

EXECUTIVE SUMMARY

This report contains the results of the comparison of primary gas standards prepared by NPL and the National Institute of Standards and Technology (NIST). These include standards of carbon monoxide, carbon dioxide, nitrogen monoxide and propane all in nitrogen and propane in air.

1. INTRODUCTION

This report contains the results of the comparisons of primary gas standards carried out between NPL and the National Institute of Standards and Technology (NIST).

2. RESULTS

The results are presented in Figures 1 to 7. The value of each primary standard from NPL, or CRM from NIST, is given in terms of its nominal concentration together with its expanded uncertainty (expressed as a 95% confidence interval). The result of the analysis of each primary standard is shown with its associated uncertainty (expressed as a 95% confidence interval). The analytical values are presented in terms of the fractional deviation between the gravimetric value and the analytical value expressed as a percentage of the gravimetric value.

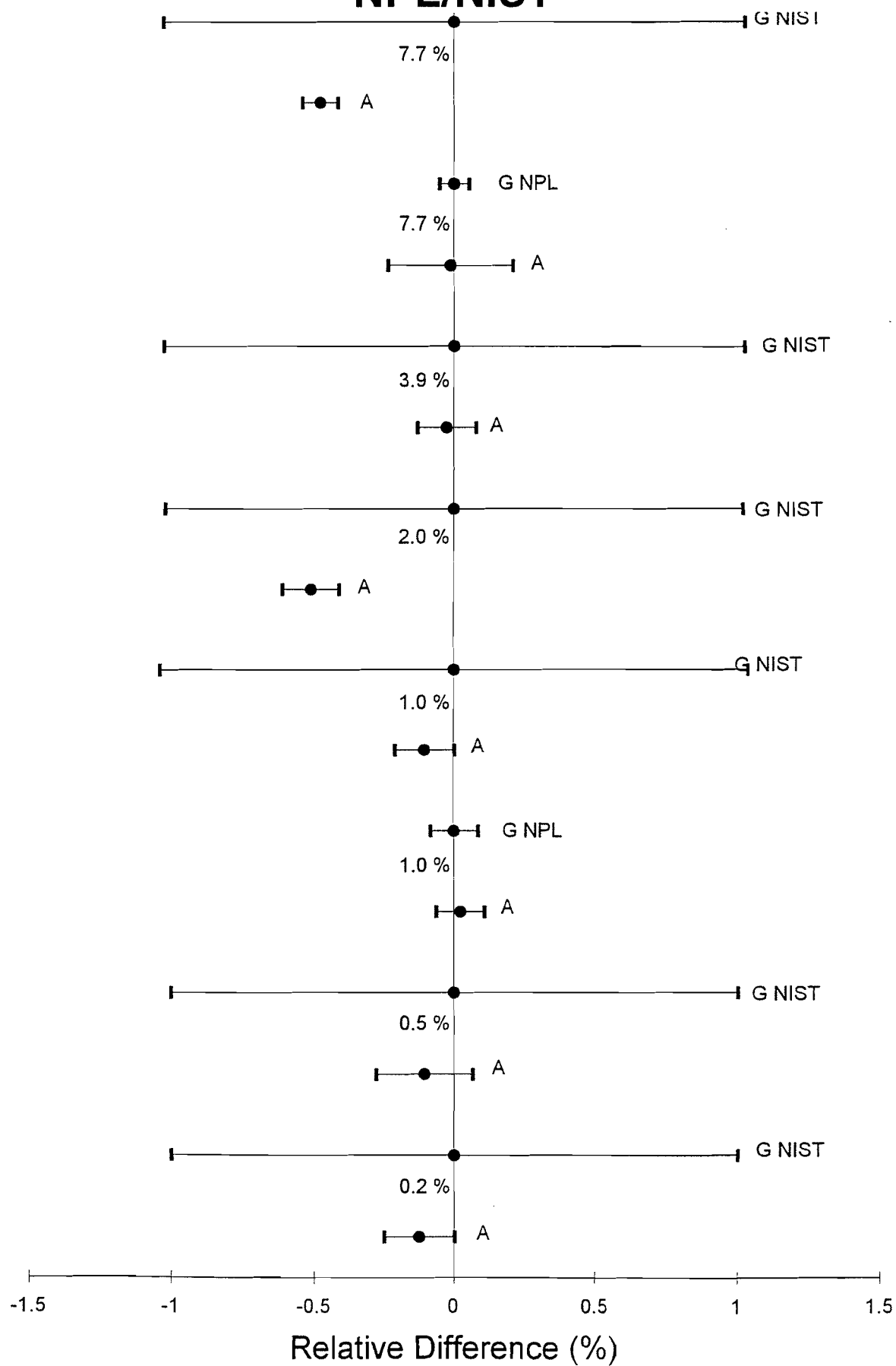
Annex 1 is a refereed publication that incorporates some of the results included in this report.

3. ACKNOWLEDGEMENTS

The active collaboration with staff at NIST including Franklin Guenther and William Dorko is gratefully acknowledged.

NPL's participation in this work was funded by the National Measurement System Policy Unit of the UK Department of Trade and Industry as part of its Valid Analytical Measurement Programme.

Figure 1: Carbon Monoxide In Nitrogen NPL/NIST



**Figure 2: Carbon Monoxide In Nitrogen
NPL/NIST (ppm levels)**

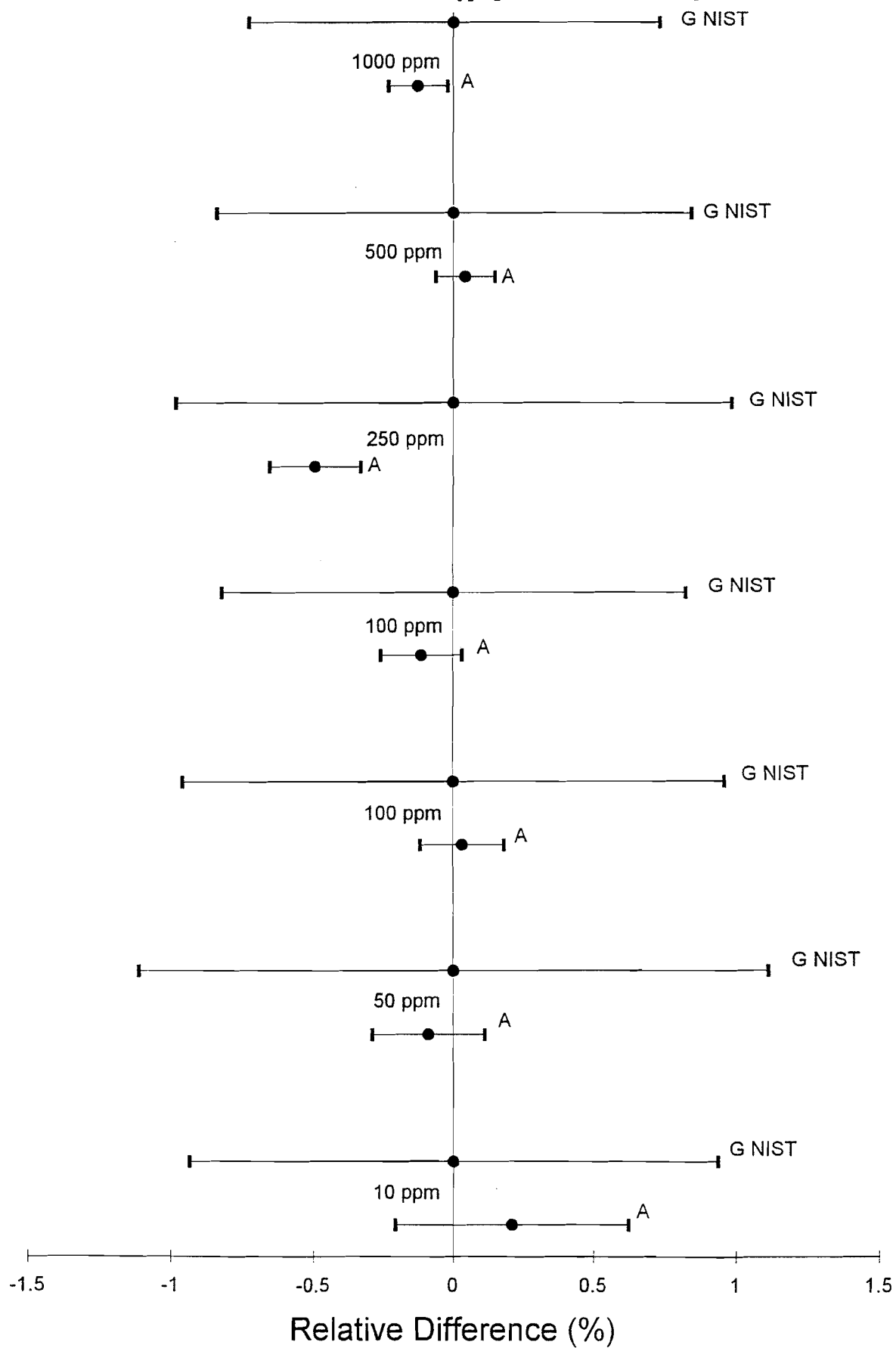


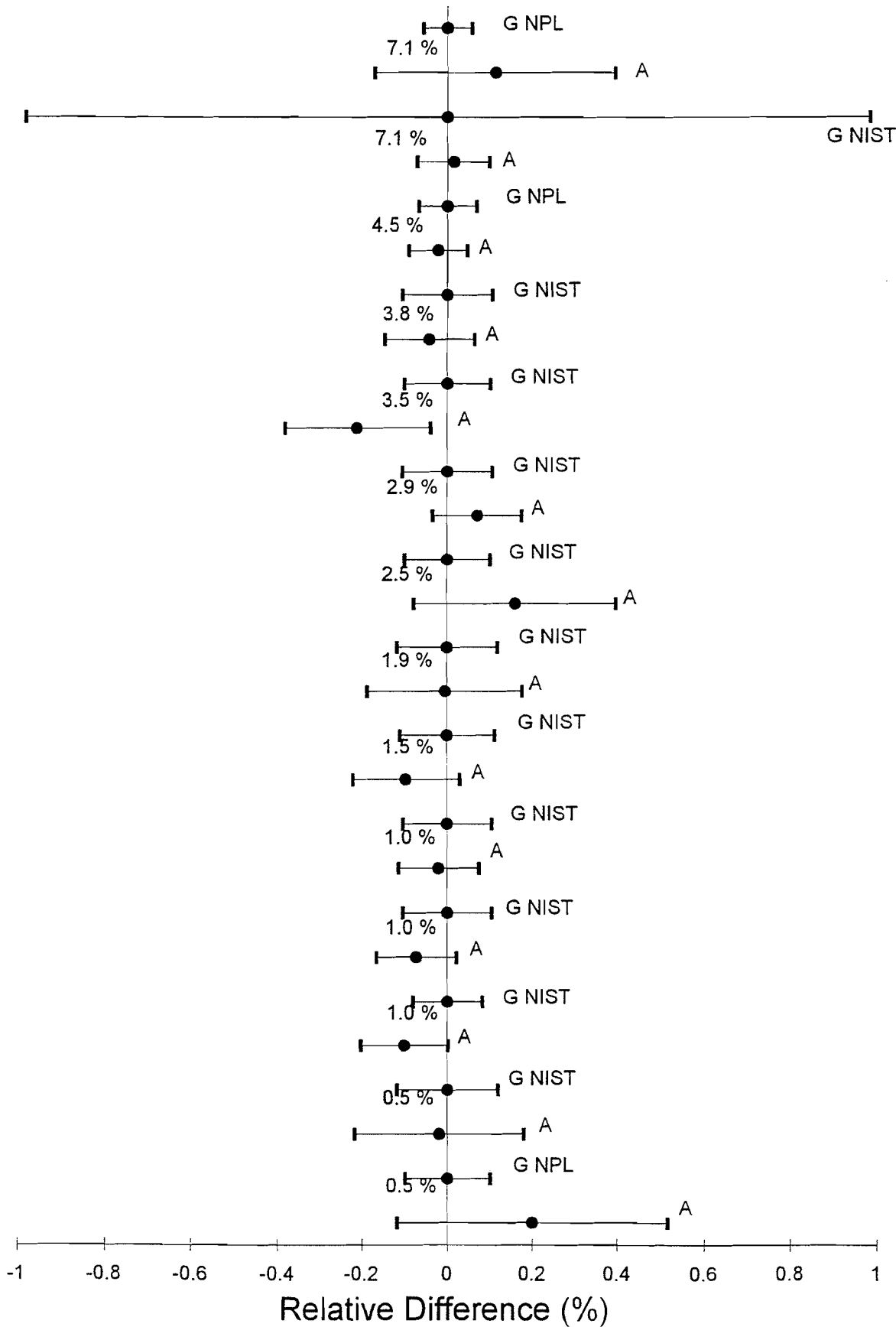
Table 1: Carbon Monoxide in Nitrogen NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction m mol/mol	Uncertainty m mol/mol	Analytical Amount Fraction m mol/mol	Uncertainty m mol/mol	Relative Difference %
80 m mol/mol CO/N ₂	NIST	77.6700	0.8000	77.3000	0.0500	-0.48
80 m mol/mol CO/N ₂	NPL	76.7900	0.0040	76.7800	0.0400	-0.01
40 m mol/mol CO/N ₂	NIST	38.9400	0.4000	38.9300	0.0400	-0.03
20 m mol/mol CO/N ₂	NIST	19.5600	0.2000	19.4600	0.0200	-0.51
10 m mol/mol CO/N ₂	NIST	9.6000	0.1000	9.5900	0.0100	-0.10
10 m mol/mol CO/N ₂	NPL	9.4490	0.0080	9.4510	0.0080	0.02
5 m mol/mol CO/N ₂	NIST	4.6800	0.0470	4.6750	0.0080	-0.11
2 m mol/mol CO/N ₂	NIST	2.3970	0.0024	2.3940	0.0030	-0.13

Table 2: Carbon Monoxide in Nitrogen NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction μ mol/mol	Uncertainty μ mol/mol	Analytical Amount Fraction μ mol/mol	Uncertainty μ mol/mol	Relative Difference %
1000 μ mol/mol CO/N ₂	NIST	956.00	7.00	954.80	1.00	-0.13
500 μ mol/mol CO/N ₂	NIST	475.00	4.00	475.20	0.50	0.04
250 μ mol/mol CO/N ₂	NIST	243.60	2.40	242.40	0.40	-0.49
100 μ mol/mol CO/N ₂	NIST	97.10	0.80	96.99	0.14	-0.11
100 μ mol/mol CO/N ₂	NIST	93.80	0.90	93.83	0.14	0.03
50 μ mol/mol CO/N ₂	NIST	44.90	0.50	44.86	0.09	-0.09
10 μ mol/mol CO/N ₂	NIST	9.62	0.09	9.64	0.04	0.21

Figure 3: Carbon Dioxide In Nitrogen NPL/NIST



**Figure 4: Carbon Dioxide In Nitrogen
NPL/NIST (ppm levels)**

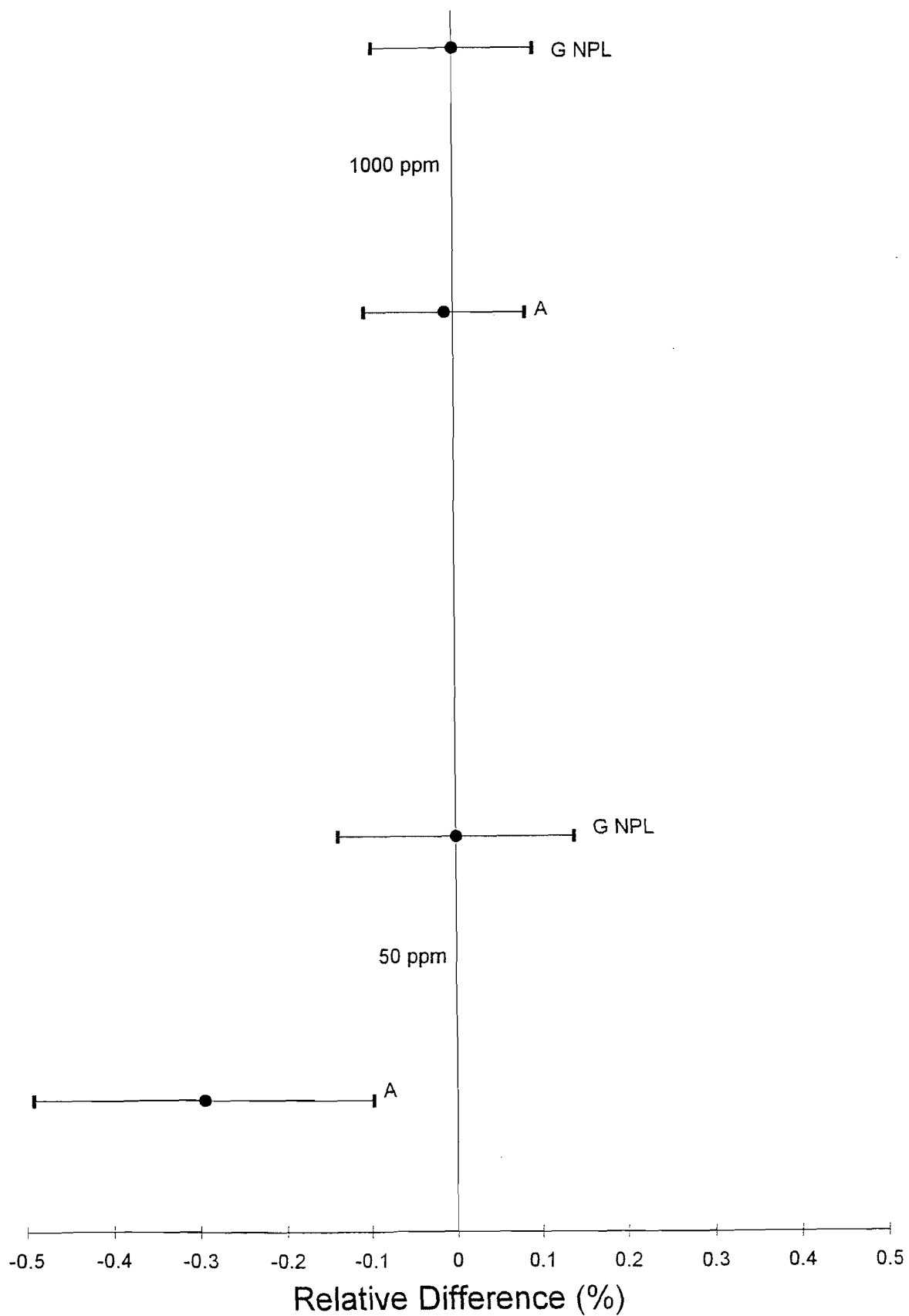


Table 3: Carbon Dioxide in Nitrogen NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction m mol/mol	Uncertainty m mol/mol	Analytical Amount Fraction m mol/mol	Uncertainty m mol/mol	Relative Difference %
70 m mol/mol CO ₂ /N ₂	NPL	71.0200	0.0400	71.1000	0.2000	0.11
70 m mol/mol CO ₂ /N ₂	NIST	71.0200	0.7000	71.2100	0.0600	0.27
45 m mol/mol CO ₂ /N ₂	NPL	44.7900	0.0300	44.7800	0.0300	-0.02
40 m mol/mol CO ₂ /N ₂	NIST	38.2460	0.0400	38.2300	0.0400	-0.04
35 m mol/mol CO ₂ /N ₂	NIST	35.0740	0.0350	35.0000	0.0600	-0.21
30 m mol/mol CO ₂ /N ₂	NIST	28.7200	0.0300	28.7400	0.0300	0.07
25 m ol/mol CO ₂ /N ₂	NIST	25.2000	0.0250	25.2400	0.0600	0.16
20 mmol/mol CO ₂ /N ₂	NIST	18.8310	0.0220	18.8300	0.0340	-0.01
15 m mol/mol CO ₂ /N ₂	NIST	14.5190	0.0160	14.5050	0.0180	-0.10
10 m mol/mol CO ₂ /N ₂	NIST	9.6450	0.0100	9.6430	0.0090	-0.02
10 m mol/mol CO ₂ /N ₂	NIST	9.6450	0.0100	9.6380	0.0090	-0.07
10 m mol/mol CO ₂ /N ₂	NPL	9.8720	0.0080	9.8620	0.0100	-0.10
5 m mol/mol CO ₂ /N ₂	NIST	5.0620	0.0060	5.0610	0.0100	-0.01
5 m mol/mol CO ₂ /N ₂	NPL	5.0390	0.0050	5.0490	0.0160	0.20

Table 4: Carbon Dioxide in Nitrogen NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction μ mol/mol	Uncertainty μ mol/mol	Analytical Amount Fraction μ mol/mol	Uncertainty μ mol/mol	Relative Difference %
1000 μ mol/mol CO ₂ /N ₂	NPL	958.30	0.90	958.20	0.90	-0.01
50 μ mol/mol CO ₂ /N ₂	NPL	50.85	0.07	50.70	0.10	-0.29

Figure 5: Nitric Oxide In Nitrogen NPL/NIST

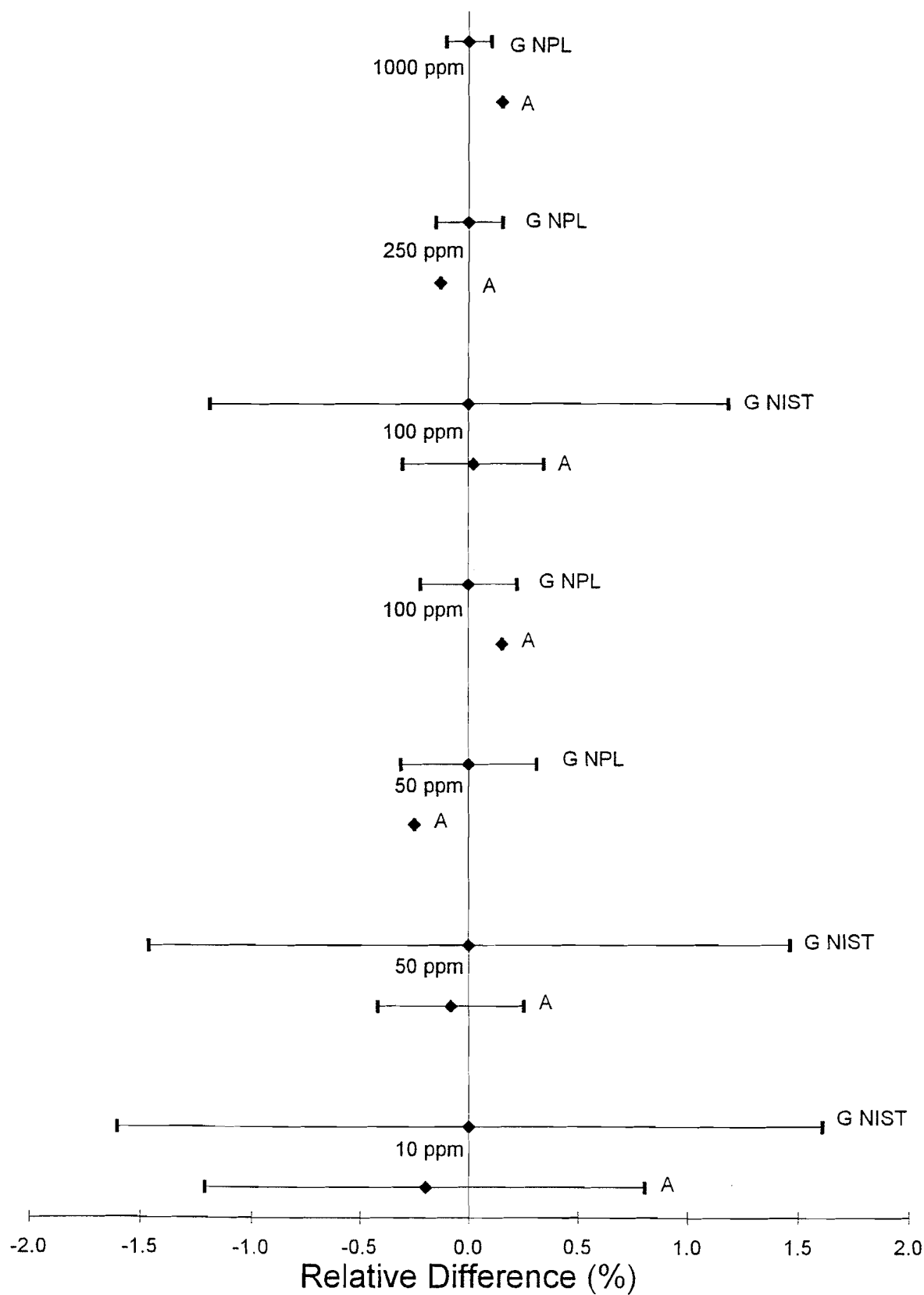


Table 5: Nitric Oxide in Nitrogen NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction $\mu\text{ mol/mol}$	Uncertainty $\mu\text{ mol/mol}$	Analytical Amount Fraction $\mu\text{ mol/mol}$	Uncertainty $\mu\text{ mol/mol}$	Relative Difference %
1000 $\mu\text{ mol/mol NO/N}_2$	NPL	980.50	1.00	982		0.15
250 $\mu\text{ mol/mol NO/N}_2$	NPL	230.6	0.35	230.3		-0.13
250 $\mu\text{ mol/mol NO/N}_2$	NIST	235	3	235.4	0.4	0.17
100 $\mu\text{ mol/mol NO/N}_2$	NIST	93	1.1	93.02	0.3	0.02
100 $\mu\text{ mol/mol NO/N}_2$	NPL	91.16	0.2	91.3		0.15
50 $\mu\text{ mol/mol NO/N}_2$	NPL	48.42	0.15	48.3		-0.25
50 $\mu\text{ mol/mol NO/N}_2$	NIST	47.9	0.7	47.86	0.16	-0.08
10 $\mu\text{ mol/mol NO/N}_2$	NIST	9.95	0.16	9.93	0.1	-0.20

Figure 6: Propane In Nitrogen NPL/NIST

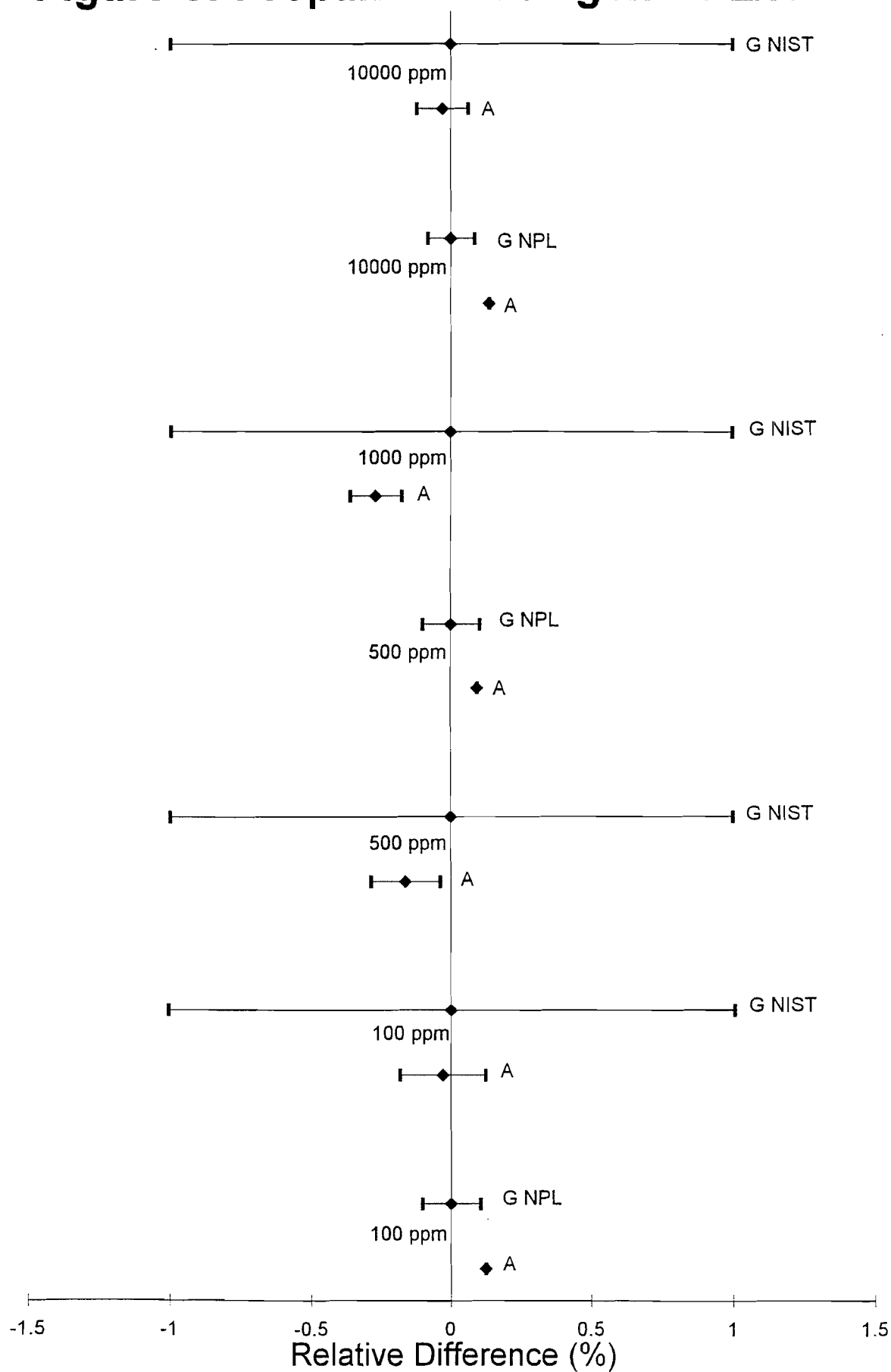


Figure 7: Propane In Air NPL/NIST

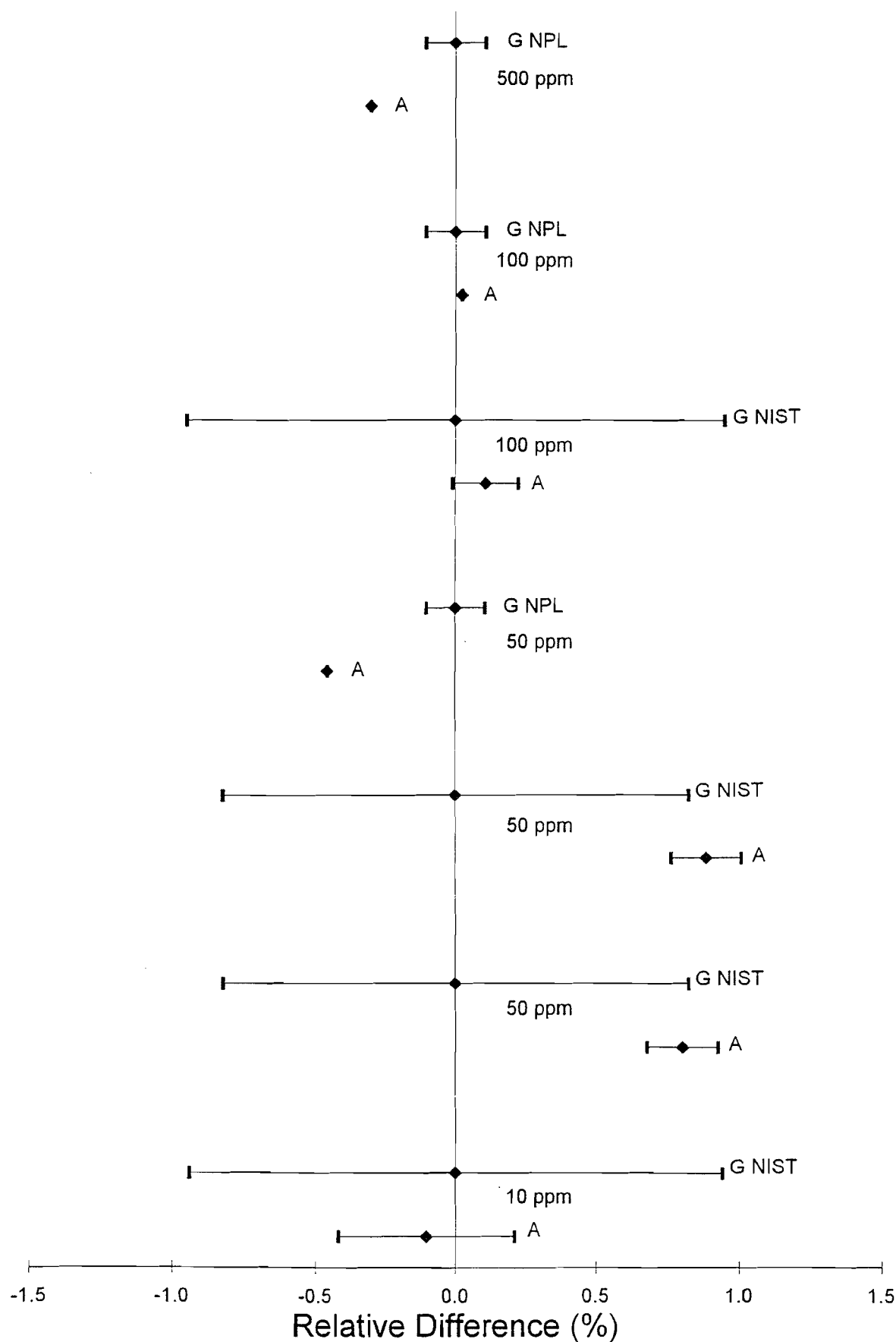


Table 6: Propane in Air NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction $\mu\text{ mol/mol}$	Uncertainty $\mu\text{ mol/mol}$	Analytical Amount Fraction $\mu\text{ mol/mol}$	Uncertainty $\mu\text{ mol/mol}$	Relative Difference %
500 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NPL	474.42	0.50	473.00		-0.30
100 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NPL	95.08	0.10	95.10		0.02
100 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NIST	94.80	0.90	94.90	0.11	0.11
50 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NIST	48.60	0.40	49.03	0.06	0.88
50 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NIST	48.60	0.40	48.99	0.06	0.80
50 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NPL	48.32	0.05	48.10		-0.46
10 $\mu\text{ mol/mol C}_3\text{H}_8/\text{AIR}$	NIST	9.57	0.09	9.56	0.03	-0.10

Table 7: Propane in Nitrogen NPL/NIST

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction $\mu\text{ mol/mol}$	Uncertainty $\mu\text{ mol/mol}$	Analytical Amount Fraction $\mu\text{ mol/mol}$	Uncertainty $\mu\text{ mol/mol}$	Relative Difference %
10000 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NIST	9814.00	98.00	9811.00	9.00	-0.03
10000 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NPL	9617	8	9630		0.14
1000 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NIST	973.7	9.7	971.1	0.9	-0.28
500 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NPL	492.54	0.5	493		0.09
500 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NIST	490.3	4.9	489.5	0.6	-0.16
100 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NIST	98.5	0.99	98.47	0.15	-0.03
100 $\mu\text{ mol/mol C}_3\text{H}_8/\text{N}_2$	NPL	97.18	0.1	97.3		0.12

ANNEX 1

Intercomparison of a Range of Primary Gas Standards of Carbon Monoxide in Nitrogen and Carbon Dioxide in Nitrogen Prepared by the National Institute of Standards and Technology and the National Physical Laboratory

Intercomparison of a Range of Primary Gas Standards of Carbon Monoxide in Nitrogen and Carbon Dioxide in Nitrogen Prepared by the National Institute of Standards and Technology[†] and the National Physical Laboratory

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■ Measurements were carried out by the National Physical Laboratory (NPL) in the United Kingdom and the National Institute of Standards and Technology (NIST) in the United States to intercompare the primary gravimetric gas standards developed by these two laboratories. These intercomparisons involved analyses of a set of CO and CO₂ NIST Standard Reference Materials by the NPL, and of a similar set of NPL primary standards by the NIST. In each case, the exact concentrations of the exchanged sets were unknown to the analyzing laboratory. The CO and CO₂ standards ranged in nominal concentration from 8% to 10 ppm and from 8% to 0.5%, respectively. The analyses were carried out using primary gravimetric standards, which were independently produced by the two laboratories. The mean difference between the values assigned by the supplying laboratory and the values determined by the analyzing laboratory was less than 0.2% relative for both sets of CO and CO₂ standards. The results confirmed that standards produced by NPL and NIST have a high degree of consistency, and that measurements obtained using these standards for measurements of levels of atmospheric CO and CO₂ may be directly intercompared.

Introduction

An increasing number of national laboratories around the world are preparing primary gas standards in order to provide a basis for ensuring the quality and intercomparability of measurements of pollutant gases in ambient

air. These primary standards, prepared by absolute gravimetric methods, are used to accurately determine and certify the concentrations of certified gas mixtures. These are then used as reference standards for the calibration of instruments employed for monitoring atmospheric pollution and air quality, and for the development and evaluation of improved monitoring methods. Applications involving certified gas standards include measurements of pollutant gas emissions from stationary and mobile sources, assessments of air quality in urban and workplace environments, and quantitative evaluations of changes in the trace gas composition of the atmosphere.

To ensure that such measurements are comparable throughout the world, it is necessary that gas standards prepared by different national laboratories agree with one another. One example where international uniformity is required is for measurements of gaseous pollutants produced by vehicles and aircraft, since these generally are manufactured for the international market. The predominant gaseous pollutants emitted from these sources include carbon monoxide, carbon dioxide, oxides of nitrogen and sulfur, and hydrocarbons. Reference standards for each of these gases are prepared at concentrations ranging from ~10% to several parts per million (ppm) in a balance gas of nitrogen or air.

The National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, in the United States has been preparing a wide range of gas standards since the late 1960s. The National Physical Laboratory (NPL) in the United Kingdom has been engaged in a similar program since 1976. Both laboratories supply certified gas reference standards in order to provide the basis for measurement quality assurance and to demonstrate intercomparability of measurements made by industry and government organizations. These standards are certified by direct comparison to the primary gravi-

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^{||} National Physical Laboratory.

Table I

(A) NPL Analysis of Purity of Parent Gases

component	concn, ppmv ^a
Carbon Monoxide	
methane	3 ± 1.5
ethane	0.1 ± 0.05
propane	0.07 ± 0.035
CO ₂	0.5 ± 0.025
O ₂	≤ 3
N ₂	74 ± 23
total impurity	79 ± 23
CO purity ^b	99.992 ± 0.008 mol %
Nitrogen Balance Gas	
CO	≤ 0.03
hydrocarbons	≤ 0.07
NO _x	< 0.2
CO ₂	≤ 0.03
argon	≤ 0.5
H ₂ O	≤ 0.1
O ₂	10 ± 2
total impurity	11 ± 2
N ₂ purity ^b	99.9989 ± 0.0011 mol %

(B) NIST Analysis of Purity of Carbon Dioxide Parent Gas

component ^c	concn, mol %
Carbon Dioxide	
N ₂	0.062 ± 0.0024
O ₂	0.019 ± 0.0008
H ₂ O	0.013 ± 0.002
hydrocarbons	< 0.001
CO ₂ purity ^b	99.906 ± 0.006

^a ppm by volume. ^b Purity determined by difference. ^c The CO₂ reagent was analyzed by mass spectrometry to identify its major impurities (nitrogen, oxygen, water vapor, and hydrocarbons), which were subsequently individually measured; the concentrations of nitrogen, oxygen, and hydrocarbons were determined by gas chromatography, while that of the water vapor was determined with a coulometric analyzer.

metric standards that are independently prepared and maintained at the two laboratories.

To assess the agreement between the gravimetric standards of NIST and NPL, a series of blind intercomparisons were carried out, involving the exchange of standards between the two laboratories. This report outlines the procedures used for the preparation of the gravimetric standards, describes the estimation of the total uncertainty assigned to the certified concentrations, discusses the methodology associated with the intercomparisons, and presents the results obtained from a range of CO/N₂ and CO₂/N₂ mixtures.

Experimental Section

Preparation of Primary Gas Standards at NPL

Primary gas standards are prepared at NPL in specially passivated, aluminum alloy cylinders. These are evacuated before use, and impurities are monitored with an on-line mass spectrometer. The parent gases used to prepare the gas mixtures are definitively analyzed for impurities by gas chromatographic and spectroscopic techniques. An example of the results obtained when analyzing the purity of CO, CO₂, and nitrogen is given in Table IA.

A set of three or more gas mixtures having a nominal concentration of ~10 mol % is prepared by accurate, consecutive transfers of known weights of the parent gases into each cylinder. A dilution of ~10:1 is then similarly made from one or more of the 10% mixtures to produce a set of mixtures having nominal concentrations of 1 mol

%, such that these mixtures are directly traceable to the parent 10% gravimetric standards. This process is repeated using sequential dilutions of approximately 10:1 to develop a hierarchy comprising sets of accurate standards ranging in concentration from 10 mol % down to a few ppm by mole. The sets of standards prepared at each dilution are repeatedly intercompared to demonstrate their internal consistency. Many such independent hierarchies of gas standards have been prepared for each gas mixture, with members of different hierarchies compared with those of similar concentration in other hierarchies to verify the self-consistency of the complete range of primary standards. Whenever new gravimetric standards are prepared to replace depleted ones, a stringent protocol of intercomparisons is followed to confirm that these new standards are consistent with the existing ones. A more detailed description of this process for preparing NPL primary standards has been reported (1).

Uncertainties in the Preparation of NPL Primary Gas Standards. The principal sources of error associated with the gravimetric preparation of primary gas standards at NPL fall into two general categories.

The first concerns uncertainties associated with the purity of the parent gases used to prepare the standards. Impurities in the parent gases would, if unaccounted for, give rise to systematic errors in the gravimetric concentrations of the primary standards. Hence, careful analyses of the parent gases are carried out to minimize such errors. Data obtained on the levels of impurities in all the components are then used to make the necessary corrections to the molar concentrations of the prepared standards. The remaining uncertainties in this category are due to the imprecision of the analyses of the impurities in the parent gases. These are used to estimate the uncertainty in the purity value assigned to each of the parent gases.

The second category is associated with the weighing procedures used during the preparation of the primary standards. These include the systematic uncertainty in the accuracy of the weights used, the statistical imprecisions in the individual weighings, the repeatability of the weighing process, and the uncertainty of atmospheric buoyancy corrections.

A more detailed analysis of these errors has been carried out (1). It is clear that the total uncertainty assigned to the concentration of different primary standards will be influenced by the purities of the parent gases and the number of dilutions used to prepare different standards. The total uncertainties in the NPL primary standards used in this intercomparison study, expressed at the 95% confidence level, are summarized in Tables II and III.

Preparation of Gas Standards at NIST. The methods used for the preparation of gaseous primary gravimetric standards at NIST are similar to those outlined above for NPL. The parent gases used to prepare the standards comprise at least one primary gas (e.g., CO or CO₂) and a balance gas (nitrogen or air). Initially, definitive analyses are carried out to determine the trace composition of each of the parent gases in order to determine their respective purities (see example for CO₂ in Table 1B). The balance gas is also analyzed to determine whether it contains any trace level of the primary gas of interest (e.g., CO or CO₂). These analyses provide information that is needed to calculate the concentration of the standards on a molar basis. Since the primary standards are used in the certification analysis of NIST gaseous Standard Reference Materials (SRMs), the results of the analyses of the parent gases are used also to verify that trace gas impurities are not present at levels that may

Table II. NPL Analysis of NIST SRMs of Carbon Monoxide in Nitrogen Using NPL Primary Standards^a

NIST SRM no.	2642	2641	2640	2639	2638	2637	
NIST sample no.	51-27-A	52-14-A	53-21-A	54-46-A	55-42-A	56-25-A	
NIST certified concn ^b	7.767 (0.08)	3.894 (0.04)	1.956 (0.02)	0.960 (0.010)	4679 ppm (47 ppm)	2397 ppm (24 ppm)	
NPL result ^b	7.730 (0.005)	3.893 (0.004)	1.946 (0.002)	0.959 (0.001)	4675 ppm (8 ppm)	2394 ppm (3 ppm)	
difference (NPL - NIST) ^b	-0.037	-0.001	-0.010	-0.001	-4 ppm	-3 ppm	
% difference	-0.48	-0.03	-0.51	-0.10	-0.09	-0.13	
NPL gravimetric uncertainty ^b	0.004	0.003	0.0015	0.0008	4.3 ppm	2.2 ppm	
NPL analytical uncertainty ^b	0.003	0.002	0.001	0.0005	6.9 ppm	2.6 ppm	
NIST SRM no.	1681	1680	2636	1679	1679	1678	1677
NIST sample no.	01-05-D	02-10-D	57-17-A	03-23-E	03-79-B	04-34-E	05-12-C
NIST certified concn ^c	956 (7)	475 (4)	243.6 (2.4)	97.1 (0.8)	93.8 (0.9)	44.9 (0.5)	9.62 (0.09)
NPL result ^c	954.8 (1.0)	475.2 (0.5)	242.4 (0.4)	96.99 (0.14)	93.83 (0.14)	44.86 (0.09)	9.64 (0.04)
difference (NPL - NIST) ^c	-1.2	+0.2	-1.2	-0.11	+0.03	-0.04	+0.02
% difference	-0.13	+0.04	-0.49	-0.11	+0.03	-0.09	+0.21
NPL gravimetric uncertainty ^c	0.90	0.50	0.33	0.13	0.13	0.07	0.03
NPL analytical uncertainty ^c	0.32	0.08	0.13	0.05	0.05	0.05	0.02

^aUncertainties (including those in parentheses) are expressed at the 95% confidence level. ^bValues are percent unless otherwise noted. ^cIn ppm by mole.

Table III. NPL Analysis of NIST SRMs of Carbon Dioxide in Nitrogen Using NPL Primary Standards^{a,b}

NIST SRM no.	1674	2626	2625	2624	2623	2622	2621	2620	2620	2619
NIST sample no.	7-21-B	37-16-B	36-24-A	35-40-B	34-05-A	33-42-B	32-03-B	31-19-B	31-34-B	30-09-B
NIST certified concn	7.12 (0.07)	3.8246 (0.0040)	3.5074 (0.0035)	2.8720 (0.0030)	2.5200 (0.0025)	1.8831 (0.0022)	1.4519 (0.0016)	0.9645 (0.0010)	0.9645 (0.0010)	0.5062 (0.0006)
NPL result	7.121 (0.006)	3.823 (0.004)	3.500 (0.006)	2.874 (0.003)	2.524 (0.006)	1.8830 (0.0034)	1.4505 (0.0018)	0.9643 (0.0009)	0.9638 (0.0009)	0.5061 (0.0010)
difference (NPL - NIST)	+0.001	-0.002	-0.007	+0.002	+0.004	-0.0001	-0.0014	-0.0002	-0.0007	-0.0001
% difference	+0.01	-0.04	-0.21	+0.07	+0.16	-0.01	-0.10	-0.02	-0.07	-0.02
NPL gravimetric uncertainty	0.004	0.003	0.0025	0.002	0.002	0.0015	0.0012	0.0008	0.0008	0.0005
NPL analytical uncertainty	0.005	0.003	0.005	0.002	0.006	0.003	0.0013	0.0005	0.0005	0.0009

^aUncertainties (including those in parentheses) are expressed at the 95% confidence level. ^bValues in percent.

affect the magnitude of an instrumental response to the primary gas during the SRM certification process.

The primary standards are prepared with a pressure-vacuum manifold system by consecutive transfer of accurately weighed amounts of the parent gases into pre-weighed, evacuated, specially passivated new aluminum alloy cylinders. Set of three or more primary standards are prepared gravimetrically in this manner, at concentrations ranging from several percent down to 200–300 ppm, such that a given set of standards brackets a specified concentration of interest. Primary standards down to several ppm are prepared from the higher concentration primary standards by accurate, consecutive dilutions, such that the lower concentration standards are directly traceable to the higher concentration standards. In all cases, primary standards prepared within each concentration level and between concentration levels are analyzed to verify that a high degree of consistency exists with respect to concentration. In some cases, larger sets of up to 20 standards are gravimetrically prepared to cover an entire range of concentrations of interest (e.g., CO₂/air standards covering a range from 300 to 400 ppm for global monitoring of atmospheric CO₂). In all cases, the sets of primary standards are intercompared by using a precise analytical method that has low instrumental noise and drift (e.g., nondispersive infrared analysis or gas chromatography). Consistent analytical data are obtained by carrying out repeated analyses within and between days, such that analytical imprecision is minimized and any observed instrumental drift is corrected. Existing standards are included in these intercomparisons to verify that newly

prepared standards demonstrate a consistent relationship with respect to concentration.

In common with the NPL procedure, the molar concentration assigned to a gravimetric primary standard prepared by NIST is calculated from the weights of the gases transferred into the cylinder and their respective molecular weights, corrected for the purity of the gases.

Uncertainties in the Preparation of NIST Primary Gas Standards. The random error associated with the preparation of the gravimetric standards can be estimated in two ways. One approach involves the summation of all systematic and statistical errors involved in the preparation, as discussed earlier. These include systematic uncertainties and imprecisions in the analysis of the purity of the parent gases, systematic uncertainties in the accuracy of the weights used, uncertainties in the estimates of buoyancy corrections during weighing, statistical imprecisions in the weighings, and the repeatability of the weighing process. Another method used to estimate the total error associated with the preparation of the gravimetric standards is to determine the standard error of the pooled differences between the gravimetric concentrations of the primary standards and their respective concentrations measured from a regression analysis of response data, developed from repeated analyses of the set of standards. This method, which includes both the random error of preparation of the gravimetric standards and the analytical imprecision of their intercomparisons, provides a more conservative estimate of the error associated with the preparation of the gravimetric standards. It represents a simple method for estimating the preparation error and

Table IV. NIST Analysis of NPL Primary Standards of Carbon Monoxide in Nitrogen Using NIST Primary Standards^a

	NPL cylinder no.			
	235	78	56	169
NPL gravimetric concn	7.679% (0.004%)	0.9449% (0.0008%)	958.3 ppm (0.9 ppm)	50.85 ppm (0.07 ppm)
NIST result	7.678% (0.017%)	0.9451% (0.0008%)	958.2 ppm (0.9 ppm)	50.7 ppm (0.1 ppm)
difference (NPL - NIST)	-0.001%	-0.0002	-0.1 ppm	+0.15 ppm
% difference	-0.01	-0.02	-0.01	+0.30
NIST gravimetric uncertainty	0.017%	0.0008%	0.8 ppm	0.09 ppm
NIST analytical uncertainty	0.0002%	0.0002%	0.4 ppm	0.01 ppm

^aUncertainties (including those in parentheses) are expressed at the 95% confidence level.

simultaneously provides a verification that all standards have been consistently prepared. When this method is used, numerous analyses are carried out to obtain an accurate measure of the instrumental response for each primary standard with respect to all other primary standards in the set. The estimated uncertainty obtained from these analyses reflects the total of all random errors associated with the preparation of a set of gravimetric standards. Systematic errors are minimized by correcting the gravimetric concentration for the purity of the gases and the presence of trace levels of the primary gas in the balance gas.

Another potential source of systematic error in primary gravimetric standards can arise due to sorption of a small amount of the primary gas of interest by the internal wall of the cylinder. The magnitude of this error is usually small for passivated aluminum cylinders, generally amounting to less than 0.2 ppm. Further, since the total uncertainty limit specified for most gas SRMs is in the order of 1% (95% confidence limit) relative to their certified concentrations, this error represents an insignificant contribution. This potential source of error must be considered, however, when primary standards are used for the certification of certain high-accuracy gas SRMs in the ppm range in which the total uncertainty limit is 0.1% (95% confidence limit) relative to their certified concentrations (i.e., CO₂/air SRMs in the concentration range of 300–400 ppm, but not for CO₂/nitrogen SRMs in the concentration range of 0.5–4.0% used in the present study.)

The uncertainties assigned to the NIST primary gravimetric standards that were used to analyze the NPL primary standards are given in Tables IV and V.

Use of NIST Primary Standards for Certification of SRMs. The primary gravimetric standards prepared and maintained by NIST are used to certify the accuracy of the concentration of a wide variety of gas SRMs, which are subsequently employed as national reference standards by industry and by government laboratories. These SRMs are prepared in homogeneous batches by specialty gas companies in accordance with NIST technical specifications. At NIST, all members of each batch are intercompared analytically to NIST primary gravimetric standards.

The procedure used for certifying gas SRMs involves three categories of analysis: (a) intercomparative analyses of the primary gravimetric standards to be used, (b) analytical comparisons of the primary standards with a cylinder selected at random from the batch (the "batch standard"), and (c) analytical comparison of the batch standard with all remaining cylinders in the batch. Step a is used to verify the stability and consistency of the respective concentrations of the primary standards. Step b is used to determine the concentration of the batch standard. Step c is used to determine the concentration of each of the remaining cylinders in the batch. Additional analyses are carried out over time, prior to certification,

Table V. NIST Analysis of NPL Primary Standards of Carbon Dioxide in Nitrogen Using NIST Primary Standards^{a,b}

	NPL cylinder no.			
	176	134	128	139
NPL gravimetric concn	7.102 (0.004)	4.479 (0.003)	0.9872 (0.0008)	0.5039 (0.0005)
NIST result	7.11 (0.020)	4.478 (0.003)	0.9862 (0.0010)	0.5049 (0.0016)
difference (NPL - NIST)	-0.008	+0.001	+0.0010	-0.0010
% difference	-0.11	+0.02	+0.10	-0.20
NIST gravimetric uncertainty	0.013	0.002	0.0004	0.0013
NIST analytical uncertainty	0.015	0.002	0.0009	0.0008

^aUncertainties (including those in parentheses) are expressed at the 95% confidence level. ^bValues in percent.

to verify the stability of the SRMs for periods of 2 years or more.

The total uncertainty (95% confidence level) assigned to the certified concentrations of gas SRMs is determined by doubling the quadrature summation of three principal sources of error in the certification process, viz.: (i) the uncertainty associated with the preparation of the NIST primary standards, (ii) the imprecision in intercomparing the batch standard to the primary standards, and (iii) the imprecision in intercomparing the batch standard to the remaining cylinders in the batch.

The total uncertainties of the certified concentrations of the SRMs used in this study are given in Tables II and III. It should be noted that the actual estimate of the total uncertainty made by NIST is typically lower than reported by NIST on an SRM certificate. It has been a NIST convention to report conservatively a total uncertainty that is in the order of 1% relative to the certified concentrations for most gas SRMs, and that is in the order of 0.1% for certain high-accuracy gas SRMs. Hence, the total uncertainties indicated for the high-accuracy CO₂ SRMs in Table III (SRMs 2619–2626) are nominally 0.1% relative to the certified concentrations, while those for all other SRMs listed in Tables II and III are nominally 1.0% relative.

Further details on the procedures used for certifying gas SRMs and for estimating the total uncertainty in NIST primary standards and SRMs have been described earlier (2).

Results and Discussion

Measurements of NIST SRMs at NPL. This study involved definitive analyses of 13 samples of SRMs of CO in nitrogen, ranging in CO concentration from 8% to 10 ppm, and 10 samples of SRMs of CO₂ in nitrogen, ranging

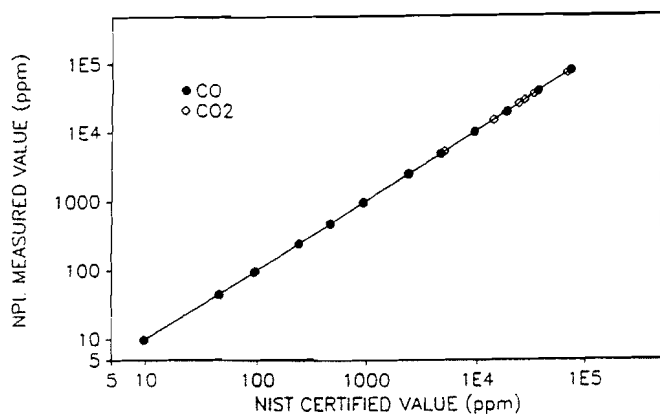


Figure 1. NPL analysis of NIST SRMs.

in CO₂ concentration from 7% to 0.5%, using primary standards prepared at NPL. While the nominal concentration of each SRM is specified in the NIST SRM catalog, the exact concentrations of the particular SRM cylinders submitted to NPL for this study were not specified. The procedure adopted was to bracket the nominal concentration of each SRM sample (by about $\pm 2\%$ of the relative value) by two or more NPL primary gravimetric standards. The gas mixtures were precisely intercompared by non-dispersive infrared (NDIR) analysis. Details of the methodology and instrumentation used in the intercomparison were similar to those outlined previously (1). However, it is appropriate to outline those aspects of the measurements that relate to the accuracy of the results. Several sources of uncertainty are present in the measurement procedure. One source of uncertainty in the analysis is due to the preparation of the NPL primary standards, as discussed earlier. Two additional sources of uncertainty are due to statistical and systematic errors that arise from the NDIR measurements used to compare the NPL primary standards with the NIST SRM samples.

Statistical uncertainties occur from NDIR analyzer noise and drift characteristics. The measurement procedure involves automatic data collection by a minicomputer system, which samples the NDIR signal numerous times within each measurement. This results in a small statistical uncertainty (typically, $\leq 0.1\%$ of value at one standard deviation).

Systematic uncertainties can arise if nonlinearities are present in the NDIR response. These errors, if unevaluated, can be significant, since a linear interpolation procedure is generally employed at NPL to derive the concentration of an unknown gas sample from the bracketing primary standards. In this study, however, the magnitude of this type of uncertainty was evaluated at all gas concentrations by employing a five-point calibration method to generate NDIR response curves. From these curves, values were derived to determine how close the concentration of the bracketing standards had to be to the unknown gas mixture to reduce this uncertainty to $\leq 0.05\%$ of value. Clearly, the magnitude of the bracketing concentration range depends on the analyzer used and the concentrations of the gases being analyzed. Based on the results, the concentrations of the bracketing cylinders were chosen typically to be within $\pm 2\%$ of the value of the unknown. This was verified by comparing the NDIR responses for a set of three NPL primary standards with their gravimetric values. No systematic differences were observed between measured and gravimetric values, indicating the absence of significant systematic differences due to the NDIR analyzers.

The concentrations determined for 13 NIST SRMs of CO/NO₂ and for 10 of CO₂/N₂ are shown in Tables II and

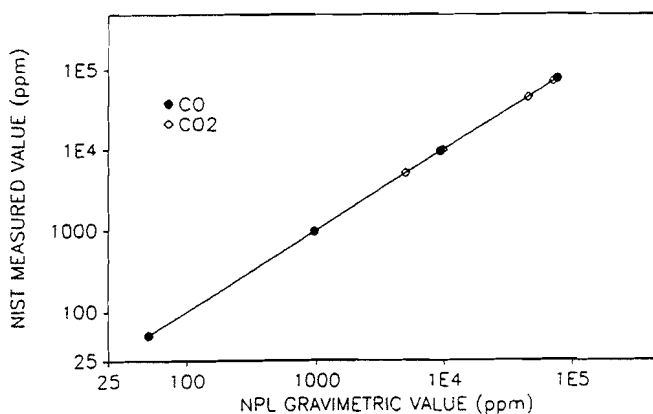


Figure 2. NIST analysis of NPL standards.

III, respectively. In each case, there is excellent agreement between the NPL measured value and the respective SRM certified value (Figure 1). The mean difference between these two values was less than 0.2% for the 13 CO/N₂ SRMs, and less than 0.1% for the 10 CO₂/N₂ SRMs. These results provide strong evidence that a high degree of consistency exists over a wide concentration range between primary standards prepared by NPL and NIST primary standards used to certify SRMs.

Measurements of NPL Primary Gravimetric Standards at NIST. Primary NPL standards, ranging in nominal concentration from 8% to 50 ppm for CO in nitrogen and from 7% to 0.5% for CO₂ in nitrogen, were submitted as unknown concentrations to NIST. The exact NPL concentrations of these standards were previously determined at NPL against the range of primary standards maintained by NPL. NIST employed both NDIR and gas chromatographic methods for analytically intercomparing the NIST primary gravimetric standards to the NPL primary standards. A set of four to six NIST primary standards was used in the analysis of each NPL primary gravimetric standard. The concentration of each NPL standard was measured by comparing its instrumental response with the regression curve formed by comparing the gravimetric concentrations of the NIST primary standards against their respective instrumental responses.

The results are summarized in Tables IV and V. Excellent agreement was found for each NPL standard between the NIST measured value and the NPL value (Figure 2). The mean difference between these two values was less than 0.2% relative for both sets of NPL primary standards.

Conclusions

A comprehensive set of measurements has been carried out to compare, for the first time, the primary gas standards of the NIST in the United States and the NPL in the United Kingdom. The results confirm that a high degree of consistency exists between primary gravimetric standards prepared by these two national standards laboratories for a wide range of concentrations of CO and CO₂ in nitrogen. They further demonstrate that standards produced by NPL and NIST for these two important pollutant gases are equivalent, and that measurements made in the United Kingdom and the United States using reference standards from these two national laboratories may be directly intercompared. This study also supports the concept that gravimetry is an excellent technique that may be used by national laboratories for producing accurate primary gas standards, and that reference standards traceable to these types of primary standards can be used to provide pollutant gas measurements that can be intercompared on an international basis.

Acknowledgment in Memorium. This paper is dedicated to Ernie Hughes, who pioneered the scientific development of the NIST gas SRM program, and who contributed so much of his technical knowledge to numerous interactions with experts in the gas analysis field, worldwide. In the present study, Ernie carried out the analyses of the NPL standards and supplied the SRMs that were analyzed by NPL, but passed away before this paper could be written. His unique insight into the requirements for accuracy in gas standards and trace gas analysis will be sorely missed by his many friends and scientific colleagues both in the United States and abroad.

Registry No. CO, 630-08-0; CO₂, 124-38-9.

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