

**The Preparation and Certification of Secondary Gas Standards
by the
National Physical Laboratory**

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Approved on behalf of Managing Director, NPL
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CONTENTS

	Page
1. INTRODUCTION	1
2. THE NPL PRIMARY GRAVIMETRIC FACILITY.....	2
2.1 PREPARATION PROCEDURE.....	2
2.1.1 Purity Analysis of Gaseous Components.....	2
2.1.2 Instrumentation for Preparing Gas Standards	2
2.1.3 Gravimetric Preparation Process.....	3
2.1.4 Validation of NPL Primary Gravimetric Standards.....	4
3. SECONDARY GAS STANDARDS.....	5
3.1 PREPARATION PROCEDURE.....	5
3.2 CERTIFICATION PROCESS	5
3.2.1 Apparatus.....	6
3.2.2 Experimental Procedure	6
4. CALCULATION OF MOLE FRACTION CONCENTRATIONS AND THE UNCERTAINTIES IN THE CONCENTRATIONS OF SECONDARY GAS STANDARDS	6
4.1 UNCERTAINTY BUDGET OF AN NPL GRAVIMETRIC STANDARD	7
4.1.1 Uncertainties arising from the Weighing Procedure.....	7
4.1.2 Uncertainties arising from Gas Purity.....	7
4.1.3 Uncertainties arising from Component Relative Molar Masses	8
4.1.4 Combination of the Uncertainty Components to Obtain the Overall Gravimetric Uncertainty	8
4.2 UNCERTAINTIES IN THE CERTIFICATION OF SECONDARY STANDARDS....	8
5. PERIOD OF CERTIFICATION AND RE-CERTIFICATION.....	10
6. SUMMARY	10
7. REFERENCES	11
8. LIST OF TABLES.....	12
9. LIST OF FIGURES.....	26

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1. INTRODUCTION

Atmospheric pollution, arising from sources such as motor vehicles, aircraft, and power generation and other industrial plants, is of increasing concern throughout the world. As a result, new and progressively more stringent legislation is being introduced to control its impact on the environment. Successful implementation of such legislation requires instruments that measure pollution levels accurately. This accuracy is most readily realised by making measurements which are traceable to recognised national or international measurement or calibration standards. Such standards are the subject of this Report.

Examples include measurements of:

- exhaust emissions from automobile and aircraft engines;
- emissions from chemical and combustion processes;
- air quality in rural and urban areas and work place atmospheres;
- natural gas for determination of calorific value and relative density.

Traceability is generally achieved in such measurements by utilizing one or more reference gas mixtures to calibrate the monitoring instruments. These reference mixtures are themselves traceable to accurate primary gas standards produced by a national standards laboratory or a similar organisation.

The National Physical Laboratory (NPL), as the UK's national standards laboratory, prepares and maintains Primary Gas Standards, which cover a wide range of gaseous species and concentrations. These standards, which are prepared by absolute gravimetric methods, are used to certify other gas mixtures, which are known as Secondary Gas Standards. These Secondary Gas Standards are subsequently disseminated to, and employed by, UK industry and government laboratories as nationally-traceable standards.

This Report provides a short description of the NPL Primary Gas Standards Facility, discusses the methods used to prepare and certify secondary gas standards in a manner which is traceable to these Primary Standards, gives the uncertainties assigned to the concentration values of these secondary standards, and outlines the procedure used for re-certification of these secondary standards, where this is required. The Report covers gas standards with concentration ranges of greater than 1ppm. Other techniques may be used for standards which have concentrations lower than this.

More information can be obtained from our website at WWW.NPL.CO.UK/ENVIRONMENT

2. THE NPL PRIMARY GRAVIMETRIC FACILITY

Primary Gas Standards are generally prepared at the NPL in passivated aluminium-alloy cylinders using absolute gravimetric procedures. The parent gases employed for this have their purities comprehensively verified using a range of different analytical techniques. The concentrations of these prepared standards are subsequently validated using stringent accuracy and stability tests. An outline of these is given below.

2. PREPARATION PROCEDURE

2.1.1 Purity Analysis of Gaseous Components

The components employed in the preparation of gas standards are all analysed before use with the following instrumentation.

- (i) A high-resolution, rapid-scanning, fourier-transform spectrometer coupled to a multi-pass absorption gas cell, which can be operated with path lengths between 4 and 120 metres. This facility identifies and measures quantitatively any gaseous species present which has an infrared absorption spectrum in the wavelength range 600 to 4000 cm^{-1} , as this covers the strong absorption bands of virtually all infrared-active gases. Additional measurements may be carried out in the ultraviolet spectral region where this is required. By comparing the amount of absorption from a gas of unknown concentration with that from similar gases with known concentrations the unknown concentration can be determined. Examples of trace gas detection limits achieved with this facility are given in Table 1.
- (ii) Gas chromatography involves passing the test gas through a column coated with a suitable adsorbent material. Components in a mixture have different tendencies to adsorb onto the column surface and will hence traverse the column at different rates. The components will therefore elute from the column at different times after the test gas was first injected. Typical detection limits are shown in Table 2. The values shown in Table 2 can be improved by at least three orders of magnitude for volatile species such as hydrocarbons by using a cryogenic pre-concentration technique.

Table 3(i) shows the maximum permissible impurity levels in minor component gases used in the preparation of NPL Secondary Standards. Table 3(ii) contains similar information for the major component gases.

2.1.2 Instrumentation for Preparing Gas Standards

As mentioned previously, all Primary Gas Standards are prepared gravimetrically in aluminium-alloy cylinders. These cylinders are currently obtained from BOC Ltd, SCOTT, or Air Products depending on their application, and are passivated using their own proprietary processes. (Specific cylinder suppliers are used for different gaseous species). Tests carried out at NIST (National Institute of Standards and Technology USA), NPL, and elsewhere have shown that the concentrations of many gas mixtures stored in these types of cylinders remains stable in excess of two years, and in many cases for more than five years.

NPL have shown certain gases to be more stable in cylinders that have undergone specific passivation processes. Thus, as noted above, a specific cylinder treatment is chosen for a particular

requirement. Over the past years NPL has worked closely with the different passivated cylinder manufacturers to improve these passivation techniques, in order to increase the stability of the more stable gases (eg CO, CO₂, C₃H₈ and CH₄), and more recently also to improve the stability for reactive gases (eg NH₃, Cl₂ and HCl).

High-vacuum apparatus is used to evacuate the passivated cylinders prior to their filling. These cylinders may be 'baked' at elevated temperatures under vacuum, where appropriate, to further ensure that no contamination is present. A computer controlled mass spectrometer is connected to the vacuum apparatus and is used daily for on-line diagnostics of impurities and leaks. Figure 1 shows a schematic diagram of the evacuation system.

A gas blending system, which was specially developed by NPL, is used to transfer the pure parent gases and gas mixtures into the recipient cylinders. This method is used both in the preparation of primary and secondary gas standards. Figure 2 shows a schematic diagram of this gas blending system.

Calibrated pressure and on-line mass measuring instrumentation is used to indicate the gas-mixing ratio. The final gas concentration is, however, derived from the molar fraction determined from accurate mass measurements. These accurate mass measurements are performed using two-pan equal-arm off-line balances. Their specifications are listed in Table 4.

2.1.3 Gravimetric Preparation Process

Gas standards are generally first prepared by a ten-to-one dilution process from the nominally pure parent gases. These standards are then used as the sources of further dilutions.

The passivated cylinders used to contain the mixtures are initially evacuated for a period of at least 48 hours, or until a pressure of less than 10^{-5} Pa is achieved. Prior to the cylinder removal from the evacuation line, a mass spectrum is produced to check for residual concentrations of extraneous gaseous species, which may contaminate the standard in production.

Each evacuated cylinder is then weighed on a two-pan balance against a tare cylinder of nominally identical volume and mass. The cylinder is then attached to the filling line and the line is evacuated to less than 10^{-2} Pa. Approximately 10 bar of the minor gas component(s) is transferred into the cylinder, which is then re-weighed on the same two-pan balance. The cylinder is then filled with a pre-determined mass of nitrogen, synthetic air or other diluent gas using the on-line balance (Figure 2). The cylinder is finally re-weighed and the masses of the minor and major components are calculated. These values are then used by the NPL proprietary software (known as Gravcalc), which calculates the absolute mole fraction(s) and the uncertainty of the mole fractions of the new gas mixture. The equations used to determine the mole fraction and measurement uncertainty can be found in Section 4.

Standards with nominally the same value are prepared with similar concentrations (within 2% to 4% relative of value). Rigorous quality assurance measurements and analytical tests are carried out on these to validate their concentrations and stability (see Section 2.1.4 below). Using this method, a family of gas standards is produced from about 100 mmol.mol⁻¹ (10%) to below 1 μmol.mol⁻¹ (1ppm). Several independent families of standards are prepared for each type of gas standard, and these independent families are used in one aspect of the procedure for validating the accuracy of the complete range of Primary Gas Standards.

2.1.4 Validation of NPL Primary Gravimetric Standards

The procedure used to validate the absolute concentrations of the range of NPL gravimetric standards has several stages, as indicated below:

- (i) The instruments and techniques outlined in Section 2.1.1 are used to check the concentration of all gaseous constituents in the standards other than the specified minor and major components.

This verifies that no impurities or extraneous species have become entrained into the cylinders during the preparation process and that no subsequent chemical reactions have taken place.

All sources of uncertainty, both type A and B, that occur during the complete preparation process are itemised and quantified. These are then combined (see Section 4) in a square-root sum-of-squares manner to produce a combined uncertainty, which is then used to produce and expanded uncertainty with the use of an appropriate k- factor.

The value of this uncertainty will depend on a number of factors including the purity of the component gases, the complete weighing procedure, and any uncertainties arising from the relative molar masses. Table 7 gives a typical budget of the measurement uncertainties in the weighing process determined during the preparation of an individual NPL primary standard, and Table 5 summarises the expanded uncertainties generally assigned to the absolute concentrations of the NPL Primary Standards. These uncertainties are not the best achievable, but are judged to be fit-for-purpose for most cases.

The newly-prepared Primary Standard is intercompared against two or more existing Primary Standards using instruments with sufficient repeatability to demonstrate that their measured and gravimetric values are consistent within the overall uncertainties indicated in (ii) above (See table 6). (The apparatus and measurement procedure used for this intercomparison are equivalent to that used to certify the concentrations of the Secondary Standard gas mixtures. This is discussed in more detail in Section 3.2.1.) The intercomparison procedure involves using the primary standards with the smallest and largest concentrations to bracket the new Primary Standard, which is treated as an unknown. If the analytical value obtained for the new standard differs significantly from its gravimetric value, (typically $\pm 0.1\%$) it indicates an inconsistency in the new standard and it is discarded. To date, no such discrepancies have been detected.

Standards with similar concentrations from different families are also intercompared using the procedure outlined in (iii). These measurements are carried out over the entire concentration range in order to demonstrate the consistency of the complete set of standards of a given component mixture.

- (v) Repeated intercomparisons are carried out in the manner outlined in (iii) above to demonstrate the long-term stability of the set of standards.

New batches of standards are produced regularly. These are intercompared with each other and also with older standards using the procedure outlined in (iii) to confirm the accuracy of the overall process.

Validation of NPL Standards by Intercomparisons with those of other National Measurement Institutes

A wide range of international comparisons has been carried out to demonstrate the validity of NPL's Primary Gas Standards. These have included NPL's gas standards are regularly intercompared with those of other national standards laboratories. For example:

- An ongoing measurement exercise carried out with the National Institute of Standards and Technology (NIST) USA (1) demonstrated the consistency of the CO/N₂ and CO/N₂ standards prepared by NPL and NIST over a wide range of concentrations. A similar intercomparison exercise was also completed on the concentration range of NO/N₂, C₃H₈/air and C₈H₃/N₂ standards (2).
- Other intercomparisons which have also been carried out with, for example, the Netherlands Measurement Institute (NMI) (3), The Netherlands, as part of Euromet agreements.

Tables 10-14 and Figures 3-16 outline some of these results.

In addition, a range of 'round-robin' intercomparisons are organised by the Consultative Committee for Amount of Substance (CCQM) within the aegis of the International Committee for Weights and Measures (CIPM). These are carried out to investigate the international uniformity of gas standards produced by selected national standard laboratories, or other designated reference laboratories. The results of these comparisons can be found within the key comparison database on the BIPM website at WWW.BIPM.Fr

3. SECONDARY GAS STANDARDS

3. PREPARATION PROCEDURE

Secondary Gas Standards are prepared in-house using the parent gases of the same specifications as those employed for the production of the primary gravimetric standards. This ensures that the gases used are of certified purity and contain no species that would affect the certified concentration values or be detrimental to the stability of the mixtures. The purity of the parent gases are checked against the manufacturers specification using gas chromatography and fourier-transform infrared techniques.

The Secondary gas standards are blended using the same apparatus as that employed to prepare the primary gravimetric standards (Figure 2). Precise measurements of the gas pressure and gas mass at each stage in the process enables the concentrations of the mixtures to be produced to within $\pm 1\%$ of the concentration of the appropriate NPL gravimetric standard. More than three mixtures with the same nominal concentrations can be produced together. These mixtures are subjected to stability checks before their concentrations are certified with respect to the NPL's primary standards (see Section 4).

CERTIFICATION PROCESS

The gravimetrically-prepared Secondary Gas Standards are checked soon after preparation to confirm that their concentrations are as expected. They are then allowed to stand for a defined period before final certification is carried out. Following this period, all secondary standards are

certified individually against NPL's gravimetrically prepared Primary Gas Standards as discussed below.

Apparatus

An Automatic Gas Analysis System (AGAS) is used to certify the concentrations of the Secondary Standards. The AGAS contains dedicated gas analysers for each of the species used in the standards. The various analysers employ different instrumental techniques and these are summarised in Table 6.

PCs are used to control AGAS, which allows zero gas, selected Primary Gas Standards, and the unknown Secondary Gas Standard, to be directed in rapid succession into the appropriate analyser. The AGAS then records the analyser's responses for each of the gases and subsequently uses these values to calculate the concentration of the new Secondary Gas Standard, and other statistical information relating to the precision of the analysis.

Experimental Procedure

The certification procedure involves bracketing the concentration of the Secondary Standard between adjacent concentrations of two Primary Gas Standards. It assumes that a linear algebraic interpolation of the analyser response can be made between the concentrations of these two standards. However, the responses of the analysers listed in Table 6 all exhibit some non-linearity in their behaviour as a function of gas concentration. The magnitude of this non-linearity will depend both on the analyser employed and on the concentrations of the gases being analysed. Therefore, to allow for this, the response of each analyser is measured over the required range of concentrations by generating a four or five point calibration curve with appropriate known-concentration standards. The issue of the analyser non-linearity is then overcome by ensuring that the difference in the concentrations of the two bracketing standards is small enough that the uncertainty in assuming a linear response is small compared with the uncertainty of the overall certification process. To achieve this the concentrations of the bracketing standards are chosen to be within $\pm 4\%$ of each other, with the concentration of the secondary standard between them, so that an uncertainty of less than $\pm 0.1\%$ relative of value is achieved. This procedure is verified regularly by comparing the analytical results obtained with sets of NPL gravimetric standards with their gravimetric values.

4. CALCULATION OF MOLE FRACTION CONCENTRATIONS AND THE UNCERTAINTIES IN THE CONCENTRATIONS OF SECONDARY GAS STANDARDS

Consider the case of a gas mixture being prepared from a number of different cylinders containing different gas mixtures. Many of these gases in the starting mixtures may be regarded as impurities. The mole fraction of the prepared gas mixture may then be expressed as:

$$X_k = \frac{\sum_{j=1}^P \frac{(m_j \cdot X_{jk})}{(\sum_{i=1}^n X_{ij} \cdot M_i)}}{\sum_{j=1}^P \frac{m_j}{(\sum_{i=1}^n X_{ij} \cdot M_i)}}$$

P	=	total number of parent gases
j	=	j^{th} parent gas
n	=	number of quantified components in final mixture
i	=	i^{th} component in cylinder j
k	=	k^{th} component in final mixture
M_i	=	relative molecular mass of component i
X_{ij}	=	mole fraction of component i in parent gas j
m_i	=	mass of j^{th} parent gas in the final mixture

4.1 UNCERTAINTY BUDGET OF AN NPL GRAVIMETRIC STANDARD

The uncertainty in the accuracy of any given primary gravimetric standard is obtained from the uncertainties associated with the weighing procedure used to produce the standard, those which arise from the purity and from the relative molecular masses of its constituents, and those associated with the mole fraction uncertainty. The uncertainty due to the sequential dilution process is also incorporated into the overall uncertainty budget. A Report detailing this determination of the measurement uncertainties assigned to the NPL Primary Standard Gas Mixtures is being published.

4.1.1 Uncertainties arising from the Weighing Procedure

The sources of uncertainties arising in the weighing procedure have been grouped together into the following categories:

- Balance Repeatability
- Thermal Drift
- Time Drift
- Draught Instability
- Location of Cylinder on Balance
- Mass Piece Uncertainty
- Resolution of Balance
- Sensitivity of Balance
- Buoyancy Correction
- Expansion of Cylinder due to pressure
- Mechanical Handling of Cylinder

Each of the categories has an assigned value, which was attained from experimentation. These values comprise both type A (the repeatability or randomness of a measurement process) and type B (those that account for errors that remain constant while the measurement is made) uncertainties. The probability distributions are determined for each of the categories and an appropriate divisor is then used. The values are summated as square root sum of squares to give a combined weighing uncertainty. (See Table 7).

Uncertainties arising from Gas Purity

Purity analyses are performed for all parent gases used, and the purities and uncertainties are determined. These impurity measurements are used in the Gravcalc software to produce the calculated mole fraction of the standard. The sequential dilution of one standard to produce the corresponding lower value in the hierarchical structure incurs a greater relative uncertainty as the concentration is reduced, so that the relative uncertainty increases each time a dilution is made. It is a necessary condition of the NPL uncertainty estimation procedure that the sum of all component mole fractions are equal to 1, and under these conditions it is assumed that perfect correlation applies.

4.1.3 Uncertainties arising from Component Relative Molar Masses

The relative molar masses of the gaseous components and the associated uncertainty in the relative molar masses are given in Table 8. The relative molar mass and uncertainties are combined with the gas purity and weighing uncertainty using the GRAV CALC software.

4.1.4 Combination of the Uncertainty Components to Obtain the Overall Gravimetric Uncertainty

To obtain the combined standard uncertainty, the standard uncertainties are combined using the law of propagation of uncertainty shown below:

$$U_c^2(X_k) = dX_k^2 = \left[\sum_{t=1}^n \left(\frac{\partial X_k}{\partial M_t} \right)^2 (dM_t)^2 + \sum_{s=1}^p \left(\frac{\partial X_k}{\partial m_s} \right)^2 (dm_s)^2 + \sum_{s=1}^p \sum_{t=1}^n \left(\frac{\partial X_k}{\partial X_{ts}} \right)^2 (dX_{ts})^2 \right]$$

where:

dm_s = standard uncertainty in the weighed mass of gas from cylinders
 dM_t = standard uncertainty in the relative molar mass component t
 dX_{ts} = standard uncertainty in the mole fraction of component t in cylinders

This expression relates to standard uncertainties, which are not correlated and have a simple non-linear functional form.

All the standard uncertainties have initially been expressed with a 68% confidence level, and hence this combined standard uncertainty $U_c(X)$ will also have this level of confidence.

Table 5 shows the expanded uncertainties at a level of confidence of approximately 95% usually assigned to the absolute concentrations of NPL Primary Gravimetric Standards.

4.2 UNCERTAINTIES IN THE CERTIFICATION OF SECONDARY STANDARDS

In order to obtain a value for the concentration of a Secondary Standard, the following data is collected sequentially from the AGAS system.

A	Zero gas	Adjust to zero
B	High concentration NPL Primary Standard	Adjust to full scale
C	Zero gas	No adjustment
D	Low concentration NPL Primary Standard	No adjustment
E	High concentration NPL Primary Standard	No adjustment

F	Zero gas	No adjustment
G	Secondary Standard	No adjustment
H	High concentration NPL Primary Standard	No adjustment
J	Zero gas	No adjustment

Identical gas-flow rates and sample pressures are used for each of the operations A-J. This is achieved by using calibrated pressure regulators and a mass-flow controller. The AGAS computer samples the instrument analogue signal at a rate of 14 Hz. In addition, multiple sets of data are sampled sequentially and the mean signal obtained and its standard deviation is compared with the previous data set, which enables checks to be performed on the stability of these readings. The concentration of the Secondary Standard is then obtained from these results using the following formula:

$$X_{ss} = X_L + (X_H - X_L) \left[\frac{Y_{ss} - Y_L}{Y_H - Y_L} \right]$$

where X_L = concentration of low-value NPL Primary Standard
 X_H = concentration of high-value NPL Primary Standard
 Y_L = stabilised analogue output for low-concentration Primary Standard
 Y_H = stabilised analogue output for high-concentration Primary Standard
 Y_{ss} = stabilised analogue output for Secondary Standard

This process is repeated between six and ten times (depending on the concentration of the mixtures, and the uncertainty determined from the measurements) to form the mean value for the certified concentration of the Secondary Standard. Two such results are obtained on at least two different days with one pair of Primary Gas Standards, and the complete procedure is repeated using different pairs of standards. The concentration of the Secondary Standard is then obtained by taking the mean of these values.

The statistical uncertainty arising from the analytical measurement is derived from the automatic data collection procedure noted before. The AGAS computer performs a standard error analysis and produces both a mean and the standard error of the mean associated with that value. A computer program is used to combine the uncertainties from the primary gravimetric process with the uncertainties produced from the standard deviation of the instrument's response for each of the gas mixtures.

Thus, the uncertainty in the certification of the Secondary Standard σ_x^2 , is:

$$\sigma_x^2 = \left(\frac{1}{R_2 - R_1} \right)^2 \left[(R_2 - X)^2 \sigma_{R1}^2 + (X - R_1)^2 \sigma_{R2}^2 \right] \frac{1}{(y_2 - y_1)^2} \left\{ (y_2 - y_1)^2 \sigma_y^2 + (y_2 - y_1)^2 \sigma_{y1}^2 + (y_2 - y_1)^2 \sigma_{y2}^2 \right\}$$

where

R_1 = low reference Primary Gas Standard Gravimetric concentration value
 R_2 = high reference Primary Gas Standard Gravimetric concentration value
 X = Calculated concentration of Secondary Standard from linear interpolation
 σ_{R1} = Gravimetric uncertainty of Low Reference Standard
 σ_{R2} = Gravimetric uncertainty of High Reference Standard
 y_1 = Instrumental response to Low Reference Standard

y_2 = Instrumental response to High Reference Standard
 σ_{y1} = Standard deviation of the response of instrument to Low Reference Standard
 σ_{y2} = Standard deviation of the response of instrument to High Reference Standard
 Y = Instrumental response to Secondary Standard
 σ_Y = Standard deviation of the response of the instrument to Secondary Standard.

Measurement anomalies due to non-linearities of the gas analysers have been determined and assigned a value of $\pm 0.1\%$ relative (at 95% level of confidence). These values are added to the combined standard uncertainties.

The expanded uncertainty U is obtained by multiplying σ_x by an appropriate coverage factor (k).

Thus $U = k\sigma_x$, and the concentration of the Secondary Standard is expressed as $X_{ss} \pm U$

Table 9 gives examples of the expanded uncertainties, which are routinely assigned to the absolute concentrations of the NPL Secondary Standards, expressed at a level of confidence of approximately 95%,

5. PERIOD OF CERTIFICATION AND RE-CERTIFICATION

A long history (> 10 years in many circumstances) of stability measurements on NPL's Primary Gas Standards for CO/N_2 , CO_2/N_2 , NO/N_2 , $\text{C}_3\text{H}_8/\text{air}$ and $\text{C}_3\text{H}_8/\text{N}_2$ over the concentration range 10% to 1 ppm have demonstrated that a two-year certification period may be assumed conservatively. Then, if a customer requests re-certification of a secondary standard, or a secondary standard has not been sold after a two-year period, then re-analysis is carried out using the procedure outlined in Section 3.2.

Where re-certification is required, the following conditions are observed

- (i) The Secondary Standard must have a total pressure of greater than 30 bar.
- (ii) If the returned cylinder corresponds with a batch that has already been measured and shown to be stable, one set of validation measurements will be performed and the existing certified value re-issued.
- (iii) If there is no previous batch member available, a complete certification process will be performed.

6. SUMMARY

The National Physical Laboratory has established and, currently maintains a national facility where a wide range of Primary Gas Standards are prepared and maintained. These Primary Standards, which provide the basis for accurate, traceable measurements of industrial and transport emissions, industrial process control, calorific value determination of natural gas, occupational exposure, and atmosphere pollution, are prepared at the highest levels of precision by absolute gravimetric methods in special passivated containers, and their concentrations are directly traceable to the primary standard of mass. They are subsequently used either to verify the concentrations of Primary Reference Gas Mixtures or to certify the concentrations of Secondary Standards. Each of these Standards is certified at NPL using a precise, well-validated procedure, which entails bracketing its concentration between adjacent concentrations of Primary Gas Standards. The

resulting accuracy in the certified concentration of the Secondary Standard is generally better than $\pm 1\%$, relative of its value (at a level of confidence of 95%). Traceable Standards with better measurement uncertainties, typically $\pm 0.2\%$ relative (Primary Certified Reference Gas Mixtures) are also available. These Standards are subsequently supplied to UK industry and government laboratories where they are employed as nationally traceable working standards.

NPL also participates in appropriate international intercomparisons of gas standards with, for example, recognised European national standards laboratories eg NMI The Netherlands, and the National Institute of Standards and Technology USA, in order to demonstrate the accuracy and international uniformity of these reference gas mixtures.

7. REFERENCES

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8 LIST OF TABLES

Table 1	Trace Gas Detection Limits achieved when measuring Pure Component Gases using NPL Fourier-Transform Spectrophotometer.
Table 2:	Trace-Gas Detection Limits achieved routinely using Gas Chromatography.
Table 3:	Maximum Permissible Impurity Levels in Gases Used for NPL Secondary Standards.
Table 4:	Specifications of the Two-Pan Reverifications Balances.
Table 5	Total Expanded Uncertainties at 95% Confidence Level assigned to Absolute Concentrations of NPL Primary Gravimetric Standards.
Table 6:	Manufacturers' Specifications for Analytical Instrumentation used by NPL.
Table 7:	Lists the Major Contributors to the Weighing and Physical Handling Uncertainty at 68% Confidence Limits.
Table 8:	Typically used Relative Molar Masses and their Uncertainties.
Table 9:	NPL Secondary Standards and their Expanded Uncertainties (95% Confidence Level).
Table 10:	Standard Gas Comparisons with NMi, The Netherlands at % levels.
Table 11	Standard Gas Comparisons with NMi, The Netherlands at ppm levels.
Table 12:	Comparison of Multi-component Motor Vehicle Exhaust Mixtures with NMi, The Netherlands.
Table 13:	Standard Gas Comparisons with NIST, USA at % levels.
Table 14:	Standard Gas Comparisons with NIST, USA at ppm levels.

TABLE 1**TRACE GAS DETECTION LIMITS ACHIEVED ROUTINELY WHEN MEASURING
PURE COMPONENT GASES USING NPL FOURIER-TRANSFORM
SPECTROPHOTOMETER**

Gas	Mole fraction (ppm)
CO	0.003
CO ₂	0.001
NO	0.1
NO ₂	0.01
N ₂ O	0.01
CH ₄	0.001
C ₂ H ₄	0.001
Other VOCs	0.001
H ₂ O	0.1
SO ₂	0.01
H ₂ S	0.5

TABLE 2**TRACE-GAS DETECTION LIMITS ACHIEVED USING GAS CHROMATOGRAPHY**

GAS	MOLE FRACTION (ppm)
H ₂	< 0.01
O ₂	< 0.05
N ₂	< 0.05
Ar	< 0.05
CH ₄	< 0.01
C ₂ H ₆	< 0.001
Other VOCs	< 0.0001
NO	< 0.01
N ₂ O	< 0.01
CO ₂	< 0.01
CO	< 0.02
H ₂ O	0.2

TABLE 3**MAXIMUM PERMISSABLE IMPURITY LEVELS IN GASES USED FOR NPL
SECONDARY STANDARDS****(i) Minor Component Gases**

Carbon Monoxide	Carbon dioxide	Nitric oxide	Propane
CH ₄ ≤ 2 ppm	C _n H _m ≤ 1 ppm	CO ₂ ≤ 100 ppm	C _n H _m ≤ 20 ppm
C _n H _m ≤ 1 ppm	CO ≤ 1 ppm	Ar ≤ 100 ppm	N ₂ ≤ 1000 ppm
CO ₂ ≤ 1 ppm	Ar ≤ 1 ppm	N ₂ ≤ 2500 ppm	O ₂ ≤ 100 ppm
Ar ≤ 1 ppm	N ₂ ≤ 1 ppm	N ₂ O ≤ 1500 ppm	H ₂ O ≤ 3 ppm
N ₂ ≤ 80 ppm	O ₂ ≤ 1 ppm	NO ₂ ≤ 100 ppm	
O ₂ ≤ 10 ppm	H ₂ ≤ 1 ppm		
H ₂ ≤ 10 ppm	H ₂ O ≤ 3 ppm		
H ₂ O ≤ 10 ppm			
Purity ≥ 99.99%	Purity ≥ 99.999%	Purity ≥ 99.7%	Purity ≥ 99.9%

(ii) Major component gases (Nitrogen)

Gas	Mole Fraction (ppm)
CO	≤ 0.1
CO ₂	≤ 0.1
C _n H _m	(for C ₃ H ₈ mixtures this should not exceed 0.1 ppm expressed as C ₃ equivalent)
NO _x	≤ 0.1
N ₂ O	≤ 0.1
Ar	≤ 50
O ₂	≤ 1 (for NO/ N ₂ ≤ 0.1 ppm)
H ₂ O	≤ 1 (for NO/ N ₂ ≤ 0.1 ppm)
Sulphur compounds	≤ 10

TABLE 4

SPECIFICATIONS OF THE TWO-PAN REVERIFICATIONS BALANCES

Type	Two pan, equal arm
Load	25 kg
Sensitivity	0.001 g
Repeatability	0.005 g

TABLE 5

TOTAL EXPANDED UNCERTAINTIES AT 95% CONFIDENCE LEVEL ASSIGNED TO ABSOLUTE CONCENTRATIONS OF NPL PRIMARY GRAVIMETRIC STANDARDS.

Normal Concentration	Gas mixtures				
	CO/N ₂	CO ₂ /N ₂	NO/N ₂	C ₃ H ₈ /air	C ₃ H ₈ /N ₂
7%	0.004%	0.004%			
5%		0.004%			
4%	0.003%	0.003%			
3.5%		0.002%			
3%		0.0025%			
2.5%		0.002%			
2%	0.0015%	0.0015%			
1.5%		0.0012%			
1%	0.0008%	0.0008%	0.0008%	0.0008%	0.0008%
5000 ppm	4.3 ppm	5 ppm	4.4 ppm		
2500 ppm	2.2 ppm		2.3 ppm	2.2 ppm	
1000 ppm	0.9 ppm		1.0 ppm	0.9 ppm	0.9 ppm
500 ppm	0.50 ppm		0.60 ppm	0.50 ppm	0.50 ppm
250 ppm	0.33 ppm		0.35 ppm		
100 ppm	0.13 ppm		0.20 ppm	0.10 ppm	0.10 ppm
50 ppm	0.07 ppm		0.15 ppm	0.05 ppm	
10 ppm	0.03 ppm		0.10 ppm	0.01 ppm	

TABLE 6**MANUFACTURERS' SPECIFICATIONS FOR ANALYTICAL INSTRUMENTATION USED BY NPL**

Carbon Monoxide (Non-dispersive infrared)					
Analyser	Ranges Available (FSD)	Repeatability (FSD)	Zero Drift (FSD over 24 hours)	Stability (FSD over 24 hours)	Response Time (90% FSD)
Hartmann and Braun URAS 10E	20%	$\pm 0.5\%$	$\pm 1\%$	$\pm 1\%$	8 secs
Beckman 864-12	2.5% 1.0% 0.5%	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	2.5 secs
Hartmann and Braun URAS 3G	1000 ppm 500 ppm 100 ppm	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	8 secs
Horiba GA 360E	10 ppm 5 ppm 2 ppm 1 ppm	$\pm 1\%$	$\pm 0.01\%$	$\pm 0.4\%$	180 secs
Rosemount NGA 2000	1.2% 1000 ppm 100 ppm 10 ppm	$\pm 1\%$	$\pm 1\%$	$\pm 1.0\%$	2-15 secs

Carbon Dioxide (Non-dispersive infrared)					
Analyser	Ranges Available (FSD)	Repeatability (FSD)	Zero Drift (FSD over 24 hours)	Stability (FSD over 24 hours)	Response Time (90% FSD)
Hartmann and Braun URAS 10E	10% 5.0% 2.5%	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	<8 secs
Rosemount NGA 2000	2000 ppm 100 ppm	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	<2-15 secs

Methane (Non-dispersive infrared)					
Analyser	Ranges Available (FSD)	Repeatability (FSD)	Zero Drift (FSD over 24 hours)	Stability (FSD over 24 hours)	Response Time (90% FSD)
Horiba GA 360E	10 ppm 5 ppm 2 ppm 1 ppm	$\pm 1\%$	$\pm 0.01\%$	$\pm 0.4\%$	180 secs

Nitric Oxide (Chemiluminescence)					
Analyser	Ranges Available (FSD)	Repeatability (FSD)	Zero Drift (FSD over 24 hours)	Stability (FSD over 24 hours)	Response Time (90% FSD)
Rosemount NGA 2000	1% 5000 ppm 500 ppm 50 ppm	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	2-15 secs

Methane and Propane (Flame Ionisation Detection)					
Analyser	Ranges Available (FSD)	Repeatability (FSD)	Zero Drift (FSD over 24 hours)	Stability (FSD over 24 hours)	Response Time (90% FSD)
Beckman 400	1% 1000 ppm 100 ppm 10 ppm 1 ppm	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	0.5 sec
Rosemount NGA 2000	1% 5000 ppm 500 ppm 50 ppm	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	2-15 secs

TABLE 7

LISTS THE MAJOR CONTRIBUTORS TO THE WEIGHING AND PHYSICAL HANDLING UNCERTAINTY AT 68% CONFIDENCE LIMITS.

Source of Uncertainty	Type A or B Uncertainty	Uncertainty Value (mg)	Probability Distribution	Divisor
<u>Balance and Weights</u> <u>Uncertainty</u>				
1. Balance Repeatability	A	12.0	Normal	1
2. Thermal Drift of Balance	A	17	Normal	1
3. Time Drift of Balance	A	5.0	Normal	1
4. Draught Instability of Balance	A	6.0	Normal	1
5. Location of Cylinder on Balance	A	15	Normal	1
6. Uncertainty in mass pieces	A	1.1	Normal	1
7. Resolution of Balance	B	0.1	Rectangular	$\sqrt{3}$
8. Sensitivity of Balance	B	20	Rectangular	$\sqrt{3}$
9. Buoyancy Correction	B	0.3	Rectangular	$\sqrt{3}$
Combined weighing Uncertainty		27		
Cylinder expansion due to pressure	B	5.0	Rectangular	$\sqrt{3}$
Physical Handling of Cylinder	A	6.0	Normal	1
Combined weighing/ Physical Handling of Cylinder		28		

TABLE 8**TYPICALLY USED RELATIVE MOLAR MASSES AND THEIR UNCERTAINTIES**

Species	Formula	Relative Molar Mass	Uncertainty in Relative Molar Mass
Hydrogen	H ₂	2.015880	0.000099
Helium	He	4.002602	0.000002
Methane	CH ₄	16.0428	0.0010
Water	H ₂ O	18.01528	0.00032
Carbon Monoxide	CO	28.0104	0.0010
Nitrogen	N ₂	28.01348	0.00010
Nitric Oxide	NO	30.00614	0.00031
Ethane	C ₂ H ₆	30.0696	0.0010
Oxygen	O ₂	31.99880	0.00042
Argon	Ar	39.948	0.001
Propane	C ₃ H ₈	44.0965	0.0017
Carbon Dioxide	CO ₂	44.0098	0.0011
Nitrous Oxide	N ₂ O	44.01288	0.00032
Nitrogen Dioxide	NO ₂	46.00554	0.00043
Sulphur Dioxide	SO ₂	64.0648	0.0060
Benzene	C ₆ H ₆	78.1136	0.0025
Toluene	C ₆ H ₅ -CH ₃	92.1405	0.0027
Xylene	C ₆ H ₄ (CH ₃) ₂	106.1674	0.0028

TABLE 9

**NPL SECONDARY STANDARDS AND THEIR EXPANDED UNCERTAINTIES
(95 % CONFIDENCE LEVEL)**

Nominal Conc	Gas mixtures and their Expanded Uncertainties					
	CO/N ₂	CO ₂ / N ₂	NO/N ₂	C ₃ H ₈ /air	C ₃ H ₈ / N ₂	CH ₄ / air
7%	0.04%	0.04%	-	-	-	-
5%	0.03%	0.03%	0.03%	-	0.03%	-
2.5%	0.018%	0.018%	0.018%	-	0.018%	0.018%
1%	0.008%	0.008%	0.008%	0.008%	0.008%	0.008%
5000 ppm	40 ppm	40 ppm	40 ppm	40 ppm	40 ppm	40 ppm
2500 ppm	20 ppm	20 ppm	20 ppm	20 ppm	20 ppm	20 ppm
1000 ppm	8 ppm	8 ppm	8 ppm	8 ppm	8 ppm	8 ppm
500 ppm	4 ppm	4 ppm	4 ppm	4 ppm	4 ppm	4 ppm
250 ppm	2 ppm	2 ppm	2 ppm	2 ppm	2 ppm	2 ppm
100 ppm	0.9 ppm	0.9 ppm	0.9 ppm	0.9 ppm	0.9 ppm	0.9 ppm
50 ppm	0.5 ppm	0.5 ppm	0.5 ppm	0.5 ppm	0.5 ppm	0.5 ppm
10 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm

TABLE 10

**STANDARD GAS COMPARISONS WITH NMi, THE NETHERLANDS
AT % LEVELS**

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction %	Uncertainty %	Analytical Amount Fraction %	Uncertainty %	Relative Difference
6.0 % CO/N ₂	NMi	5.997	0.006	5.996	0.0070	-0.02
4.5 % CO/N ₂	NMi	4.507	0.004	4.510	0.0068	0.07
1.0 % CO/N ₂	NPL	0.994	0.001	0.993	0.0022	-0.10
0.1 % CO/N ₂	NMi	0.0998	0.0001	0.0999	0.0001	0.10
15 % CO ₂ /N ₂	NMi	15.011	0.015	15.030	0.0250	0.13
10 % CO ₂ /N ₂	NMi	9.998	0.010	10.008	0.0100	0.10
10 % CO ₂ /N ₂	NPL	9.751	0.004	9.746	0.0200	-0.05
1.0 % CO ₂ /N ₂	NMi	1.001	0.001	1.001	0.0014	0.00
1.0 % CO ₂ /N ₂	NPL	0.979	0.001	0.980	0.0022	0.10
0.5 % CO ₂ /N ₂	NPL	0.498	0.001	0.499	0.0011	0.20
0.1 % CO ₂ /N ₂	NMi	0.1000	0.0001	0.1001	0.0003	0.10
0.1 % CO ₂ /N ₂	NMi	0.0994	0.0001	0.0999	0.0003	0.50
0.4% NO/N ₂	NMi	0.4003	0.0008	0.3995	0.0009	-0.20
0.3 % NO/N ₂	NPL	0.2872	0.001	0.2870	0.0010	-0.07
0.1 % NO/N ₂	NPL	0.0983	0.0002	0.0979	0.0005	-0.41
0.1 % NO/N ₂	NMi	0.1000	0.0001	0.1002	0.0004	0.23
0.1 % SO ₂ /N ₂	NMi	0.1000	0.0001	0.1000	0.0003	0.03
0.1 % SO ₂ /N ₂	NMi	0.0999	0.0001	0.0999	0.0003	-0.03
22 % O ₂ /N ₂	NMi	21.952	0.022	21.980	0.0600	0.13
10 % O ₂ /N ₂	NMi	10.006	0.010	10.010	0.0300	0.04

TABLE 11

**STANDARD COMPARISONS WITH NMi, THE NETHERLANDS
AT ppm LEVELS**

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction ppm	Uncertainty ppm	Analytical Amount Fraction ppm	Uncertainty ppm	Relative Difference %
800 ppm CO/N ₂	NMi	800.0	0.8	800.1	4.0	
200 ppm CO/N ₂	NMi	200.4	0.2	200.1	0.6	
100 ppm CO/N ₂	NMi	101.1	0.1	101.1	0.5	
50 ppm CO/N ₂	NPL	50.1	0.08	50.1	0.3	
100 ppm CO ₂ /N ₂	NPL	97.1	0.13	96.9	0.3	
100 ppm CO ₂ /N ₂	NMi	100.0	0.1	100.5	0.5	
500 ppm NO/N ₂	NMi	500.1	0.5	499.5	2.1	
500 ppm NO/N ₂	NPL	495.2	1.0	493.4	2.4	
100 ppm NO/N ₂	NMi	100.1	0.1	100.0	0.4	
500 ppm SO ₂ /N ₂	NMi	500.4	0.5	499.5	2.5	
100 ppm SO ₂ /N ₂	NMI	110.2	0.1	110.2	0.5	
500 ppm C ₃ H ₈ /N ₂	NPL	485.6	0.5	485.6	1.5	

TABLE 12

**COMPARISON OF MULTI-COMPONENT MOTOR VEHICLE
EXHAUST MIXTURES WITH NMI, THE NETHERLANDS**

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction	Uncertainty	Analytical Amount Fraction	Uncertainty	Relative Difference
3.5 % CO,	NPL	3.545%	0.010%	3.549%	0.018%	0.11%
2000 ppm C ₃ H ₈ ,		1996.3ppm	4.0ppm	2004ppm	10ppm	0.39%
14 % CO ₂ /N ₂		13.863%	0.030%	13.850%	0.060%	-0.09%

TABLE 13

STANDARD GAS COMPARISONS WITH NIST, USA AT % LEVELS

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction %	Uncertainty %	Analytical Amount Fraction %	Uncertainty %	Relative Difference
8.0 % CO/N ₂	NIST	7.7670	0.0800	7.7300	0.0050	-0.48
7.7 % CO/N ₂	NPL	7.6790	0.0040	7.6780	0.0040	-0.01
7.1 % CO ₂ /N ₂	NPL	7.1020	0.0040	7.1100	0.0200	0.11
7.0 % CO ₂ /N ₂	NIST	7.1200	0.0700	7.1210	0.0060	0.01
4.5 % CO ₂ /N ₂	NPL	4.4790	0.0030	4.4780	0.0030	-0.02
3.9 % CO/N ₂	NIST	3.8940	0.0400	3.8930	0.0040	-0.03
3.8 % CO ₂ /N ₂	NIST	3.8246	0.0040	3.8230	0.0040	-0.04
3.5 % CO ₂ /N ₂	NIST	3.5074	0.0035	3.5000	0.0060	-0.21
2.9 % CO ₂ /N ₂	NIST	2.8720	0.0030	2.8740	0.0030	0.07
2.5 % CO ₂ /N ₂	NIST	2.5200	0.0025	2.5240	0.0060	0.16
2.0 % CO/N ₂	NIST	1.9560	0.0200	1.9460	0.0020	-0.51
1.9 % CO ₂ /N ₂	NIST	1.8831	0.0022	1.8830	0.0034	-0.01
1.5 % CO ₂ /N ₂	NIST	1.4519	0.0016	1.4505	0.0018	-0.10
1.0 % CO/N ₂	NIST	0.9600	0.0100	0.9590	0.0010	-0.10
1.0 % CO ₂ /N ₂	NIST	0.9645	0.0010	0.9643	0.0009	-0.02
1.0 % CO ₂ /N ₂	NIST	0.9645	0.0010	0.9638	0.0009	-0.07
1.0 % CO/N ₂	NPL	0.9449	0.0008	0.9451	0.0008	0.02
1.0 % CO ₂ /N ₂	NPL	0.9872	0.0008	0.9862	0.0010	-0.10
0.5 % CO ₂ /N ₂	NIST	0.5062	0.0006	0.5061	0.0010	-0.02
0.5 % CO ₂ /N ₂	NPL	0.5039	0.0005	0.5049	0.0016	0.20
0.5 % CO/N ₂	NIST	0.4680	0.0047	0.4675	0.0008	-0.11
0.2 % CO/N ₂	NIST	0.2397	0.0002	0.2394	0.0003	-0.13

TABLE 14**STANDARD GAS COMPARISONS WITH NIST, USA AT ppm LEVELS**

Nominal Value of Standard	Source Laboratory	Gravimetric Amount Fraction ppm	Uncertainty ppm	Analytical Amount Fraction ppm	Uncertainty ppm	Relative Difference %
1000 ppm CO/N ₂	NIST	956.00	7.00	954.80	1.00	-0.13
1000 ppm CO ₂ /N ₂	NPL	958.30	0.90	958.20	0.90	-0.01
500 ppm CO/N ₂	NIST	475.00	4.00	475.20	0.50	0.04
250 ppm CO/N ₂	NIST	243.60	2.40	242.40	0.40	-0.49
100 ppm CO/N ₂	NIST	97.10	0.80	96.99	0.14	-0.11
100 ppm CO/N ₂	NIST	93.80	0.90	93.83	0.14	0.03
50 ppm CO/N ₂	NIST	44.90	0.50	44.86	0.09	-0.09
50 ppm CO ₂ /N ₂	NPL	50.85	0.07	50.70	0.10	-0.29
10 ppm CO/N ₂	NIST	9.62	0.09	9.64	0.04	0.21

9. LIST OF FIGURES

- Figure 1: Cylinder Evacuation System.
- Figure 2: Gas Blending System.
- Figure 3: Results of Intercomparison of NPL's Carbon Monoxide in Nitrogen standards with NMi.
- Figure 4: Results of Intercomparison of NPL's Carbon Dioxide in Nitrogen standards with NMi.
- Figure 5: Results of Intercomparison of NPL's Nitric Oxide in Nitrogen standards with NMi.
- Figure 6: Results of Intercomparison of NPL's Sulphur Dioxide in Nitrogen standards with NMi.
- Figure 7: Results of Intercomparison of NPL's Propane in Nitrogen standards with NMi.
- Figure 8: Results of Intercomparison of NPL's Oxygen in Nitrogen standards with NMi.
- Figure 9: Results of Intercomparison of NPL's Hydrogen Sulphide in Nitrogen standards with NMi.
- Figure 10: Results of Intercomparison of NPL's Carbon Monoxide in Nitrogen standards with NIST (% Levels).
- Figure 11: Results of Intercomparison of NPL's Carbon Dioxide in Nitrogen standards with NIST (% Levels).
- Figure 12: Results of Intercomparison of NPL's Carbon Monoxide in Nitrogen standards with NIST (ppm Levels).
- Figure 13: Results of Intercomparison of NPL's Carbon Dioxide in Nitrogen standards with NIST (ppm Levels).
- Figure 14: Results of Intercomparison of NPL's Propane in Air standards with NIST.
- Figure 15: Results of Intercomparison of NPL's Nitric Oxide in Nitrogen standards with NIST.
- Figure 16: Results of Intercomparison of NPL's Propane in Nitrogen standards with NIST.

Figure 1: Cylinder Evacuation System

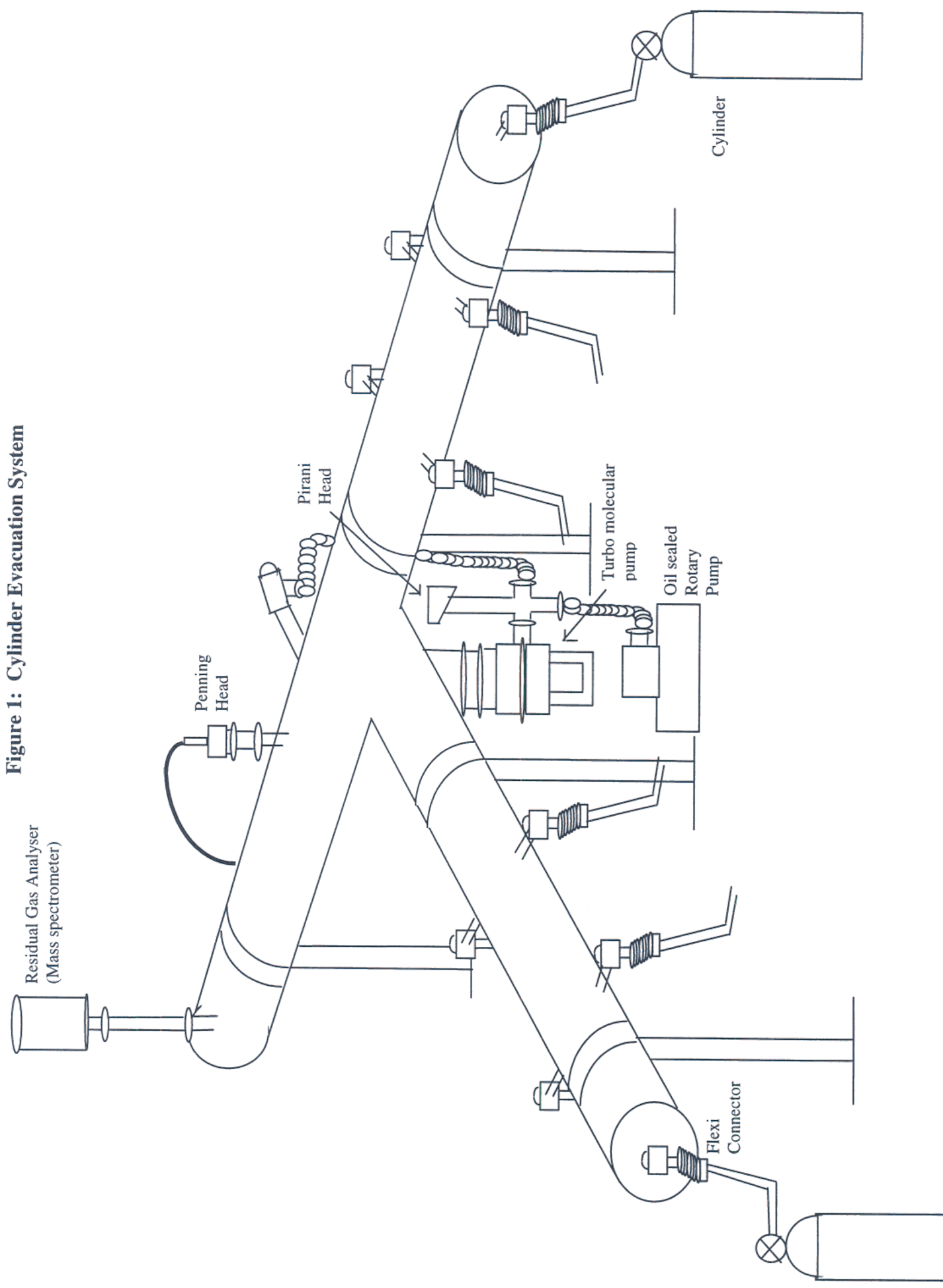


Figure 2: Gas Blending System

KEY.

-  1/4 Turn shut off valves.
-  Needle valve

Filter

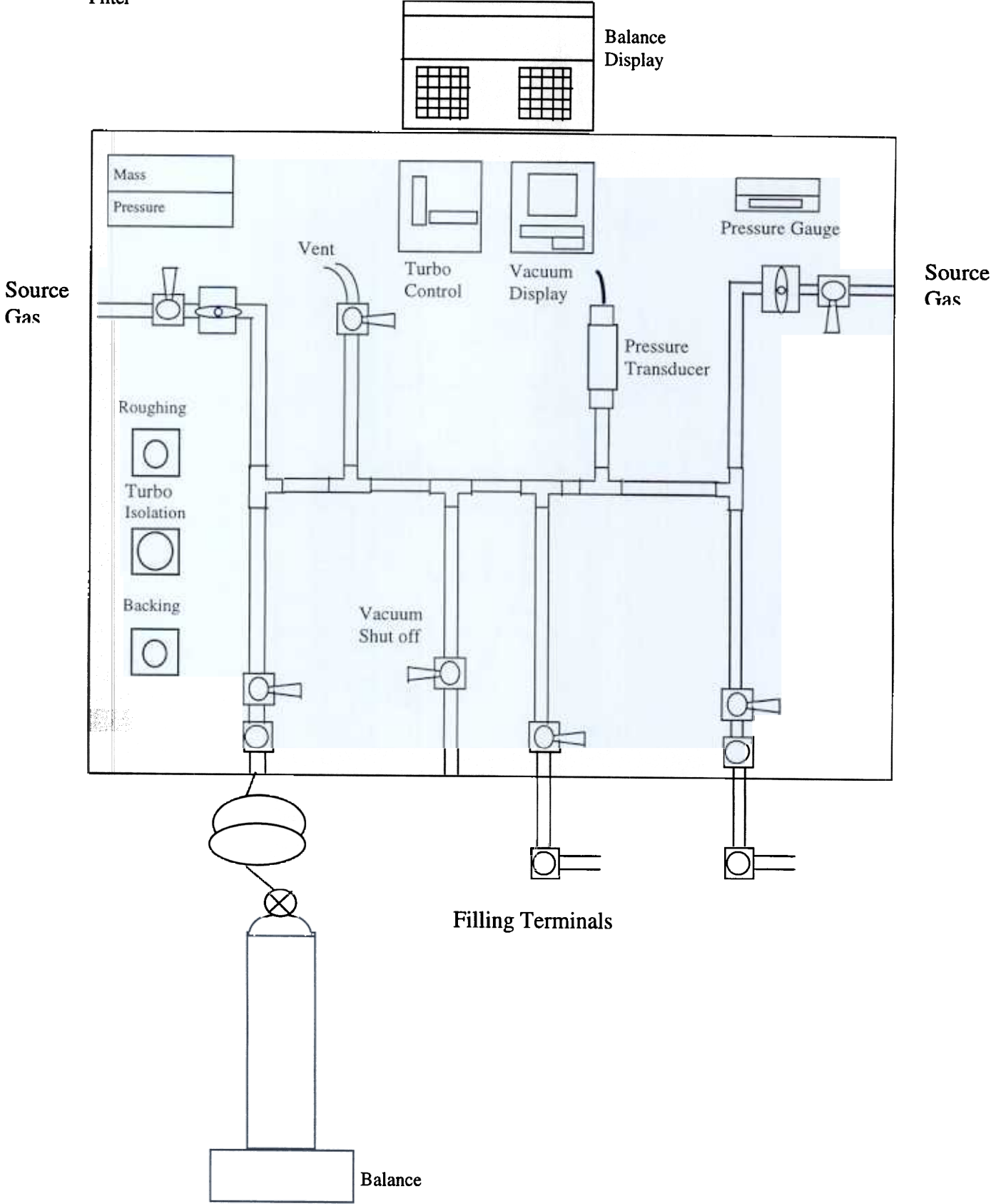
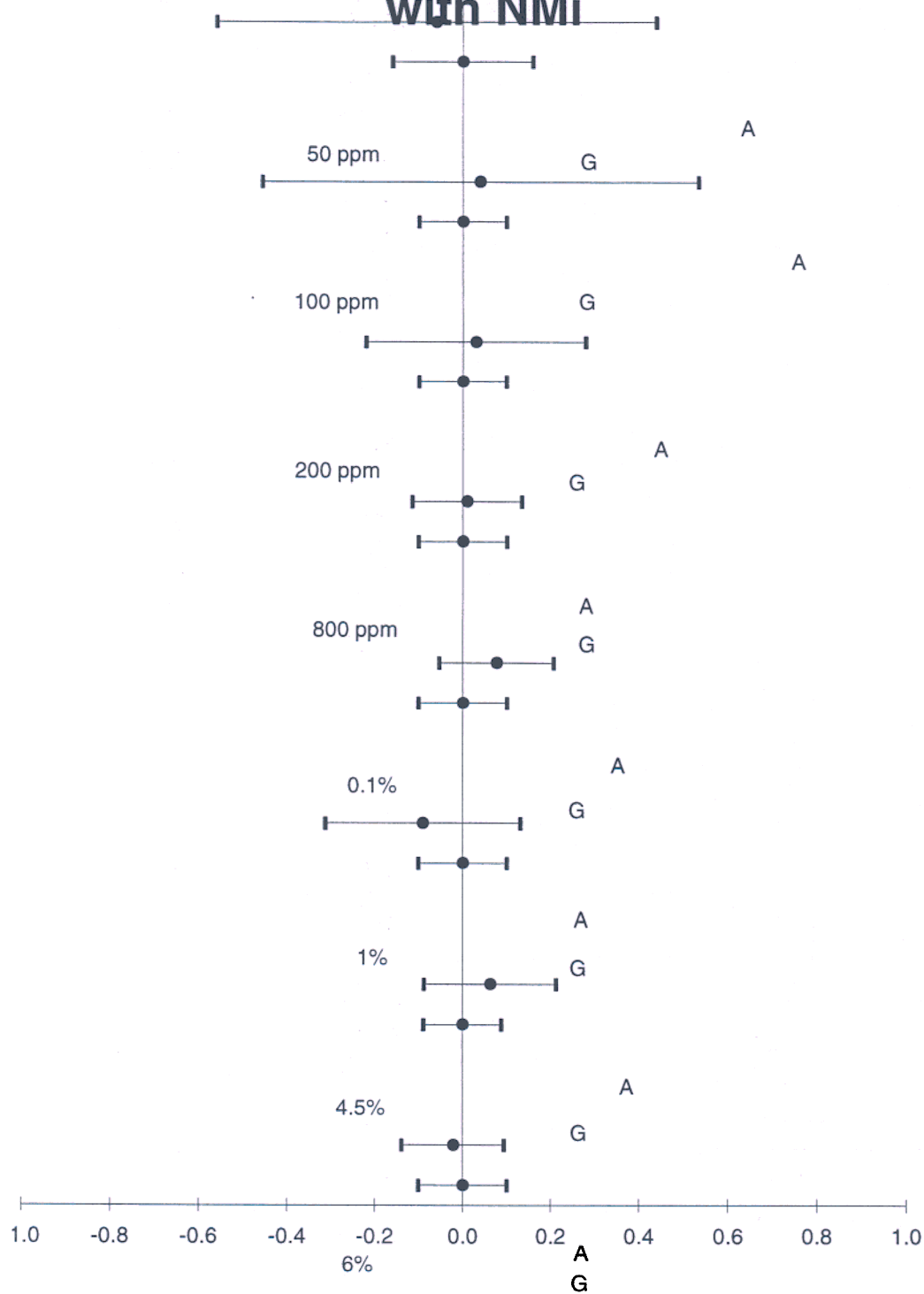


Figure 3- Carbon Monoxide in Nitrogen with NMI



Relative Difference (%)

Figure 4 - Carbon Dioxide in Nitrogen with NMI

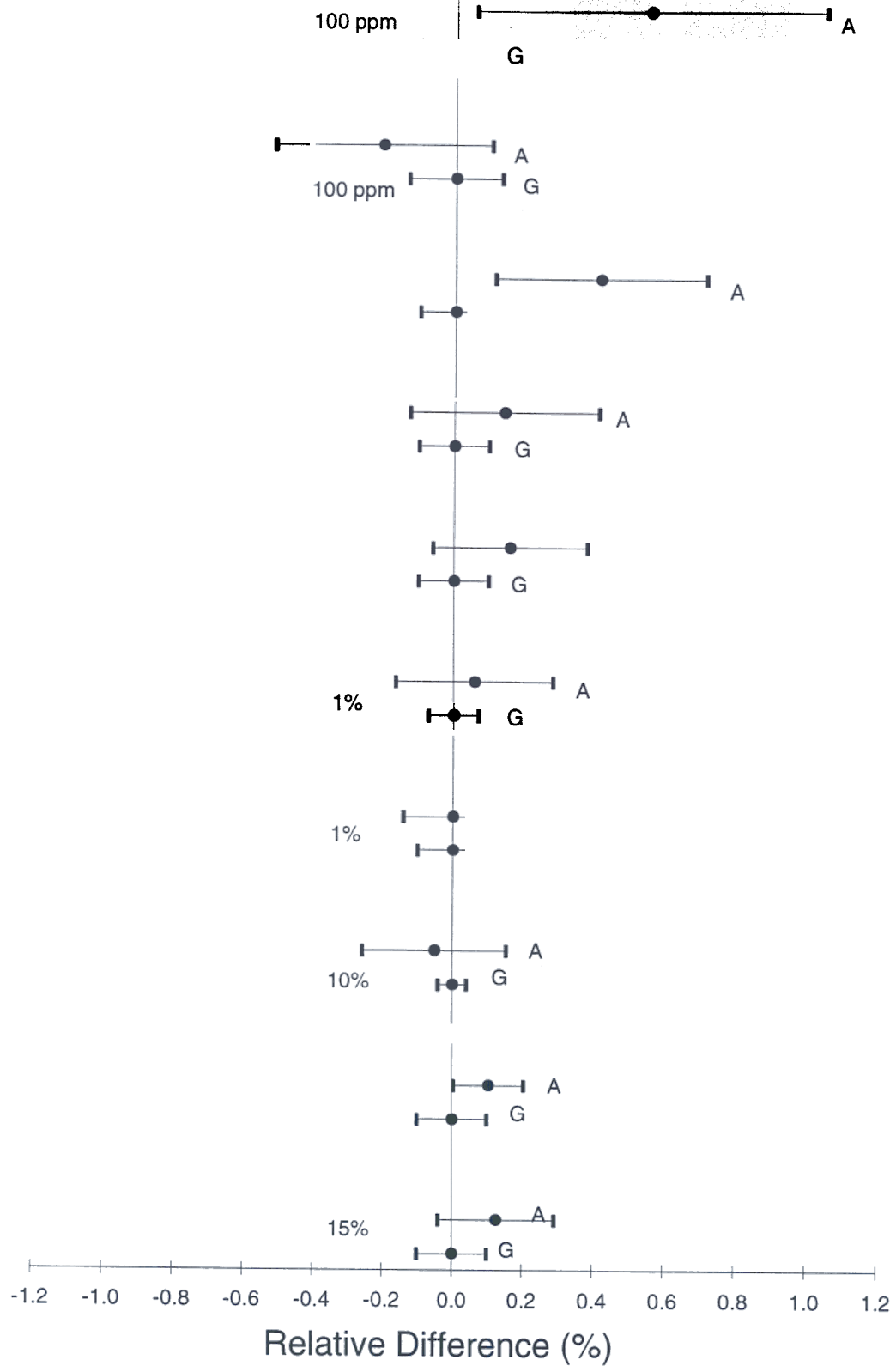


Figure 5 Nitric Oxide in Nitrogen with

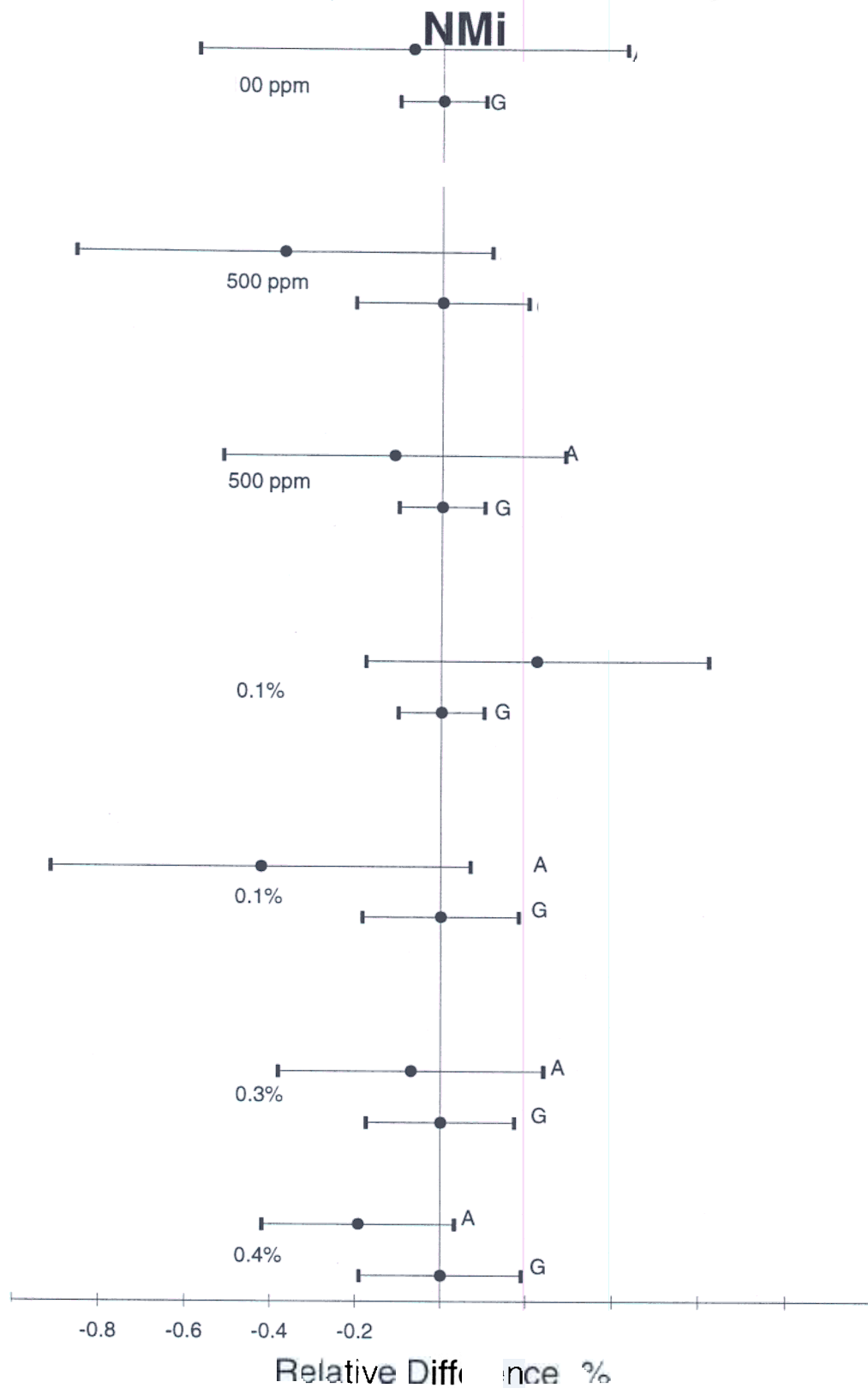


**Figure 6 - Sulphur Dioxide in Nitrogen
with NMI**

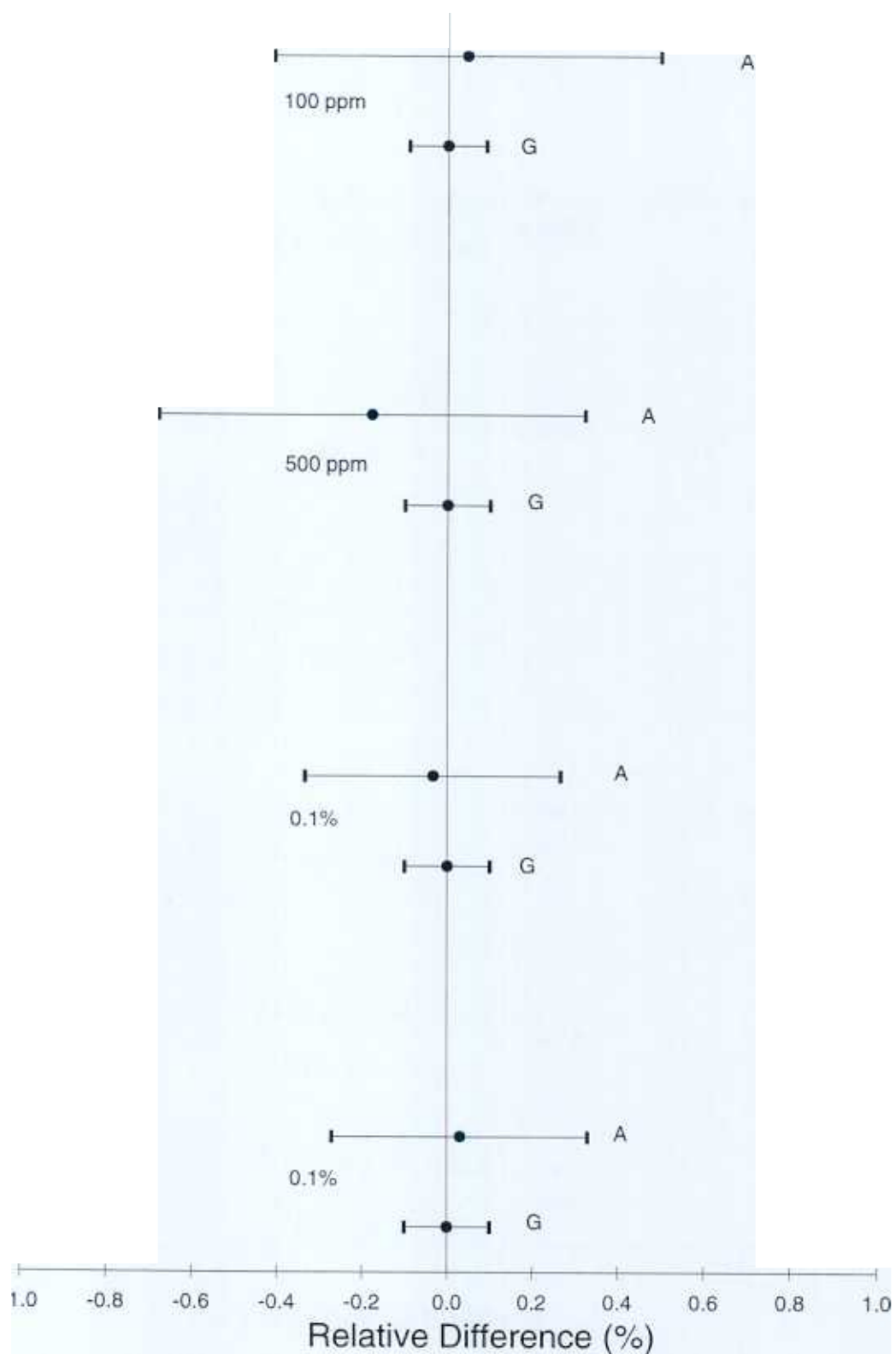


Figure 7 - Propane in Nitrogen with NMI

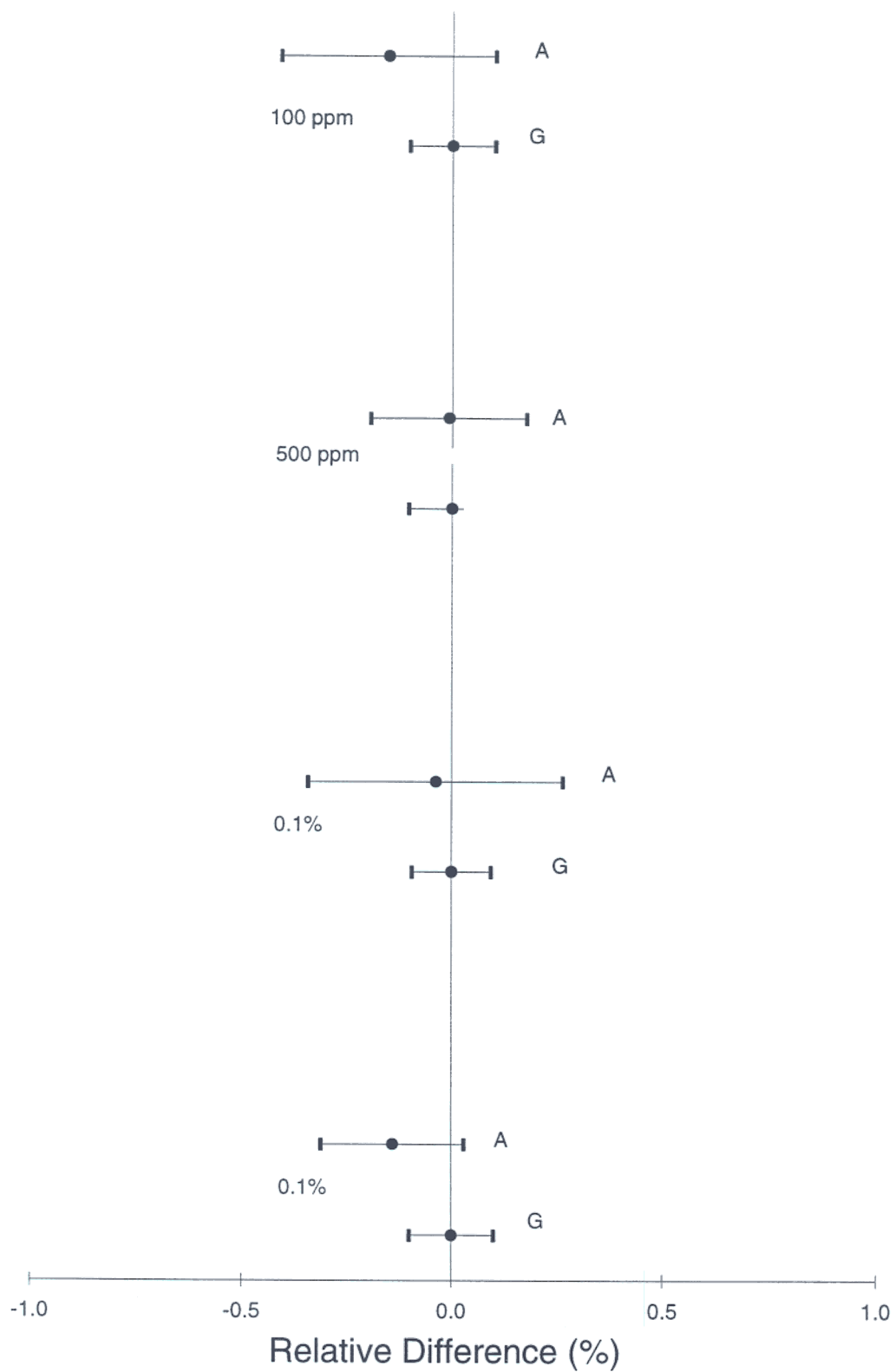


Figure 8 - Oxygen in Nitrogen with NMi

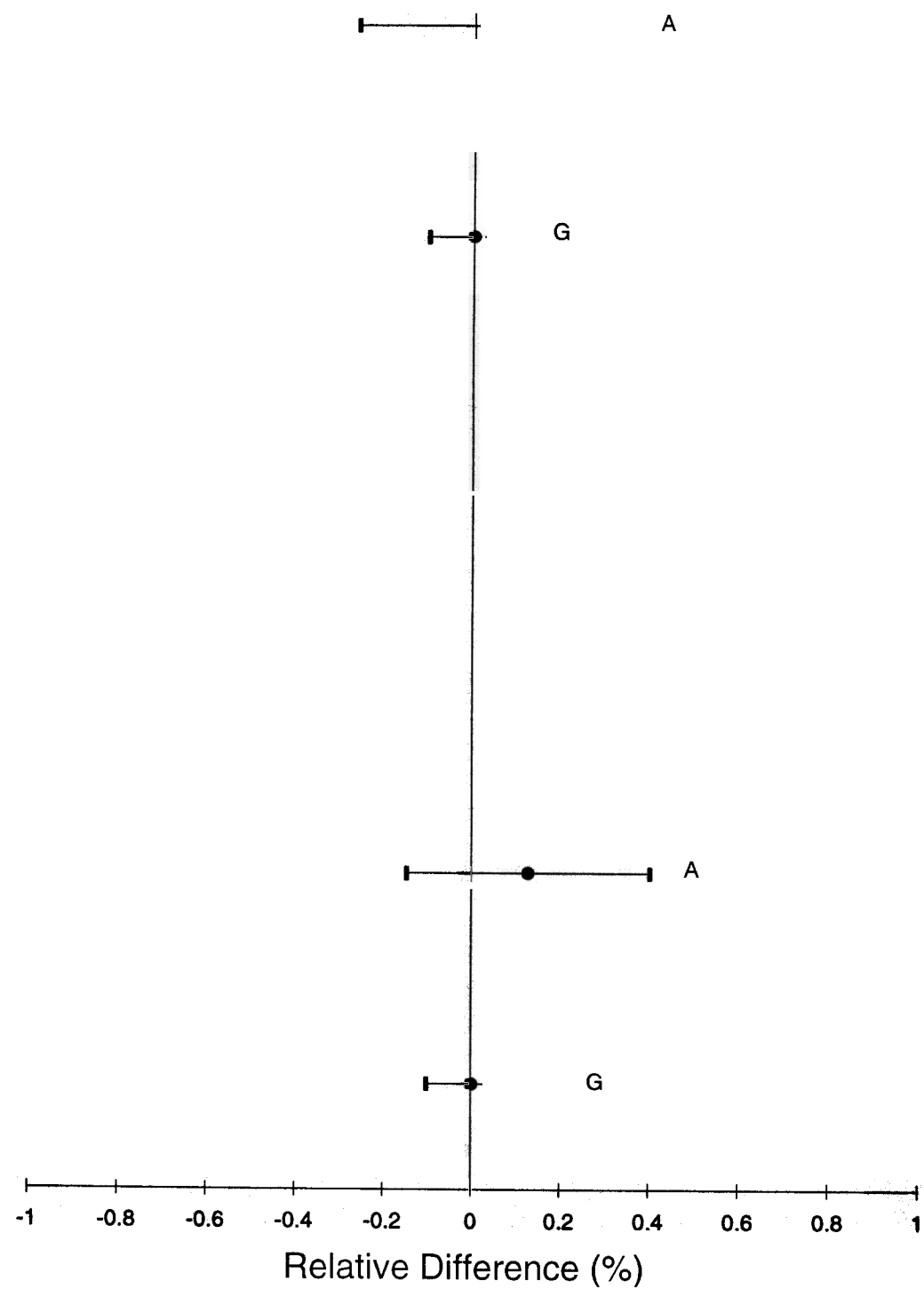


**Figure 9 - Hydrogen Sulphide in Nitrogen
with NMI**

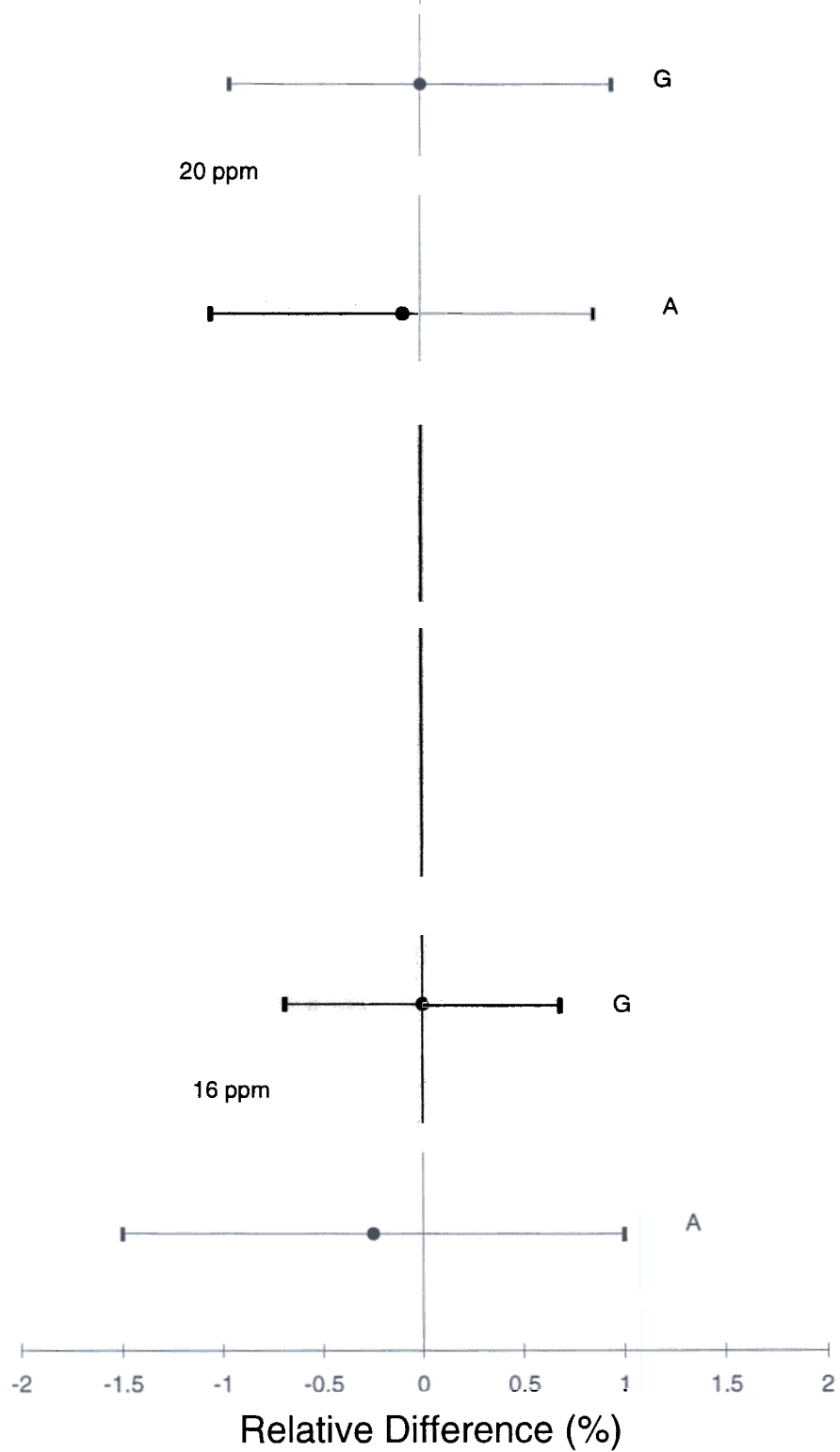


Figure 10 - Carbon Monoxide with NIST (% Levels)

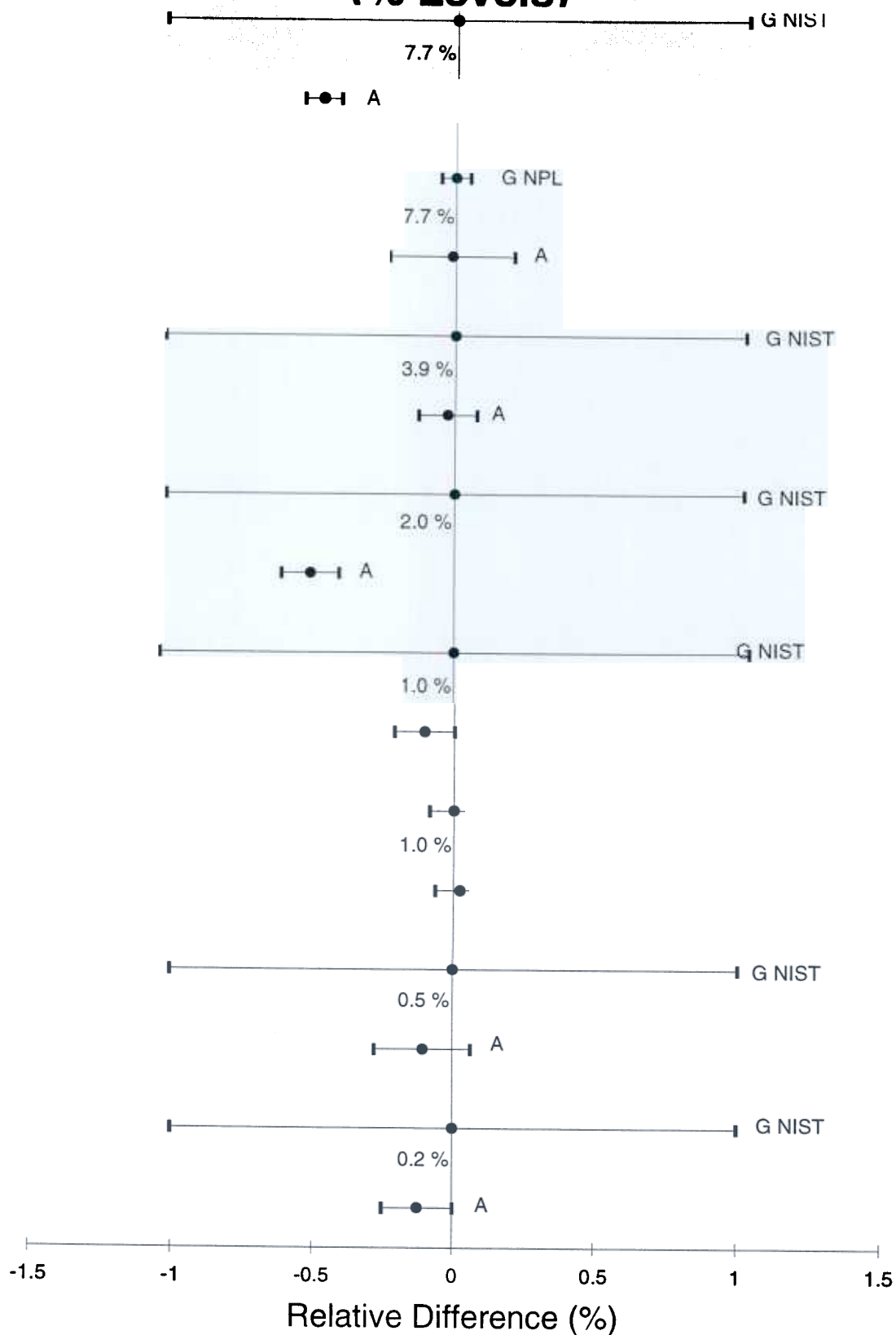


Figure Carbon Dioxide with NIST (%Levels)

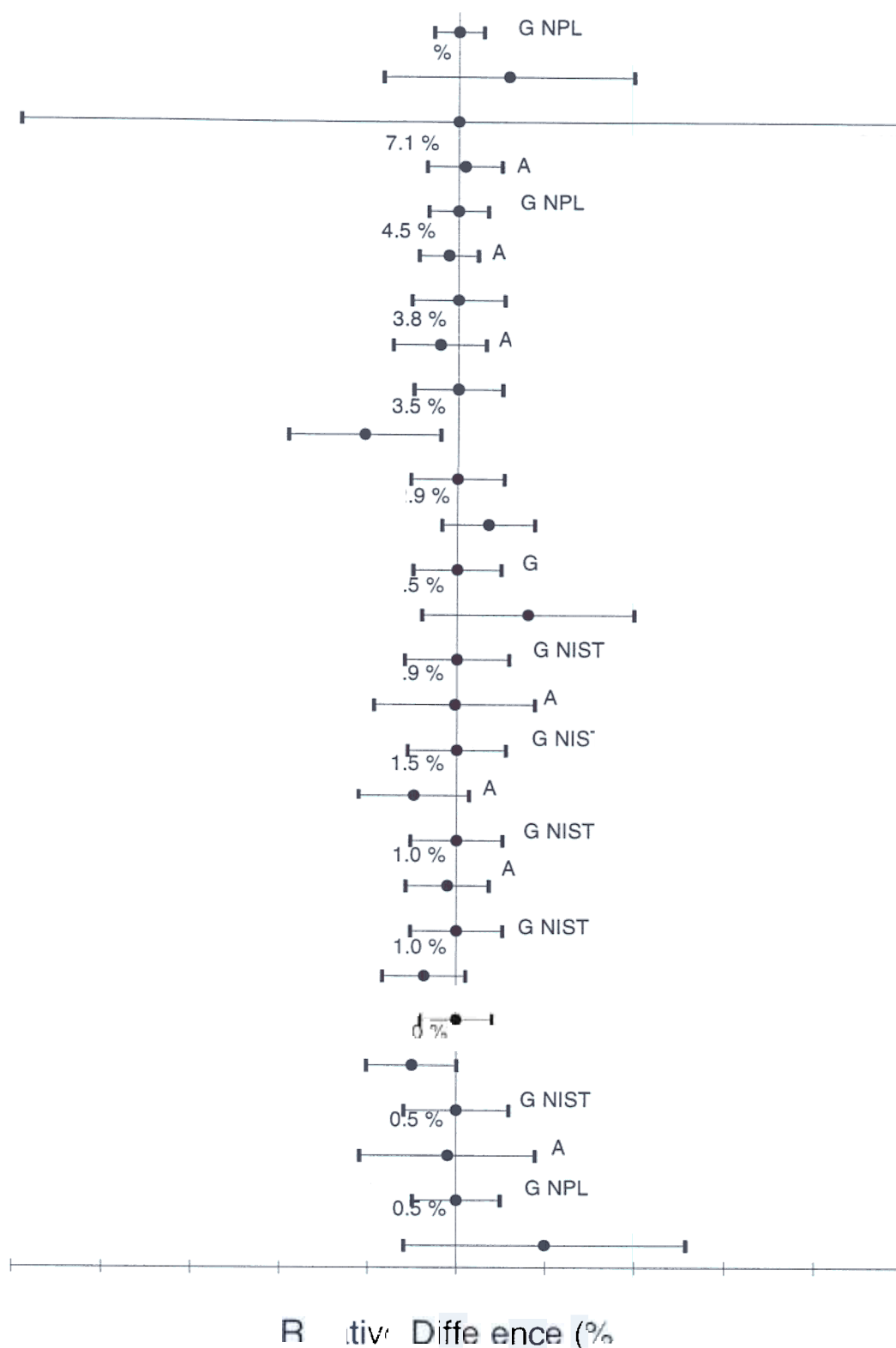


**Figure 12 - Carbon Monoxide with NIST
(ppm levels)**

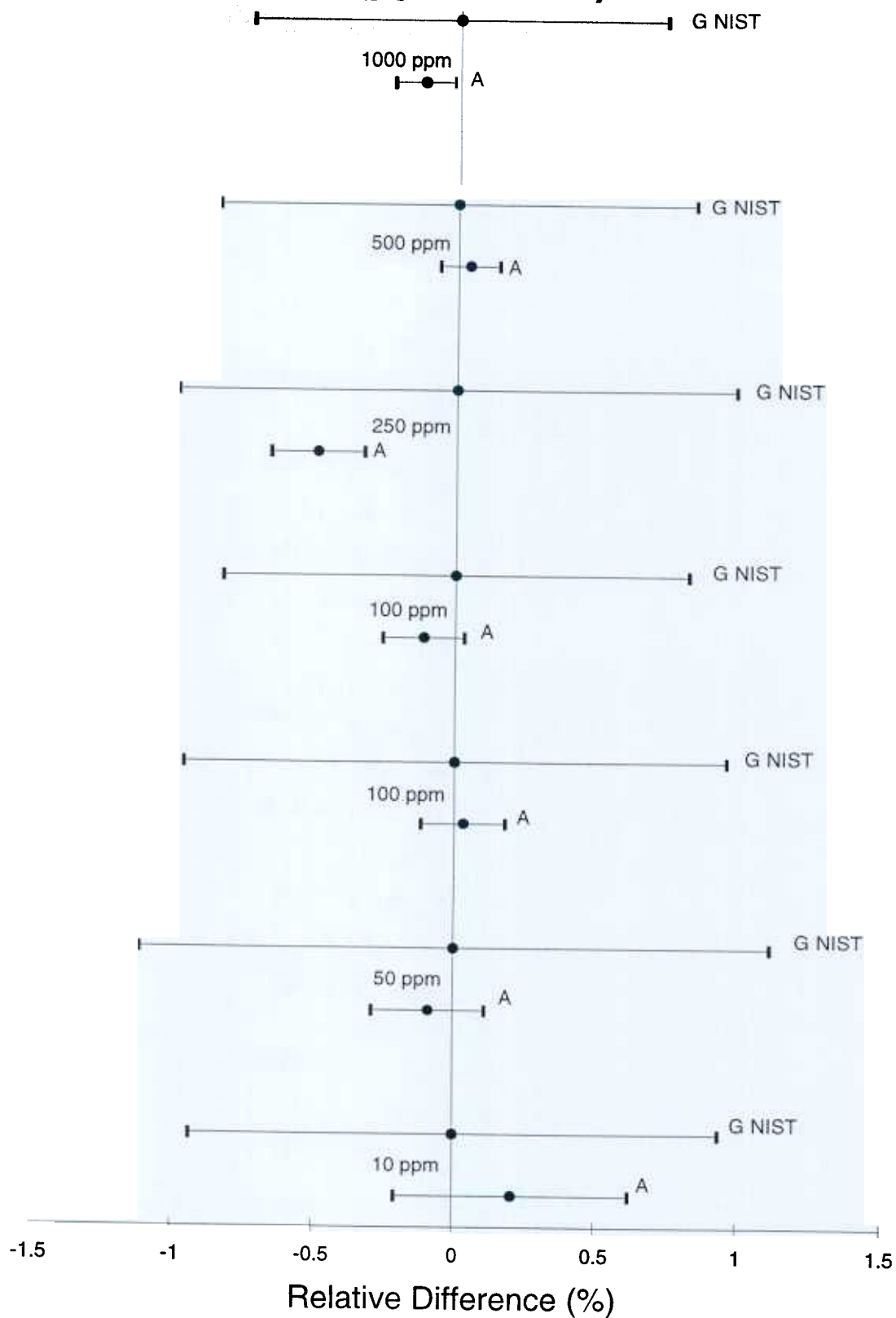


**Figure 13 - Carbon Dioxide with NIST
(ppm levels)**

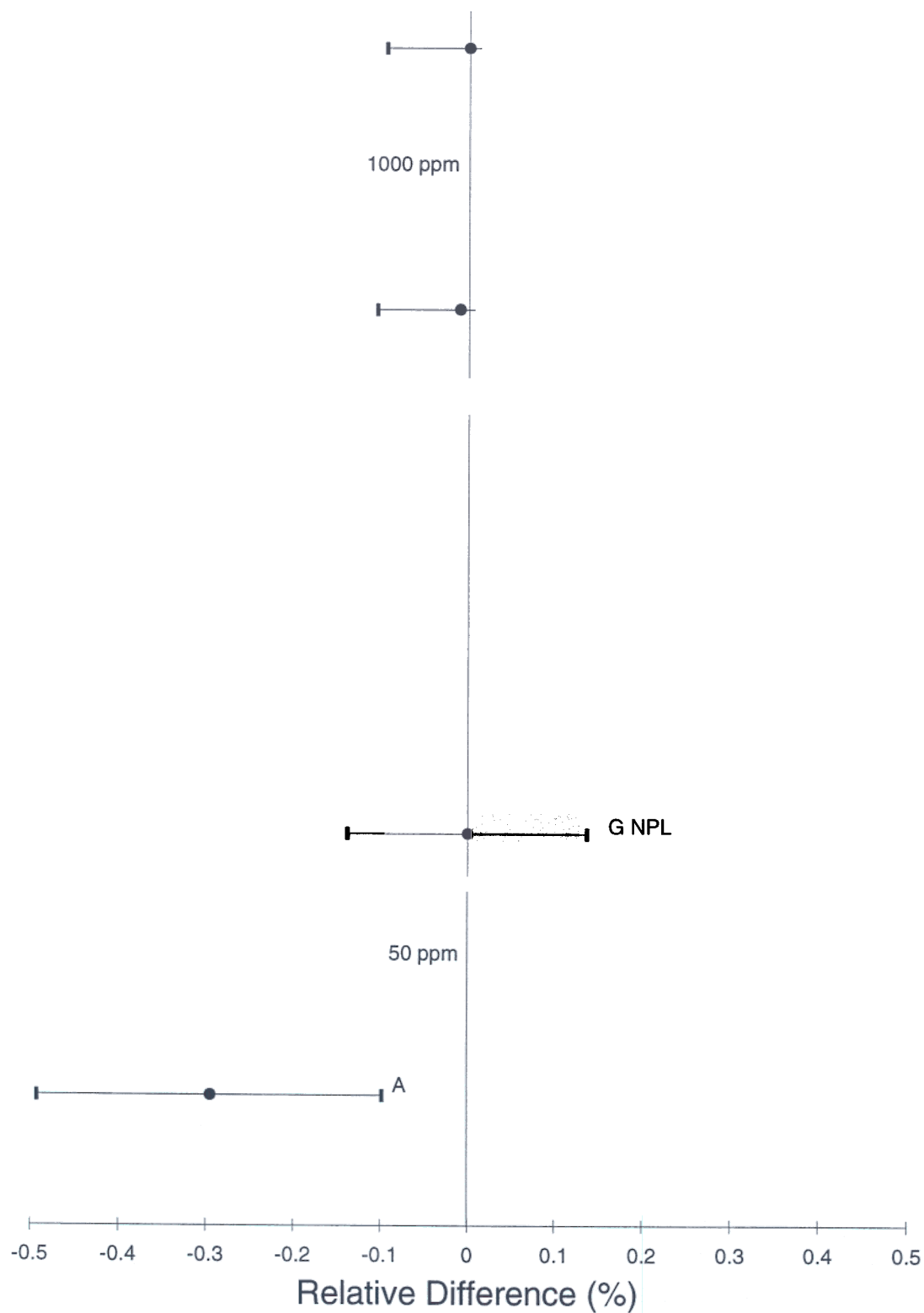


Figure 14 - Results of Intercomparison of NPL's Propane in Air standards with NIST

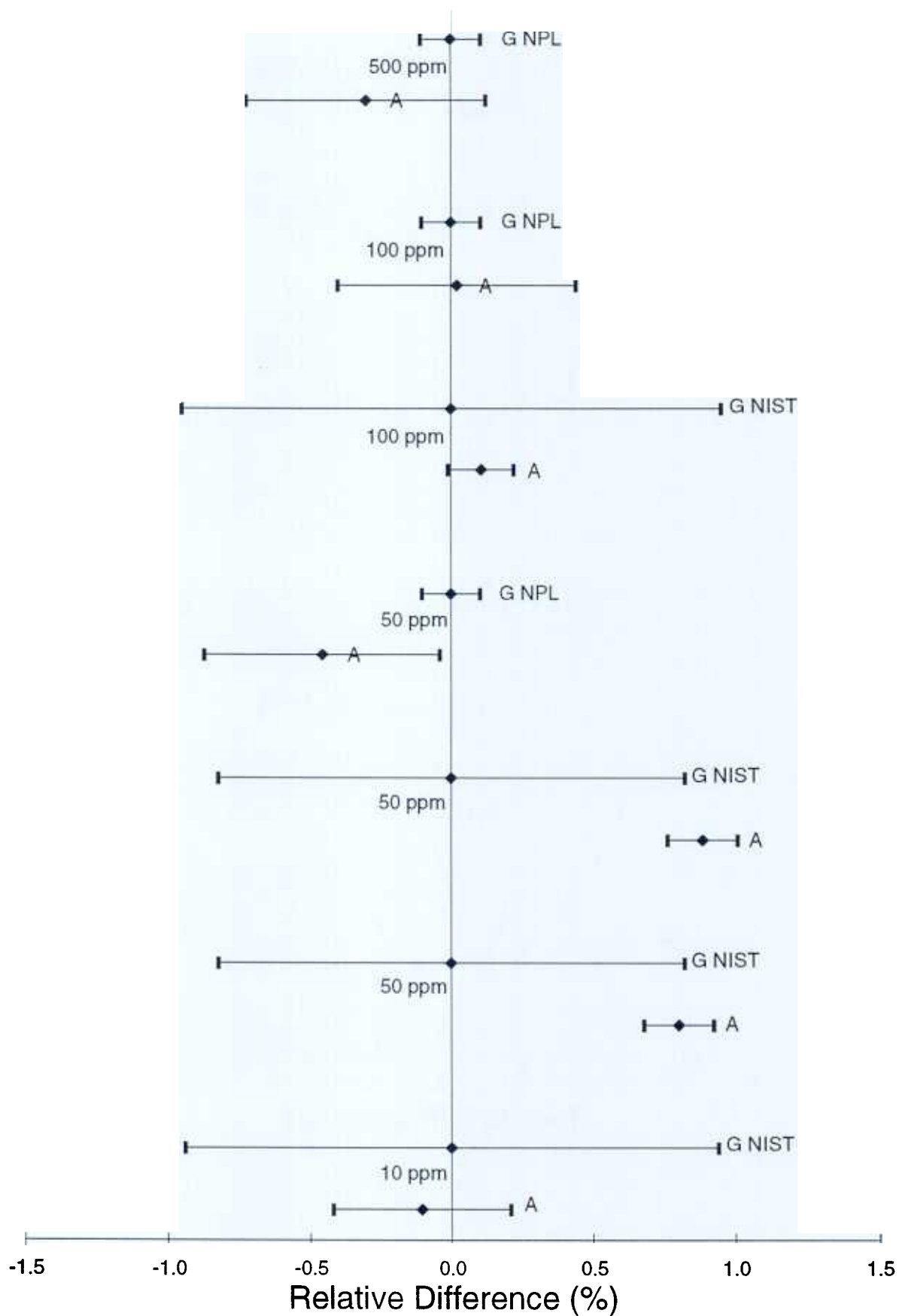


Figure 15 - Results of Intercomparison of NPL's Nitric Oxide in Nitrogen standards with NIST

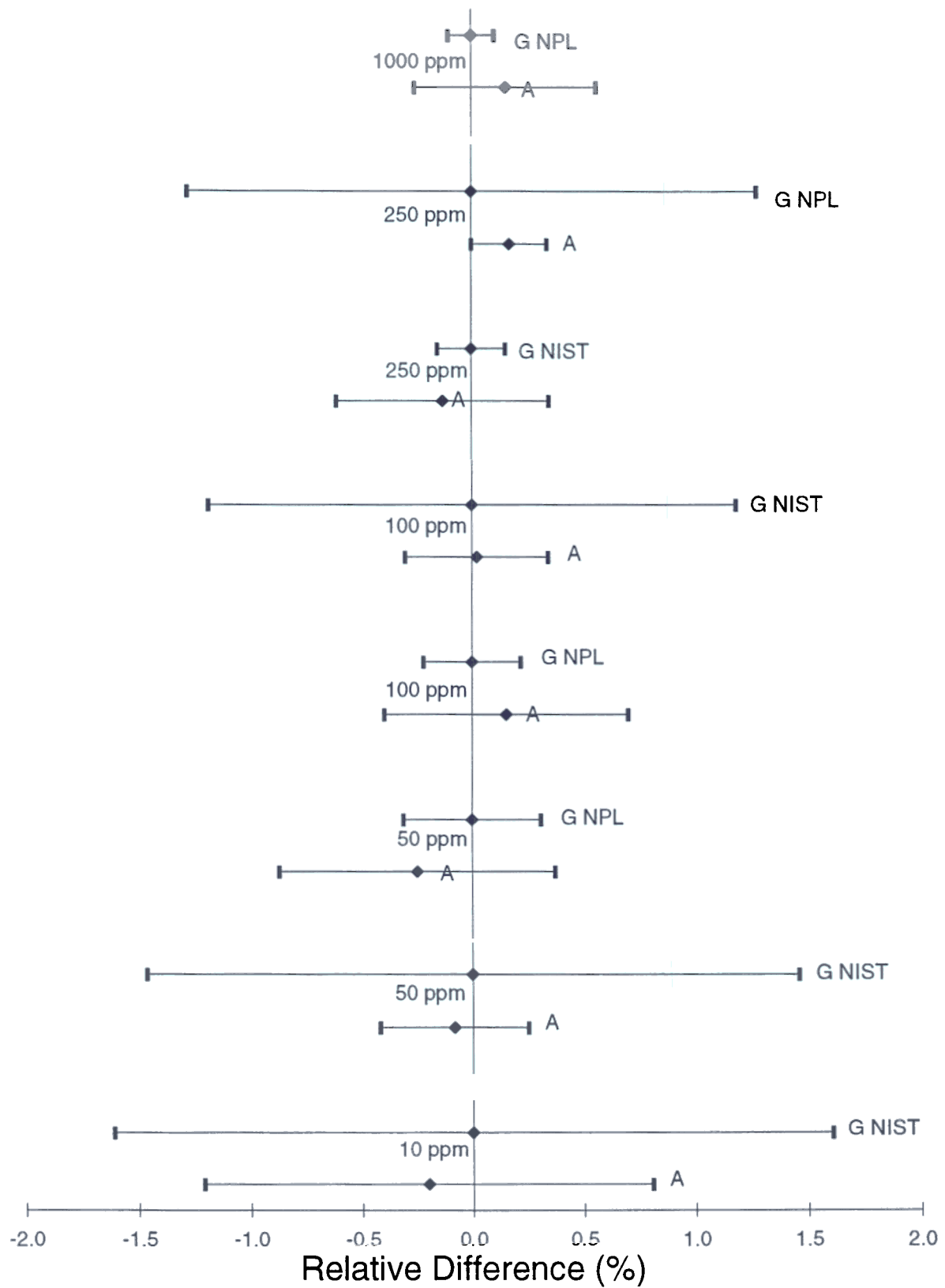


Figure 16 - Results of Intercomparison of NPL's Propane in Nitrogen standards with NIST

