

**First Annual Report on Standards, Measurement & Testing
Programme Project SMT4-CT96-2094**

**HARMONISATION OF AIR QUALITY MEASUREMENTS IN EUROPE
(HAMAQ)**

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Approved on behalf of Managing Director, NPL
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EXECUTIVE SUMMARY

The overall aim of the HAMAQ project is to improve the consistency of air quality measurements made by EU member states. The project will achieve this by assessing, and subsequently improving, the comparability of a range of 'primary' methods used throughout Europe to certify gas calibration mixtures - mainly those produced in high pressure cylinders. These standards are then used as transfer standards for the calibration of instruments deployed at air-quality monitoring sites. The specific objectives of this project are therefore:

- a) to develop the methodology whereby internationally-acceptable gas mixtures can be produced for use as calibration standards and certified in concentration so as to promote widespread uniformity and accuracy of air quality measurements throughout Europe;
- b) to demonstrate the equivalence of different 'primary' methods available in different member states for providing nationally traceable calibrations of air quality measurements of atmospheric pollutants (CO, NO, NO₂, SO₂ and C₆H₆) in order that these methods can be employed to certify the stable gas calibration mixtures produced commercially;
- c) to develop improved gas cylinder passivation treatments by means of the industrial partners, and to evaluate their effectiveness in order to provide more accurate, stable long lifetime calibration gas mixtures of CO, NO, NO₂, SO₂ and C₆H₆;
- d) to provide technology transfer, in order to promote improved measurements in Member States where the air quality measurement infrastructure is not yet fully mature or is not yet of demonstrated accuracy.

The work programme of the project comprises four workpackages (WPs). WP1 has been completed and involved the production of compressed gas mixtures in high pressure cylinders by two leading commercial gas companies: Scott Speciality Gases of the Netherlands, and Messer of Germany in the United Kingdom. Subsequently, batches of these gas mixtures (fifteen for each compound) were shipped to designated pilot laboratories selected from the project partners. For the potentially unstable mixtures (SO₂, NO₂ and C₆H₆) stability tests were conducted on a subset of each batch (six or more cylinders) during the period February-October 1997. These measurements showed good stability with typical measurement standard deviations for SO₂, NO₂ and C₆H₆ of less than $\pm 1.3\%$, $\pm 2.3\%$ and $\pm 1.2\%$ respectively. There was one exception in the case of one cylinder of NO₂.

WP2 has also been completed and was concerned with intercomparison measurements. These intercomparisons were organised such that each participant was sent an individual cylinder by the designated pilot laboratory for each species. This was returned to the pilot laboratory after each measurement. An additional cylinder was circulated to all participants. The results of the intercomparisons are summarised in the figure below. The largest disagreements between the laboratories involved are 2.1%, 2.4%, 7.1%, 5.4% and 3.0% for CO, NO, SO₂, NO₂ and C₆H₆ respectively.

The results of these intercomparisons were discussed at the first annual progress meeting held in Madrid on the 3rd and 4th November 1997. A number of technical investigations were formulated in order to investigate, understand, and reduce these initial discrepancies. These investigations were concerned with:

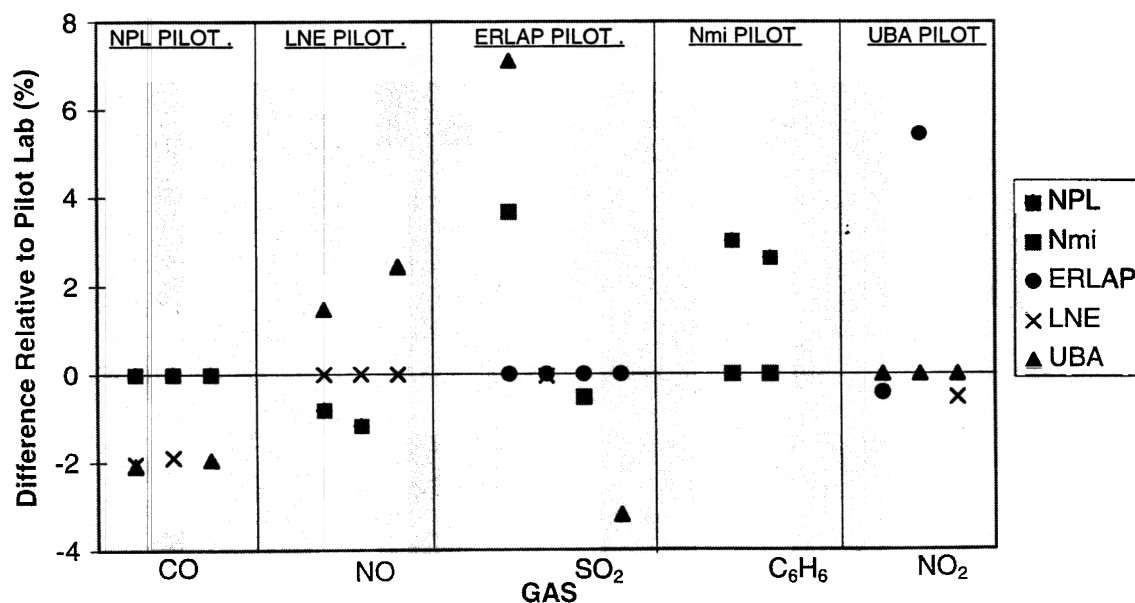
- (i) investigating the effects of CO analyses carried out using the non-dispersive infrared (NDIR) technique, as to whether the balance gas used is air or nitrogen,
- (ii) investigating, in the case of SO₂ and NO₂ analyses whether apparent upward trends in the measured concentrations observed during the intercomparisons could be real and due to effects arising from cylinder preconditioning and subsequent handling.

The results of these investigations will be reported in the mid-term review report.

WP3, which will take place during the period January-October 1998, will involve a second set of intercomparisons. The aim of these will be to demonstrate consistency between all the partners for all gaseous species to a target level of agreement of $\pm 1\%$. A schedule for the second set of intercomparisons has now been agreed by all the partners

WP4 involves disseminating the results and findings of the HAMAQ project through a technical workshop to the large number of other key organisations within Europe responsible for air quality monitoring. Plans were made at the annual progress meeting to involve these institutes. Progress will be reported in the mid-term review report.

RESULTS OF FIRST HAMAQ INTERCOMPARISON



1. INTRODUCTION

The overall aim of the HAMAQ project is to assess and improve the consistency of air quality measurements made within the member states of the EU in support of the recent Air Quality Framework Directive and its subsequent 'Daughter' Directives. This aim is first addressed within this project by assessing the comparability of the primary reference methods for gas calibration mixtures of CO, NO, NO₂, SO₂, and C₆H₆ maintained in a number of metrological institutes within Europe. Most air quality measurements within Europe are traceable, through the use of transfer standards in the form of compressed gases in cylinders, to these national facilities. The partners within this project are:

1. The National Physical Laboratory (NPL), United Kingdom, which develops and maintains a large range of primary gas standards, and is responsible for underpinning air quality measurements made as part of the national rural and urban monitoring networks, as well as local measurements made under the auspices of local and regional authorities.
2. The Nederlands Meetinstituut (NMI), the Netherlands, which is responsible for providing primary reference mixtures to the national institute responsible for the management of national air quality monitoring networks (mainly RIVM, Ministry of Public Health and the Environment). In addition, NMI provide primary reference mixtures and certified reference materials to local environmental authorities.
3. The European Reference Laboratory for Air Pollution (ERLAP) at the EC Joint Research Centre, Ispra, which has responsibility for the harmonisation of air pollution measurements within European air-quality monitoring networks. This is achieved through a number of activities including: preparatory work for future regulations; harmonisation of current directives; development and validation of new monitoring techniques; organisation of pilot studies; development of measurement strategies; participation in international air monitoring programmes and standardisation activities (CEN/ISO). ERLAP have organised round-robin tests in the past with the objective of ensuring the quality and comparability of European air pollution measurements in the past.
4. The Laboratoire National d'Essais (LNE, France) is part of a group of institutes, including INERIS and Ecole de Mines de Douai which are known collectively as the French central laboratory (LCSQA). These are responsible for the validation of measurements made as part of national and local air quality monitoring networks.
5. Umweltbundesamt Offenbach Pilotstation (UBA) is one of two German institutes responsible for the harmonisation of air quality monitoring networks throughout the country. Each German Bundesland has a central laboratory in which transfer standards for CO, SO₂, and NO₂ are calibrated by reference methods. Once or twice each year comparison measurements are organised by either UBA or LUA (North Rhine - Westfalia) to ensure the consistency of measurements between these required networks.

6. VTT Chemical Technology (Finland) together with The Finnish Meteorological Institute (FMI) have been involved with air quality monitoring since 1970. At present, FMI manages seven national and international networks which include a total of nineteen monitoring stations.
7. Instituto de Salud Carlos (ISC III) is the reference laboratory of the Spanish Atmospheric Pollution Network, and organises intercomparison exercises throughout the country. As part of its international quality assurance activities ISC III have worked in conjunction with ERLAP, NILU and the US EPA.

2. OBJECTIVES OF THE HAMAQ PROJECT

The specific objectives of the project are:

- a) to develop the methodology whereby internationally-accepted calibration gas standards can be produced and certified in concentration so as to promote widespread uniformity and accuracy of air quality measurements throughout Europe;
- b) to demonstrate the equivalence of different 'primary' methods available in different member states for providing nationally traceable calibrations of air quality measurements of atmospheric pollutants (CO, NO, NO₂, SO₂ and C₆H₆) in order that these methods can be employed to certify stable gas calibration mixtures produced commercially;
- c) to develop improved gas cylinder surface passivation treatments by means of the industrial partners, and to evaluate their effectiveness in order to provide more accurate, stable long-lifetime calibration gas mixtures for CO, NO, NO₂, SO₂ and C₆H₆;
- d) to provide technology transfer, in order to promote improved measurements across Europe - particularly in Member States where the air quality measurement infrastructure is not yet fully mature or is not yet of demonstrated accuracy.

The technical work programme is divided into four workpackages:

- (i) **Workpackage 1 (WP1): Production and stability test of a first set of gas mixtures**

This workpackage has involved:

One specialist gas company (Messer) preparing, testing and supplying 15 cylinders of each of NO, NO₂ and SO₂ to the partners responsible for the relevant intercomparisons (piloted by LNE, UBA and ERLAP, JRC respectively)

Another specialist gas company (Scott Gases) preparing, testing and supplying 15 cylinders of each of CO and C₆H₆ to the partners responsible for the relevant intercomparison (piloted by NPL and NMi respectively).

Measurements of the stability of the prepared mixtures of NO_2 , SO_2 and C_6H_6 , and the characterisation of their decay, if detected.

(ii) Workpackage 2 (WP2): Intercomparisons using the first set of gas mixtures

This workpackage required:

NPL, ERLAP-JRC, NMi, UBA and LNE to coordinate intercomparisons for the gases CO , SO_2 , C_6H_6 , NO_2 and NO respectively;

The 3 or 4 partners involved in each of the intercomparisons to make measurements through comparison with their national primary standard facilities and determine their measurement uncertainties in accordance with the ISO document "Guide to the Expression of Uncertainty in Measurements" (GUM);

To report their results to the appropriate pilot laboratory;

The project coordinator to organise a meeting to discuss the results of the exercise about 12 months from the start of the contract.

(iii) Workpackage 3 (WP3): Intercomparisons using a second set of gas mixtures

The partners responsible for each type of gas mixture will produce a new set of gas mixtures and will distribute or circulate these to Partners 1 to 7 for a second set of intercomparisons.

Each participant will analyse the gas mixtures using their designated primary method plus any other methods available to them. They will provide their results in the form of concentration values with estimates of measurement uncertainties in accordance with the ISO guidelines ("GUM").

The results will be collated and processed initially for each gas by the responsible partners, and subsequently by the coordinator.

(iv) Workpackage 4 (WP4) Dissemination and Technology Transfer

The findings of the project will be disseminated to all European national network operators through a technical workshop, organised by the coordinator, at a time and place agreed by the Commission.

Workpackages 1 and 2 were due for completion within the period, 1st December 1996 - 30th November 1997.

3. RESULTS OBTAINED DURING THE REPORTING PERIOD

3.1 WORK PACKAGE 1: GAS MIXTURE PRODUCTION AND STABILITY TESTS

Fifteen cylinders of each of NO, NO₂ and SO₂ were delivered on schedule directly to the appropriate pilot laboratories (LNE, UBA and ERLAP respectively) by Messer during February 1997.

Preparations for the production of these gas mixtures started during July/August 1996 at the Messer production facility at Duisberg, Germany. Prior to filling the empty cylinders assigned to this project were conditioned at the Messer Krefeld-Gelep plant where the empty aluminium cylinders were evacuated and treated using a combination of chemicals (including HF) to passivate the surface of the cylinder. Following this a valve was fitted to the passivated cylinder, which was then baked at 50°C in order to remove residual water. At the Duisberg facility empty cylinders were then initially filled with gas mixtures at a concentration of 10ppm of SO₂ and NO₂ which was used to passivate the internal walls of the cylinders. In this 'soaking' process the cylinders were left for 2-3 months to allow the concentration of the mixtures within the cylinders to stabilise. This has the effect of saturating, and thereby deactivating, otherwise active sites which could potentially cause decay at some later time. The cylinders were then evacuated and then filled with a small amount of a parent mixture to be used for the gas concerned - at a concentration of 10 ppm. This was then diluted, using high pressure, with zero gas to give the correct nominal concentration, in this case ~200 ppb.

In the case of NO mixtures, stability was not considered to be a problem and no pre-conditioning was thus carried out.

Fifteen mixtures of CO and C₆H₆ were prepared by Scott Speciality Gases and delivered to the pilot laboratories (NPL and NMI) during February and March. The CO mixtures were prepared using a dynamic blending technique (using the Scott 'Acublend' process). The benzene standards were produced gravimetrically and by a multistage dilution process.

The subsequent stability tests on the concentrations of the SO₂, NO₂ and C₆H₆ mixtures carried out by the appropriate pilot laboratories are discussed in the relevant sections (3.2.3, 3.2.4 and 3.2.5) below.

3.2 WORK PACKAGE 2: FIRST INTERCOMPARISONS

3.2.1 CO Intercomparison

Fifteen CO gas mixtures in synthetic air were delivered for use as transfer standards on schedule to NPL during February 1997. Initial measurements were made on all fifteen cylinders during the period 11th-25th March 1997. A further three measurements were made on four of these cylinders during the period 10th April-16th May 1997. During June, one cylinder was shipped to each of the participants involved in the intercomparison, (LNE and UBA). In addition, a further circulation cylinder was shipped to LNE and then

to UBA and subsequently back to NPL. The following measurement methods were used to determine the concentration of the CO mixtures in the intercomparison cylinders:

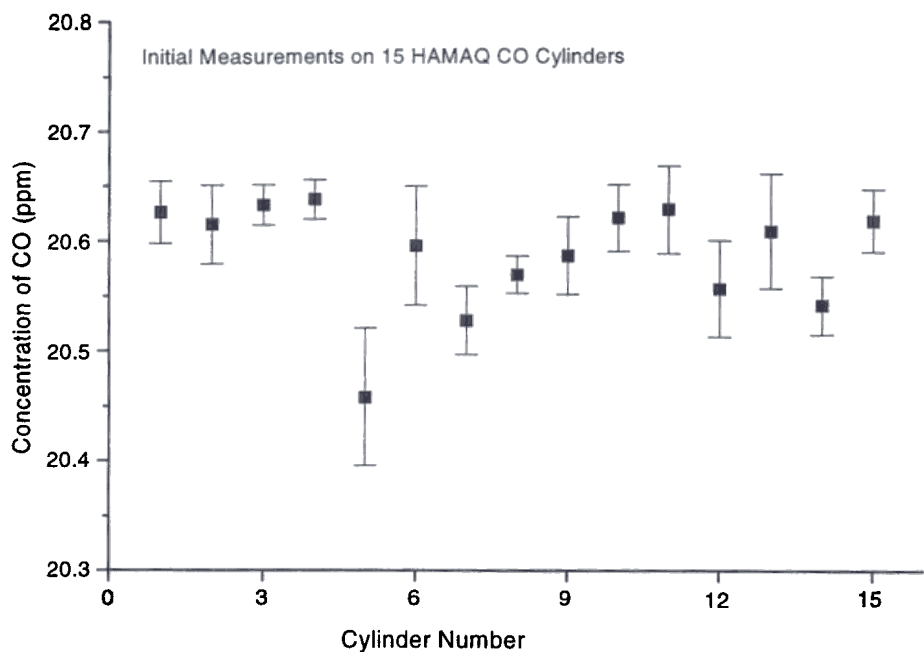
- 1. At NPL, a non-dispersive infrared (NDIR) analyser was used, which was calibrated using gravimetrically prepared mixtures of CO in diluent N₂.
- 2. At LNE, an NDIR analyser was used, which was calibrated using gravimetrically-prepared standard mixtures of CO in synthetic air.
- 3. At UBA, an NDIR analyser was used, which was calibrated against standards generated using a static injection method.

The results obtained, together with associated uncertainties are summarised in Table 1 below.

Table 1: Summary of results from the CO intercomparison

Cylinder 5701207				
Laboratory	Mean/ppm	Standard Dev./ppm	2σ Uncertainty/ppm	Diff. Rel. NPL
NPL	20.64	0.07	0.11	---
UBA	20.21	0.06	0.40	2.1%
LNE	20.22	0.02	0.35	2.0%
Cylinder 5701217				
Laboratory	Mean/ppm	Standard Dev./ppm	2σ Uncertainty/ppm	Diff. Rel. NPL
NPL	20.64	0.04	0.11	---
LNE	20.25	0.04	0.35	1.9%
Cylinder 5701219				
Laboratory	Mean/ppm	Standard Dev./ppm	2σ Uncertainty/ppm	Diff. Rel. NPL
NPL	20.61	0.04	0.11	---
UBA	20.21	0.06	0.40	2.1%

Measurements on the fifteen cylinders are shown in Figure 1 below (It should be noted that the cylinder numbers are not revealed in order to maintain the unknown nature of the concentrations in the cylinders throughout the second phase intercomparisons which will involve the other partners.



A Summary of the measurement procedures carried out by the individual laboratories involved in the first CO intercomparison are given below.

(i) Measurements carried out by the National Physical Laboratory

Primary standards of CO in **nitrogen** are maintained at NPL in the concentration range 7%-10 ppm, with uncertainties of $\pm 0.06\%$ to $\pm 0.3\%$ respectively (95% confidence limits). These standards are prepared gravimetrically and stored in high pressure cylinders. Their concentrations are validated by comprehensive internal and external intercomparisons.

For the measurements reported here, an initial single measurement was conducted using an NDIR analyser, which was calibrated using primary standards at concentrations of 10, 25 and 50 ppm, to establish the approximate concentration of CO gas mixtures in the cylinders of the batch. This was found to be about 20.5 ppm. Further new primary standards were then prepared at concentrations of 20.2 ppm (afterwards called C_1) and 20.8 ppm (afterwards called C_2) (about $\pm 1.5\%$ relative to unknown concentration) and subsequently used to calibrate the NDIR analyser. The unknown concentration (C_u) was then determined by linear interpolation from the measurements obtained during an automatic measurement sequence: which involved measurements of zero gas, C_2 , zero gas, C_1 , C_2 , zero gas, C_u , C_2 zero gas. This sequence is repeated six times and the mean and standard deviation reported. The results obtained are summarised in Tables 2a, 2b and 2c below.

Table 2(a): Cylinder number 5701207 (circulation cylinder)

measurement No.	date	result (μ mol/mol)	Stand Deviation (% relative)	number of sub-measurements
1	20/03/97	20.63	0.09	6
2	10/04/97	20.58	0.12	6
3	1/05/97	20.76	0.15	6
4	16/05/97	20.62	0.31	6
5	19/8/97	20.62	0.19	6

Result (assigned value) : 20.64 ppm

Assigned overall uncertainty : 0.11 ppm (95% confidence limit)

Table 2(b): Cylinder number 5701217

measurement No.	date	result (μ mol/mol)	stand. Deviation (% relative)	number of sub-measurements
1	19/03/97	20.61	0.17	6
2	10/04/97	20.60	0.17	6
3	1/05/97	20.68	0.13	6
4	15/05/97	20.69	0.13	6
5	2/09/97	20.63	0.14	6

Result (assigned value) : 20.64ppm

Assigned overall uncertainty : 0.11ppm (95% confidence limit)

Table 2(c): Cylinder number 5701219

measurement No.	date	result (μ mol/mol)	stand. Deviation (% relative)	number of sub-measurements
1	20/03/97	20.64	0.09	6
2	10/04/97	20.54	0.45	6
3	01/05/97	20.65	0.23	6
4	15/05/97	20.61	0.19	6
5	02/09/97	20.63	0.14	6

Result (assigned value) : 20.61ppm
Assigned overall uncertainty : 0.11 ppm

The uncertainties reported for these measurements are derived from:

- (i) The uncertainties in the concentration of the primary standards, which are derived from the uncertainties in the molecular masses of the components, the uncertainties in the purity analyses and the multistage weighing process itself.
- (ii) The uncertainties in the analysis process including instrumental precision and bias.

Table 3 summarises the methodology for deriving the overall uncertainty.

Table 3 : Overall uncertainties in NPL measurements of HAMAQ cylinders.

Symbol	Source & Uncertainty	Value (ppm)	Distribution	Division	C _i	U _i	V _i
C ₁	low primary standard	0.05	n	2	0.3	0.01	∞
C ₂	high primary standard	0.05	n	2	0.7	0.02	∞
a	analysis uncertainty	0.03	n	1	1	0.03	4
U(C _u)	combined uncertainty		n			0.04	
U	expanded uncertainty		n(k = 2.78)			0.11	4

(ii) Measurements carried out by the Laboratoire Nationale d’Essais

A primary standard of CO in air was generated specifically for the HAMAQ intercomparison measurements. This was done by a two-stage gravimetric procedure in

which, initially, a high concentration (~1000 ppm) CO air mixture is produced by introducing a known weight of CO into an evacuated cylinder and then by topping this up with a known mass of air. In the second stage this CO mixture was diluted again to produce a mixture at a concentration of about 40 ppm. This gravimetric mixture was then compared against previously-prepared standards at NMi to ensure its comparability with existing standards.

This mixture is used to calibrate (span) the analyser which was set at 40 ppm full scale reading. The analyser used was a COSMA BERYL 100 dual cell NDIR analyser. The following procedure was used to obtain the measurements summarised in tables 4(a) and 4(b) below. ||

- (i) Instrument calibration (zero gas and 40 ppm span).
- (ii) Three individual measurements were made on the sample.
- (iii) The above process was repeated three times.

Table 4(a): Cylinder number 5701207

measurement N°	date	result (ppm)	Standard deviation (% relative)	number of sub measurements
1	97-6-5	20.23	0.06	3
2	97-6-5	20.23	0.06	3
3	97-6-5	20.20	0.17	3

Result (assigned value) : 20.22 ppm
Assigned overall uncertainty : 0.35 ppm (95 % confidence level)

Table 4(b): Cylinder number 5701217

measurement N°	date	result (ppm)	Standard deviation (% relative)	number of sub measurement
1	97-6-6	20.27	0.06	3
2	97-6-6	20.20	0.10	3
3	97-6-6	20.27	0.12	3

Result (assigned value) : 20.24 ppm
Assigned overall uncertainty : 0.35 ppm (95 % confidence level)

The derivation used to obtain the uncertainties given above is summarised in table 5 below :

Table 5: Uncertainties for LNE measurements of CO in air mixtures

Variable	Source of uncertainty	Uncertainty (ppm)	Variance
Preparation of gas span (39.67 ppm)	Concentration of the gravimetric gas mixture (39.67 ppm)	0.26	0.016
Analyser	Repeatability	0.22	0.012
	Calibration	0	0
	Non-linearity	0.12	0.0033

(iii) Measurements carried out by Umweltbundesamt Offenbach, Pilotstation

Primary gas mixtures were generated using a static volumetric method in which a small volume of pure CO is diluted in a 14 litre chamber to produce a concentration of 29.9 ppm. This 14 litre chamber is normally filled to a pressure of 9.5 bars.

The volume of the chamber is determined by filling with water. As a quality assurance check the performance of the chamber was compared against that of a larger chamber (100 litre) in generating low concentration mixtures of SO₂. The agreement was also found to be within ± 0.18%.

As a further accuracy test low volume syringes (0.05 - 5ml capacity) were compared with other similar syringes. The deviations of the measured volumes was found to be less than ± 1%.

The resulting mixture was used to calibrate a NDIR CO analyser. This analyser was then used to measure the concentration of the CO/air mixtures within the HAMAQ cylinders. This process was repeated three times, and the results obtained are shown below in Tables 6(a) and 6(b).

Table 6(a): Cylinder number 5701207

Measurement Number	date	result (ppm)
1	97-7-5	20.20
2	97-7-5	20.17
3	97-7-5	20.25

Result (assigned value)

Assigned overall uncertainty

: 20.21 ppm

: 0.40 ppm (95 % confidence level)

Table6(b): Cylinder number 5701219

Measurement Number	date	result (ppm)
1	97-7-20	20.20
2	97-7-20	20.17
3	97-7-20	20.25

Result (assigned value) : 20.21 ppm
Assigned overall uncertainty : 0.40 ppm (95 % confidence level)

The uncertainty analysis used to derive the uncertainties given is taken from ISO 6144, and includes: uncertainty contributions from purity of the gas; the pressure measurement; the temperature measurement and the measurement of the syringe and chamber volumes.

(iv) Conclusions of the First CO Intercomparison

The largest discrepancy in the derived concentrations of CO in the three cylinders that were intercompared in the first intercomparison is 2.1% (NPL vs UBA, both circulation and individual cylinders, see Table 1). The UBA and LNE results are, however, in good agreement - 0.1% difference, which is not significant compared with the measurement uncertainties of the partner laboratories. The NPL measurements appear to be 2.0% higher than the both UBA and LNE measurements for the both the circulation and individual intercomparisons. Thus although the NPL and LNE results for cylinders 5701207 and 5701217 are in agreement within their combined measurement uncertainties (at 95% confidence levels) it is likely, given the level of agreement between UBA, LNE and the Scott assured values, that this discrepancy is real.

One possible source of this discrepancy was that CO in nitrogen primary standards were used to calibrate the NDIR analyser at NPL. The intercomparison cylinders, however, contained CO prepared in air. Additional measurements are therefore currently underway at NPL to investigate whether there is a possible difference in the NPL NDIR analyser response to standards which are prepared in air and nitrogen.

Another possibility is the existence of significant CO impurity levels in the balance gas used to generate the primary standards prepared by LNE and UBA. These laboratories are currently examining the specifications of the balance gases used and the results of in-house purity checks.

NO Intercomparison

(i) LNE Measurement Techniques and Facilities

The LNE multistage technique which was used to certify the concentrations of the NO mixtures supplied to them is summarised below.

a) Preparation of Calibration Standards :

- Preparation of source mixture of NO in nitrogen (of the order of 17 000 ppm mol)

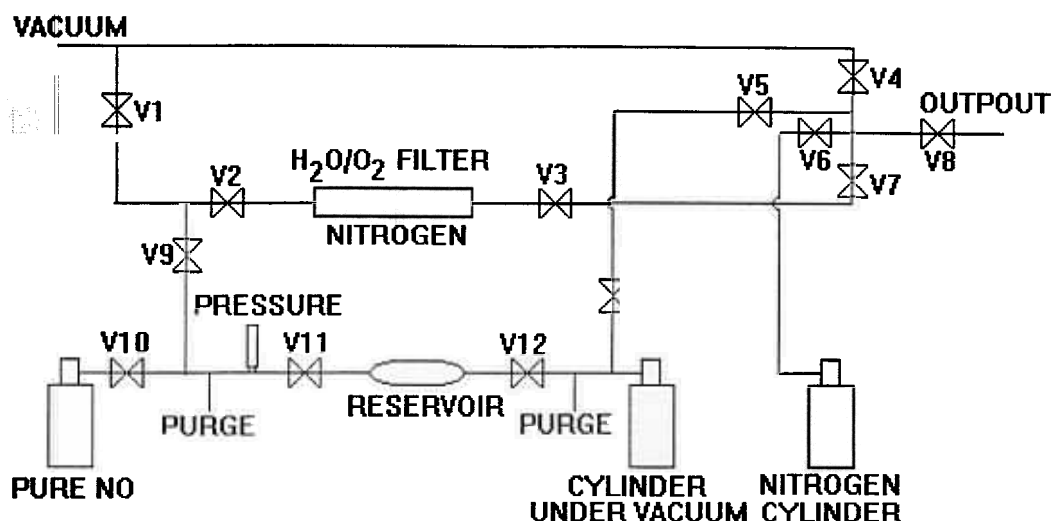


Diagram 1 : System for generating primary mixtures of NO in nitrogen

Initially, a high concentration mixture of NO in nitrogen is generated (of the order of 17 000 ppm). Preparing mixtures of NO in nitrogen is very critical as the slightest damp or oxygen in the generator system may cause parasitic reactions. To avoid these problems, nitrogen of N60 purity is passed through a specific filter designed to trap water vapour and oxygen before the nitrogen is used to generate the NO mixtures.

In addition, before generating the NO mixtures in nitrogen, it is essential to ensure that the system is not polluted. To do this, the system is evacuated and then heated. The whole of the generation system is evacuated to about 10^{-6} mbar. The system is then flushed with a small quantity of nitrogen or NO as appropriate.

The stainless-steel cylinder and reservoir are then removed from the system and weighed on two balances: the cylinder is weighed on a 15 kg balance and the reservoir on a 1.2 kg balance. The reservoir is then filled with pure NO and weighed again on the 1.2 kg balance. Because of the heating of the gas, there should be a delay between filling the reservoir and weighing.

Finally, this volume of NO is introduced into the cylinder under vacuum and the cylinder is filled with nitrogen at 150 bar. The cylinder filled with NO and nitrogen is weighed again to establish the mass of nitrogen introduced into the cylinder. Because of the heating of the gas, there should be a delay between filling the cylinder and weighing.

- Preparation of NO secondary mixture in nitrogen (of the order of 500 ppm mol)

An NO secondary mixture in nitrogen of about 500 ppm mol is then generated.

The method described in paragraph a) is used. However, the reservoir is filled from the source NO in nitrogen cylinder at about 17000 ppm mol instead of pure NO.

- Preparation of NO tertiary mixture in nitrogen (of the order of 13 ppm mol)

An NO tertiary mixture in nitrogen of about 13 ppm mol is then generated.

The method described in paragraph a) is used. However, the reservoir is filled from the source NO in nitrogen cylinder at about 13 ppm mol instead of pure NO.

- Generation of a NO mixture in nitrogen at about 400 ppb mol

The 400 ppb mixture of NO in nitrogen is generated from the source mixture of NO in nitrogen at about 13 ppm mol prepared in the laboratory (cf paragraph c) and a cylinder of nitrogen for dilution (diagram 2).

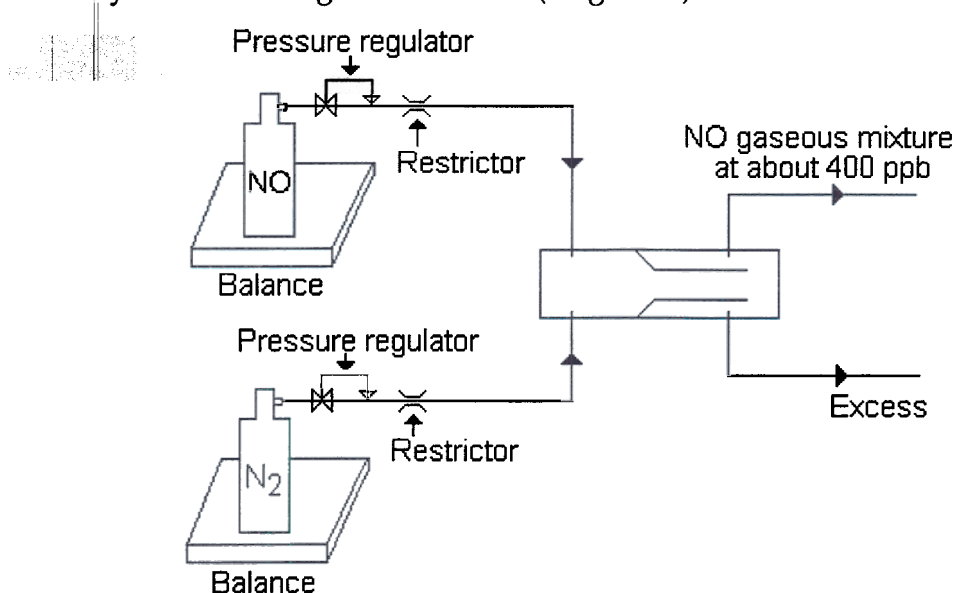


Diagram 2 : Generation of a NO mixture in nitrogen at about 400 ppb mol

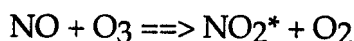
The cylinder of nitrogen for dilution is placed on a 15 kg balance and the cylinder containing the source mixture of NO in nitrogen (at about 13 ppm mol) is placed on a 6.2 kg balance. These two balances are connected to the same computer. The balances used allow real-time measurement of the flow by loss of mass against time.

The NO concentration of the gas mixture is the NO concentration at about 13 ppm mol NO multiplied by NO flow rate and divided by the sum of the NO flow rate plus the nitrogen flow rate.

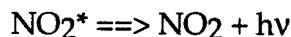
b) Measurement Method :

An Environment SA AC31M analyser is used to measure the NO. This uses chemiluminescence. It is used exclusively for this procedure.

The oxidation of NO by ozone causes chemiluminescence.



When the excited NO_2^* molecules return to their ground state, radiation is produced in the range 600 to 1200 nanometers.



c) Instrument calibration :

Stage 1: Setting The Analyser

The analyser is set at 1 point : full scale which is double the concentration to be analysed. In this case, the NO concentration is close to 200 ppb. So, the analyser is set to 400 ppb with NO.

Stage 2: Determining The NO Concentration Of An Unknown Gas Mixture

The unknown gas mixture is injected 3 times consecutively into the NO_x analyser. The NO concentration of the unknown gas mixture is equal to the NO concentration displayed by the analyser (C_{read}).

This procedure (stage 1 + stage 2) is carried out 3 times.

d) Sample Handling :

Cylinders were maintained inside a laboratory at a nominal temperature of 20 °C for all the period.

Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

(ii) NPL Measurement Techniques and Facilities

a) Primary Calibration Standards :

NO standards are prepared in the range 200ppb - 1ppm (mol/mol) by a multistage gravimetric dilution process from the pure gas. Each dilution stage involves a 10 to 1 dilution. These primary standards are prepared and stored in high pressure cylinders, and their concentrations and stabilities are validated by comprehensive internal intercomparisons and rigorous international comparisons.

The purity of the nominally pure NO is established using FTIR and GC techniques. The calculated purity of the NO used to generate the standards used for these measurements was found to be 99.6%.

The diluent gas (N_2) is analysed for residual NO and NO_2 by using a chemiluminescence analyser which has been zeroed using a scrubbed zero gas. The efficiency of the scrubber is established by measurement.

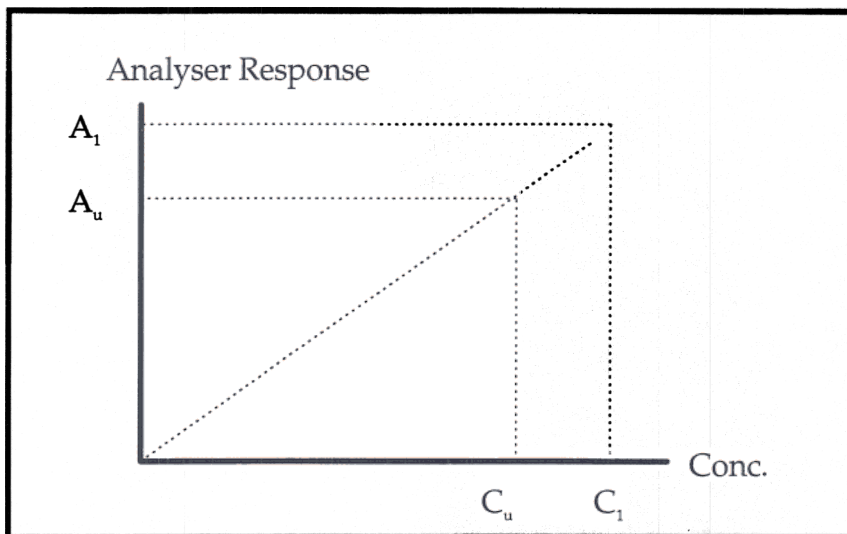
b) Measurement Method :

The measurements reported here were obtained using a calibrated chemiluminescence NO/NO₂ analyser (API model 200). Two NPL primary gravimetric standards at 500 ppb and 830 ppb were used both to calibrate the NO_x analyser and to place an upper limit estimate on the non linearity of the analyser.

For each of the 3 independant calibrations required by the protocol, 3 sub - measurements were obtained, each of these measurements were taken from an average of 5 independant readings from the analogue voltage output from the back of the analyser, using a digital data logger .

c) Instrument Calibration :

The measurements reported here were obtained from a *ratiometric* procedure. The mathematical model used to derive the concentration of the NO in the intercomparison cylinder (C_u) from the measured input parameters (C_1 and A_1 , the span gas concentration and associated analyser response, together with the analyser response for the unknown gas to be analysed A_u) is shown below:



$$C_u = A_u \cdot (C_1 / A_1)$$

d) Sample Handling:

Cylinders were maintained within a laboratory at a nominal temperature of 20°C for the period 15/4/97 - 15/6/97. Samples were introduced into the analysers via a normal gas regulator and a bypass valve. Analysers were allowed to stabilise for greater than 10 minutes prior to measurements.

(iii) UBA Measurement Techniques and Facilities

The Principle of the method is described in VDI 3490 ; Part 14.

a) Calibration Standards :**Static volumetric method :**

A glass chamber of 167 litres was used at 1.5 bar : 50 µl of pure NO (purity 2.5) were injected. This results in a pressure concentration of 299 ppbv. 50 µl volume chosen to minimize the reading error of the syringe.

b) Measurement Method :

The measurements reported here were obtained using a analyser which is a Apna 350 E, Horiba (chemiluminescence).

c) Instrument Calibration :

The NO channel and the NOx channel of the analyser are calibrated with the prepared primary NO standard: before that the conversion efficiency of the reference instrument is determined by gas phase titration. Using NO concentration gases at a concentration of about 200 ppbv, interferences of other NOx - components are negligible.

(iv) LNE Results and Measurement Uncertainties**Table 7(a):Cylinder number A9080**

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (ppb) (*)
1	97-03-06	196.7	0.6	3	196.8	2.6
2	97-03-06	196.7	0.6	3		
3	97-03-06	197.0	0.0	3		
4	97-11-12	195.7	0.6	3	195.8	2.4
5	97-11-13	195.7	0.6	3		
6	97-11-14	196.0	0	3		

Table 7(b): Cylinder number A9192 (Circulating Cylinder)

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (ppb) (*)
1	97-03-07	197.0	0.0	3	197.0	2.6
2	97-03-07	197.3	0.6	3		
3	97-03-07	196.7	0.6	3		
4	97-11-12	196.0	0	3	196.3	2.4
5	97-11-13	196.3	0.6	3		
6	97-11-14	196.7	0.6	3		

Table 7(c): Cylinder number A9206

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (ppb) (*)
1	97-03-12	196.7	0.6	3	196.9	2.6
2	97-03-12	197.0	0.0	3		
3	97-03-12	197.0	0.0	3		
4	97-11-12	195.3	0.6	3	195.7	2.4
5	97-11-13	196.3	0.6	3		
6	97-11-14	195.3	0.6	3		

(*) overall uncertainty at 95 % confidence level

The uncertainty analysis used to derive the uncertainties given in enclosure 1 above is summarised in table 9:

Table 8: Uncertainties for LNE Measurements of NO in Nitrogen Mixtures

Variable	Source of uncertainty	Uncertainty (U in ppb)	Variance
Preparation of gas span	Concentration of the gas mixture obtained by dilution of a gravimetric NO standard mixture (1)	2.05 (03/97) 1.75 (11/97)	1.05 (03/97) 0.77 (11/97)
Zero gas	Concentration of zero gas (2)	1.15	0.33
Analyser	Repeatability (3)	0.94	0.22
	Calibration (4)	0.40	0.04
	Non-linearity (5)	0.57	0.08

Notes :

1. The uncertainty on the span gas concentration is derived from an uncertainty analysis of the dilution of a gravimetrically prepared NO standard mixture (uncertainty on the purity of used pure gases, uncertainty on the weighing process, uncertainty on the molar masses, uncertainty on the dilution...).
2. The uncertainty on zero gas (nitrogen) is estimated at ± 1 ppb (rectangular distribution).

3. and 4. The uncertainties are estimated by using the ISO 5725 standard.
5. The NO_x analyser is calibrated with a gas mixture. Then, another gas mixture is injected. The uncertainty (± 0.5 ppb, rectangular distribution) is estimated from the difference between the response of the analyser and the response calculated with the calibration curve.

(v) **NPL Results and Measurement Uncertainties**

Table 9(a): Cylinder number A9080

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (ppb) (*)
1	97 - 5 - 7	194.0	0.4	3 (each av. of 5)	194.5	4.6
2	97 - 5 - 9	193.7	0.4	3		
3	97 - 6 - 10	195.7	0.3	3		

Table 9(b): Cylinder number A9192 (Circulating Cylinder)

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (ppb) (*)
1	97 - 5 - 7	194.7	0.1	3	195.4	4.6
2	97 - 5 - 9	195.7	0.1	3		
3	97 - 6 - 10	195.7	0.3	3		

(*) overall uncertainty at 95 % confidence level

The uncertainty analysis used to derive the uncertainties is summarised in the table below:

Table 10: Uncertainties for NPL Measurements of NO in Nitrogen Mixtures

Symbol	Source & Uncertainty	Value	Distribution	Divisor	C _i	U _i	v _i
c ₁ ¹	preparation of span gas (500 ppb span)	10 ppb	normal	2.0	0.4	2.0	50 ⁷
c ₀ ²	concentration of zero gas	1 ppb	rectangular	$\sqrt{3}$	0.6	0.3	∞
a ₀ ³	fluctuations in analyser response	1.5 mV	normal	2.0	0.6	0.4	15
a ₁ ⁴	fluctuations in analyser response	1.5 mV	normal	2.0	0.4	0.3	15
a ₁ ⁵	analyser non-linearity	2.0 mV	rectangular	$\sqrt{3}$	0.4	0.5	3
a _u ⁶	fluctuations in analyser response	1.5 mV	normal	2.0	1.0	0.8	15
U(CU)	combined uncertainty		normal			2.3	87 ⁸
	expanded uncertainty		normal (k=2)			4.6	87

Notes:

1. The uncertainty in the span gas concentration (10ppb) is derived from an uncertainty

analysis of the gravimetric preparation method. The main contributions to this uncertainty are :

- the uncertainty in the purity analyses.
 - the uncertainty in the weighing process (including handling effects, balance sensitivity and buoyancy effects)
2. The uncertainty here (1 ppb , rectangular distribution) is estimated based on previous determinations of the concentrations of NO within similar samples of zero gas.
 3. The uncertainty in the zero level analyser response (± 1.5 mV, 95% confidence level) is taken from a Type A evaluation of uncertainty in the analyser output.
 4. as for 3.
 5. This uncertainty (± 2.0 mV, rectangular distribution) is estimated from the difference in the analyser calibration factors derived from the two gravimetric standards produced at 830ppb and 500 ppb.
 6. as for 3.
 7. See ISO guide , Appendix A , Section A4
 8. See ISO guide, Appendix A , Section A3.

(vi) UBA Results and Measurement Uncertainties

Table 11(a): Cylinder number A9206

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (*)
1	97-7-3	201.1	-	1	200.7	< 2 %
2	97-7-3	199.0	-	1		
3	97-7-3	202.0	-	1		

(*) overall uncertainty at 95 % confidence level

Table 11(b): Cylinder number A9192 (Circulating Cylinder)

Measurement N°	Date	Result (ppb)	Standard deviation (% relative)	Number of sub measurements	Mean (ppb)	Assigned overall uncertainty (ppb) (*)
1	97-7-3	200.6	-	1	199.8	< 2 %
2	97-7-3	199.2	-	1		
3	97-7-3	199.5	-	1		

(*) overall uncertainty at 95 % confidence level

UBA have not yet developed an explicit measurement uncertainty budget in the format given by LNE and NPL above. However, ISO 6144 gives an uncertainty which is smaller than 2 % at a 95 % confidence interval : this uncertainty comprises the uncertainty of the preparation of the calibration gas (uncertainty of the volumes of the chamber and the syringe, uncertainty of the purity gases, uncertainty of pressure and temperature

measurements) and the measurement uncertainties associated with the analytical instrument.

The purity of the pure gas is given by the manufacturer as 2.5 for NO. But there is some doubt. Therefore, a research programme is initiated at PTB which should clarify that phenomena, which is due to all preparation methods (gravimetry, permeation and so on).

(vii) Summary of the Results Obtained in the NO Intercomparison

A summary of the results of the NO intercomparison is given below in table 12.

Table 12: Summary of results for the first NO intercomparison

LAB	Cylinder A9192 (circulating cylinder)		Cylinder A9080		Cylinder A9206	
	Mean (ppb)	Uncertainty (ppb)	Mean (ppb)	Uncertainty (ppb)	Mean (ppb)	Uncertainty (ppb)
LNE	197.0	2.6	196.8	2.6	196.9	2.6
NPL	195.4	4.6	194.5	4.6	-	-
UBA	199.8	4.0	-	-	200.7	4.0
LNE	196.3	2.4	195.8	2.4	195.7	2.4

3.2.3 SO₂ Intercomparison

(i) Overview and Stability Test Results

The responsible pilot laboratory for the stability tests and subsequent intercomparison was ERLAP. During the first workpackage the gas mixtures were prepared (according to the certificates) on 27 January 1997 by Messer. The fifteen cylinders arrived in Ispra on 13 February 1997. All cylinders were stored as soon as possible after arrival at a room temperature of 20°C and were rolled for several minutes before analysis. Samples were introduced into the analyser via a pressure regulator and an overflow valve.

A first measurement was carried out on 27 and 28 February, a second on 13 and 14 March, and a third one on 20 and 21 March 1997. The ERLAP measurements show in most cases lower values than the Messer certificates, and for 5 cylinders the ERLAP measurements were outside of the tolerance stated on the Messer certificates of $\pm 5\%$.

Table 13: Results Of The Measurements Of All Fifteen Cylinders On Arrival at ERLAP

Cylinder	Messer Certificates (ppb)	Pressure At Arrival	1 st analysis (ppb)	2 nd analysis (ppb)	3 rd analysis (ppb)	ERLAP Concentration Value (ppb)
4552B	204	137	201,8	202,9	205,1	203,3
6991E	213	145	203,0	198,0	202,0	201,0
A715	214	142	205,9	208,0	209,0	207,6
120C	209	143	209,1	205,9	207,0	207,3
4719A	206	142	196,0	196,0	197,1	196,4
A1345	211	143	207,0	207,0	207,3	207,1
556948	206	138	206,5	205,5	207,8	206,6
4476B	216	149	210,5	209,5	209,3	209,8
8109A	202	138	197,5	196,5	199,1	197,7
4192E	200	143	193,5	192,5	192,3	192,8
5791F	202	137	180,6			180,6
5421C	211	137	196,3			196,3
2921C	180	138	152,8			152,8
6829F	208	141	199,1			199,1
A4597	181	141	150,9			150,9

For each gas mixture of the HAMAQ project it is required that the stability of the mixtures should be monitored over a long period with a smaller set of gas cylinders. eg. measurements could be carried out every two weeks for three months and every two months for one year. The stability tests are therefore not yet completed according to this time schedule. However, the results obtained to date are presented in Table 14.

Table 14: Stability tests by ERLAP on six SO₂ gas mixtures

	4719A	4476B	4192E	8109A	A1345	556948
MG	206.0	216.0	200.0	202.0	211.0	206.0
28.02.97	196.0	210.5	193.5	197.5	207.0	205.5
14.03.97	196.0	209.5	192.5	196.5	207.0	207.8
04.04.97	197.1	209.3	192.3	199.1	207.3	206.2
04.04.97	194.6	208.7	191.6	197.5	205.8	208.8
04.04.97	197.1	210.2	194.7	199.5	209.7	206.2
04.04.97	196.0	209.2	193.6	197.5	208.2	204.1
05.04.97	196.4	209.9	192.5	196.4	204.6	203.7
05.04.97	195.9	209.5	193.0	196.4	204.7	203.0
26.06.97	195.0	211.0	194.0	196.0	210.0	204.0
26.06.97	197.0	212.0	193.0	195.0	211.0	201.4
21.07.97	193.6	208.3	191.7	194.6	208.3	204.4
21.07.97	197.5	210.2	193.4	195.6	211.2	199.0
07.08.97	194.0	209.0	192.0	195.0	209.0	207.5
20.08.97	200.5	214.0	194.5	196.5	214.0	206.5
20.08.97	199.7	214.2	194.9	197.8	212.7	202.0
23.10.97	192.6	208.5	188.9	190.7	208.5	
Average	196.2	210.3	192.9	196.4	208.7	204.8
StDev	2.06	1.78	1.48	2.05	2.68	2.60
Stdev%	1.0	0.8	0.8	1.0	1.3	1.3
Min	192.6	208.3	188.9	190.7	204.6	199.0
Max	200.5	214.2	194.9	199.5	214.0	208.8

The measurement results of these six gas cylinders showed no significant trend in concentrations during the period from February to October. The standard deviation of the sixteen concentration values for each cylinder lies between 0.8% to 1.3 %. A summary of the results obtained for the intercomparison is given in table 15 below.

Table 15: Results of WP2 – First Intercomparison for SO₂

(all results in ppb)							Mean	Uncertainty
Cylinder 120C								
	Measurement dates							U
	1997							
ERLAP	28/2, 14/3, 21/3, 3/4, 4/4	209,1	205,9	207	205,8	207,5	207,1	3,1
LNE	24/4, 25/4, 26/4	207	207	207			207,0	2,6
Cylinder A715								
ERLAP	28/2, 14/3, 21/3, 3/4, 4/4	205,9	208	209	207,3	207,5	207,5	3,1
NMi	9/7, 10/7, 26/8, 27/8, 28/8	207	207,5	204,8	207,6	204,9	206,4	1,3
Cylinder 6991 E								
ERLAP	28/2, 14/3, 21/3, 3/4, 4/4	203	198	202	198,2	203,6	201,0	3,1
LNE								
NMi	9/7, 10/7, 26/8, 27/8, 28/8	206,9	208,4	208,7	208,8	209,1	208,4	0,8
UBA	17/10	214,4	215,9	215,5			215,3	0,6
Cylinder 4552 B								
ERLAP	28/2, 14/3, 21/3, 4/4	201,8	202,9	205,1	201,6	203,6	203,0	1,3
UBA	23/5	197,8	195,8	195,8			196,5	1,5

All participants were asked to calculate the uncertainty of their results according to the ISO Guide.

The calibration and measurement procedures of the participating laboratories are described more detailed below:

(ii) Calibration standard and measurement procedure - ERLAP

A permeation tube with SO_2 is maintained in a thermostated system with a continuous flow of nitrogen over the permeation system. At regular intervals the tube is removed from the permeation system, left for 90 min at ambient conditions (20°C , 50 % r.H.) and weighed on a Mettler AT201 balance. Calibration standards are made by dilution with cleaned air. The total flow SO_2 in N_2 and air is measured with a calibrated mercury sealed piston flow meter. The SO_2 fraction in the mixture is then calculated by dividing the permeation rate by the total flow.

ERLAP maintains three permeation systems for SO_2 , each having different permeation rates. Through dilution, concentrations in a range from 50 to 800 ppb SO_2 can be generated. The SO_2 concentration is measured with an UV Fluorescence analyser AF 21 M from Environnement SA, which is calibrated by a calibration curve (linear regression) from three or four standards prepared by the permeation method.

(iii) Calibration standard and measurement procedure- NMi

A permeation tube with SO_2 is maintained in a balance under continuous weighing and an air flow along the tube of about 50 ml/min ($\rightarrow$ permeation rate in nmol/min). Calibration standards are made by dilution with synthetic air, having a total sulphur content of less than 1ppb. The total flow (air + SO_2) is measured with a calibrated mercury sealed piston flow meter (to give the total amount of moles per minute in the mixture).

The SO_2 fraction in nmol/mol in the mixture is calculated by dividing the permeation rate by the total flow, the standard uncertainty on the fraction SO_2 is 0,17%.

A permeation system in which the permeation rate is determined by continuous weighing is maintained. The current concentration range is 350-750 nmol/mol with a total uncertainty of 2%. A Thermo Electron Instruments - Pulsed Fluorescence SO_2 ambient Air Analyser, model 43A was used to determine the concentration of SO_2 in the intercomparison cylinders.

The cell is flushed for at least 15 minutes with standard or sample before recording the response of the monitor. The pressure in the cell is measured directly before recording the readout of the response, which is sampled 90 times in approximately 1,5 min. This pressure-response readout is repeated three times and the measured response is the mean of the three series.

The calibration curve is made with five to eight standards in the range from 165-215 nmol/mol SO_2 . The response is corrected for pressure; the measurement sequence is from low to high concentration. The mathematical model used for the calculation is a first order linear regression (straight line).

The cylinders were kept in the laboratory all the time ($T_{\text{lab}} = 21,5 \pm 0,5 \text{ }^{\circ}\text{C}$) and samples were transferred to the monitor by using a reducing valve and a mass-flow controller.

(iv) Calibration standard and measurement procedure- LNE

The LNE permeation bench based on permeation method consists of: a water bath whose temperature is regulated at $(30.0 \pm 0.1)^{\circ}\text{C}$ by a thermostatic immersion heater (HAAKE E8) and a refrigeration unit (HUBER); a platinum temperature sensor (100 ohms at 0°C (AOIP)) in accordance with DIN 43760, version 1/10 DIN in a stainless steel sheath to monitor the stability of the bath temperature (stability of the order of 0.02°C) and a nitrogen cylinder to provide a continuous flow of dry gas over the permeation tube.

In order to determine the permeation tube flow the SO_2 permeation tube is removed from the permeation bath at regular intervals (every month) and is left for half an hour at ambient temperature. It is then weighed on a METTLER AT 201 balance which is accurate to 0.01 mg. The measured mass is corrected for ambient RH, pressure and temperature. The slope of the permeation tube mass vs. time curve is then calculated using the last three mass measurements only, because the permeation rate decreases in the time: this gives the permeation tube rate.

The LNE permeation bench generates primary gas mixtures of SO_2 in air at different concentrations. A primary gas mixture is obtained by passing synthetic air from a cylinder on a 15 kg balance over a SO_2 permeation tube. The balance is connected to a computer, which allows the flow to be measured directly by loss of mass vs time. As the permeation rate is fixed, the air flow must be varied to obtain gas mixtures with different SO_2 concentrations. The SO_2 concentration of the primary gas mixture is the permeation tube rate divided by the permeation tube rate plus the air flow rate.

LNE does not *maintain* primary standards of SO_2 , because the method which is used to generate primary standards of SO_2 utilises the permeation method. But, the traceability of the measurements is ensured by weighing the permeation tubes every month.

A SERES SF2000 analyser is used to measure the SO_2 . This uses UV fluorescence. It is used exclusively for this procedure. UV fluorescence analysers use a source with a wavelength close to 215 nm, which excites SO_2 molecules. Excited SO_2 molecules may relax in two ways. The first way is the transfer of energy between molecules during collisions. This is a non-radiating process. The second way is transfer of energy by emission of electromagnetic radiation. This is a radiating process.

The calibration of the analyser is divided into two stages. Stage 1: setting the analyser: The analyser is set at 2 points: zero and a full scale point. Stage 2: Determining the SO_2 concentration of an unknown gas mixture. The unknown gas mixture is injected once into the SO_2 analyser. The SO_2 concentration of the unknown gas mixture is equal to the SO_2 concentration displayed by the analyser (C_{read}). This procedure (stage 1 + stage 2) is carried out three times.

Cylinders were maintained inside a laboratory at a nominal temperature of 20 °C for all the period. Samples were introduced into the analyser via normal gas regulator and an overflow valve.

(v) Calibration standard and measurement procedure - UBA

UBA uses the static dilution method, where a pure gas of SO₂ is injected into a vessel. The principle of the method is described in VDI 3490 Part 14. ISO gives a preparation uncertainty of 2 % for 95 % confidence interval including uncertainty of the syringe, volume of the vessel and uncertainty of pressure and temperature measurement. The gas is prepared and directly used for the calibration of the reference instrument. Measured uncertainty comprehends the above-mentioned parameters, but as well the uncertainty of the reference instrument. E.g. a ceramic coated chamber of 13,904 l at 1 bar; operational pressure 9 bar was used in which 50 µl of pure SO₂ (3.8) were injected. This results in a concentration of 399,6 ppb. The measurements were carried out with an APSA 360 E, Horiba, fluorescence type.

3.2.4 C₆H₆ Intercomparison

Within the frame of Work Package 1 of the HAMAQ project fifteen cylinders have been prepared containing approximately 20 ppb (mole fraction) of benzene in nitrogen. The concentrations of benzene in these cylinders have been evaluated by comparison with an appropriate range of benzene calibration standards, and have been tested for stability over a three-month period.

After this period, as a part of Work Package 2, cylinders have been send to NPL, to JRC-Ispra and to UBA for intercomparison. NPL received a second cylinder that has to circulate as follows : NMi - NPL - JRC - UBA - NMi. This summary describes the procedures used by the labs and the results obtained.

(i) NMI Intercomparison Procedure and Results

Materials And Methods

Assay cylinders

A total of 15 Gas mixtures containing approximately 20 ppb benzene in nitrogen have been prepared by Scott Specialty Gases by gravimetry in 10 liter Aculife treated aluminium cylinders. All cylinders were delivered to NMi in april 1997.

Primary Standard Materials (PSM's)

Primary standard gas mixtures of benzene in nitrogen have been prepared in a concentration range of 15 to 30 ppb by serial dilution from 2 independently prepared 'parent' PSM's containing approximately 20 ppm of benzene in nitrogen.

The parent mixtures have been prepared by injection of an amount of benzene (Merck, >99,8 % purity) in a nitrogen (Scott, 6.0 quality) flow entering an evacuated cylinder. The mass of benzene was determined by weighing the syringe before and after injection. The total mass of benzene + nitrogen was determined by weighing the cylinder after

evacuation and after pressurizing.

The set of PSM's used for the HAMAQ project are given in the table below :

Table 16: PSMs used for HAMAQ benzene measurements at NMi

cylinder i.d.	Benzene fraction (nmol/mol)	Uncertainty (%rel.)
VSL103715	15.01	0.35
VSL103716	16.91	0.35
VSL103713	20.00	0.21
VSL103714	23.04	0.21
VSL103711	30.01	0.21

The individual cylinder comparison results between ERLAP and LNE & NMi show good agreement (0 and 0.5 % rel. difference), with a 3% difference in the ERLAP - UBA comparison, which does not agree within the uncertainty tolerance. In contrast to the good results obtained with NMi and LNE, the circulation cylinder shows poor agreement. This may be the result of instability of SO₂ within the cylinder. The SO₂ cylinders were during preparation pre-conditioned with SO₂ in high concentration, so although an instability showing an upward trend in concentration would be unusual, it was not unheard of. It was pointed out that environmental conditions experienced during transportation could have adversely effected the stability of this cylinder, compared to those remaining in an air-conditioned laboratory. The circulation cylinder will now be send to LNE for analysis and all returned cylinders will be remeasured by ERLAP to complete the intercomparison.

The importance of pre-conditioning the regulator used for the SO₂ cylinder and allowing a long time (~ 45 minutes) for the analyser readings to stabilise was emphasised.

Apart from the circulation cylinder, the level of agreement is encouraging, considering that ERLAP and LNE both use regular, but infrequent weighing of permeation tubes. NMi described a continuous weighing permeation method used to make the measurements reported here. UBA described the static injection method used to make these measurements.

The uncertainty is calculated from the weighing uncertainties, uncertainty in the molar masses and from contributions of the (im)purities of the benzene and nitrogen used. The uncertainty of a possible benzene content in the nitrogen is the predominant contributor to the total uncertainty. Consistency analysis has been carried out to check for (in)stability.

Control cylinder

A gas standard of a known concentration of approximately 20 ppb volume fraction (ppbv) in dry air has been prepared to serve as an independent check on the accuracy of the PSM preparation procedure. Herefore an evacuated 1 liter stainless steel cylinder was filled

cryogenically from a dynamically generated standard atmosphere of 20 ppbv benzene in dry air. The standard atmosphere was generated by two-stage dilution of the output of a benzene diffusion cell (Aldrich, >99,5 % purity). Before use, the benzene was dried on a molecular sieve.

Analytical procedure

Sampling and analysis

The contents of all cylinders were analysed by a cryofocussing gas chromatographic procedure. The instrument used was a Varian Star 3600 CX GC, equipped with an SPT injector and a Flame Ionisation Detector.

The gasmixtures were sampled from the cylinders using a mass-flow controller (range 0 - 50 ml/min) positioned directly after the cold trap. The MFC was set to a flow rate of 25 ml/min, and was operated by cylinder pressure. For this purpose, the cylinder was directly connected to the cold trap via a 80 cm deactivated fused silica transfer line of 0,53 mm internal diameter. Before sampling, the cylinder outlet pressure was set to 2,0 bar by a pressure reducer.

The used sampling procedure consists of a 1-minute flush of the transfer line, and 3-minute trapping on a cold trap packed with silanized glass beads and held at a temperature of - 120 °C. The cold trap was subsequently heated to 200 °C and its contents were injected on a 60 m x 0,32 mm fused silica DB-1 column (J & W scient.) with a 1 µm methylsilicone stationary phase. The column was kept at 40 °C for 1 minute (after heating the trap), raised with 20 °C/min to 160 °C and held at 160 for the remaining analysis time (i.e. 1 min.).

The sequence in which the assay cylinders and calibration standards have been analyzed was set by randomization, with the exception that a PSM was analyzed after every 3 or 4 assay cylinders.

Data processing

All analysis consisted of four repetitive injections. The first injection was considered as an equilibration step; its results were not used for further processing.

Data processing was performed by peak integration using the Varian Star chromatography software. All chromatograms were manually checked, and, if necessary, reintegrated.

The necessity for reintegration depended strongly upon the correct setting of peak start and peak ends, which were governed by the baseline noise, particularly at the peak end.

The responses of the PSM's were subjected to linear regression analysis in order to evaluate (a) the linearity of the responses as function of the concentration, (b) the offset of the calibration curve at zero concentration. In all cases, responses were found to be linear related to the benzene concentrations in the PSM's, with offsets not significantly differing from zero.

The integration results of the latter three sample injections of the PSM's were used for calculation of the respons factor. This respons factor is the mean peak area divided by the PSM concentration. The mean respons factor of the five PSM's is used for calculating the unknown concentration in the assay cilinder, by dividing the respons by the respons factor.

In a three-monthl period a total of five analyses for each cylinder was performed. In this period no significant instability appeared. Therefore the mean of these five measurements is given as the final result.

Uncertainty calculations

The response factor is calculated from the response and the benzene concentration of the PSM. The uncertainty in the response is the standard deviation (approx. 0,5 % rel.).

The uncertainty in the mean response factor is the standard deviation for the five PSM's divided by $\sqrt{5}$.

The uncertainty in the concentration of the assay cylinder is calculated from the uncertainty (stand. dev.) of the response and the uncertainty in the mean response factor. For all individual analysis the total uncertainty is given as an expanded uncertainty with a coverage factor $k=2$.

The final result however is the mean of five individual analysis. The uncertainty on this result is the standard deviation divided by $\sqrt{5}$ and multiplied by the student t-factor for five measurements : $t = 2,78$. To eliminate the influence of outliers the presented uncertainty is the mean uncertainty for the 15 analysed assay cylinders.

NMI Results And Discussion

A total of fifteen cylinders are used for stability testing, and for calculating the overall uncertainty. In this summary only the results of the cylinders used in this part of the project are presented, see Table 17 below:

Table 17: NMI benzene stability measurements

cylinder	1st check		2nd check		3rd check		4th check		5th check		overall	
	ppb	U % k=2	ppb	U % k=2	ppb	U % k=2	ppb	U % k=2	ppb	U % k=2	ppb	U % t=2,78
5701214	20.9	1.1	20.5	0.9	20.7	0.8	20.8	0.6	20.4	1.4	20.7	2.0
5701204	21.1	1.8	20.6	1.2	20.8	1.9	20.9	0.8	20.5	1.5	20.8	2.0
5701236	20.7	1.3	20.6	3.0	20.7	1.3	20.3	0.8	20.6	0.9	20.6	2.0
5700527	20.9	1.7	20.6	2.7	21.0	1.6	20.6	1.2	20.7	1.0	20.8	2.0
cryo mix	20.0	1.1	20.1	1.3	20.0	1.3	19.7	0.9	20.2	1.0	20.0	2.0

The results of the control cylinder match the calculated concentration. This proves that no

systematic error is made by the preparation of the PSM's.

(iii) NPL Intercomparison Procedure and Results

Measurement Procedure

Calibration Standards:

A reference standard (BX507) containing benzene in nitrogen at a concentration of 11.69 ppb, by mole fraction, was used to make the measurements. The standard was validated against two other mixtures containing benzene at concentrations of 9.21 and 6.07 ppb. All standards were prepared by multistage dilution gravimetric techniques, using pure benzene obtained from Aldrich with a quoted purity of 99.9%. This was verified by GC analysis at NPL. The nitrogen balance gas was the highest purity supplied by Air Liquide (N60). The total detectable hydrocarbons found in the balance gas was less than 0.1 ppb.

Reference Measurement Method:

The concentration of benzene in the two HAMAQ cylinders was analysed by Gas Chromatography. Measurement of the concentration was achieved by cryogenic preconcentration of benzene. This involves trapping and retaining benzene in the gas samples on an adsorbent material (Tenax TA) held at low temperature (-99°C). The adsorbent is then heated rapidly in a stream of carrier gas to desorb the benzene directly on to GC column for subsequent analysis using an FID detector. By sampling 200cc of gas the limit of detection for benzene is less than 0.02ppb.

GC Parameter Varian 6500

Column : 50m x 0.53 megabore Plot Alumina KCL activated.

Detector : Flame ionisation set @ 250°C

Injector Oven: Set @ 250°C

Cold trap : Tenax-TA adsorbent. Trap temperature -99°C heated rapidly to 220°C maximum.

Column temperature programme: 100°C held for 1 minute, ramp to 196°C at 5°C/min and hold at 196°C

Carrier gas : high purity helium at flow rate of 15ml/min.

Detector gases: Air at flow of 300 ml/min. Hydrogen at flow rate of 30 ml/min

Sample volume: 200cc

Instrument Calibration:

The GC was calibrated against a single reference standard (BX507) with a concentration of 11.69 ppb. Assuming a zero response at zero concentration, this single standard is used to give a sensitivity for the GC, defined as the analyser response (integrated peak area) divided by concentration. This sensitivity was verified by comparison sensitivities derived from two independent benzene standards, AMOHA 1933A (6.07 ppb) and BTEX 5601467 (9.21 ppb). The sensitivity values calculated by the three separate standards agreed to within 1.7%. The concentration of the HAMAQ cylinders was then found by applying the sensitivity calculated from reference standard BX507.

The measurement protocol was not followed exactly. In an initial test measurement, four analyses of each sample were made, followed by four analyses of the calibration standard. Then in the set of measurements reported here each HAMAQ cylinder was measured once, then the reference cylinder was measured once, and this was repeated three times for each cylinder. The areas of benzene peaks in the chromatograms obtained from the analysis runs were evaluated by the Varian Star software.

Sample Handling:

The sample inlet, all the pipe work and needle valves are purged with zero grade nitrogen and an analysis of the nitrogen was performed as a blank run. The resulting chromatogram was examined for baseline stability and for any contaminants in the GC system.

The two cylinders were connected with the fittings supplied by Scott Speciality Gases and four needle valves. The sample was transferred to the GC inlet at 100cc/min. A gas flow meter measured the flow rate of sample at the GC outlet.

NPL Results

The results obtained by NPL for both the individual cylinder and circulation cylinder are given below in Table 18.

Table 18: NPL benzene results

			1st meas.		2nd meas.		3rd meas		overall	
cylinder			ppb	st.dev (% rel)	ppb	st.dev (% rel)	ppb	st.dev (% rel)	ppb	U %
5700527			21.53	0.35	21.26	0.35	21.34	0.35	21.38	3.6%
5701214			21.06	0.35	21.34	0.35	21.16	0.35	21.19	3.6%

Uncertainty:

The uncertainty in the concentration of 11.22 ppm benzene in the master BTEX mixture (BX501 cylinder 5601747) is estimated from the gravimetric techniques used to be ± 0.42%.

The mixture was then diluted in two stages to give reference standard BX507 with a concentration of 11.69 ppb. Each weighing has an uncertainty of 30mg:

1st Dilution: Mix#5601747 11.4g ⇒ 0.265%
 Nitrogen 550g ⇒ 0.006%

2nd Dilution: Mix#5601746 29.9g ⇒ 0.10%
 Nitrogen 550g ⇒ 0.006%

These uncertainties can be combined in quadrature to give a total uncertainty of 0.51% at 1σ . However, this uncertainty budget contains no allowance for stability of the standard, or loss (gain) of benzene to (from) the walls of the blending mechanism.

In order to get a better estimate of the true uncertainty of the reference standard BX507, the response of the GC to three separately prepared standards was compared, the results are summarised in Table 19 below:

Table 19: NPL Analyser sensitivity results

Reference Standard	Concentration	GC Response	Calc. Sensitivity	Mean
AMOHA 1933A	6.07 ppb	17433	2872	= 2926
BX505 (#5601467)	9.21 ppb	27316	2966	± 0.48
BX507 (#5601466)	11.69 ppb	34355	2939	$\Rightarrow (1.65\%)$

Thus if the uncertainty in the original weighing was 0.51% then the uncertainty from stability or loss (gain) of benzene to (from) the walls of the blending mechanisms = 1.57%.

A comparison of the concentration values interpolated for a response of 61400 using each of these three reference standards, gave a 1σ standard deviation of 1.66 %. Hence the uncertainty in interpolation is 0.18%. The overall uncertainty estimate is summarised in Table 20 below.

Table 20: Overall Measurement Uncertainty for NPL Benzene Measurements

Source of Uncertainty	Type A or B	Probability Distribution	Divisor	Value #570052 7	Value #570121 4
Preparation of Standard BX501	B	normal	1	0.42%	
1 st Dilution	B	normal	1	0.27%	
2 nd Dilution	B	normal	1	0.10%	
Stability of cylinders	A	normal	1	1.57%	
Interpolation of GC Response	A	normal	1	0.18%	
Std Deviation of GC Response	A	normal	1	0.64%	0.67%
Combined Uncertainty				1.78%	1.79%
Expanded Uncertainty		normal (k=2)		3.56%	3.58%

(iv) JRC- ISPRA Intercomparison Procedure and Results

Measurements are being completed and the results, together with an account of the measurement procedure will be described in the mid-term review report.

(v) UBA

Measurements are being completed and the results will be included in the mid-term review report. An account is given below of the measurement procedure used.

Measurement Procedure

A CHROMPACK GC 9000 with Auto-TCT is used for analysing benzene at the UBA laboratory. Dried sample air is sucked through the adsorption tube. After thermal desorption the compounds are cryogenic trapped. By heating the trap up the compounds are transferred to the analytical column.

Analytical conditions :

Sampling procedure	Technique	Adsorption on Carbosieve SII, Carbotrap C temperature -20 °C, cooled by liquid CO ₂
	Sampling Volume	220 ml
	Volume measurement	Time programmed mass flow controller
Desorption	Dryer	Perma pure
	Technique	Thermal desorption 3 min. at 250 °C
	Flow	2 ml/min
GC analysis	Colt trap	Fused silica Al ₂ O ₃ /KCl, 30 µm
	Carrier gas	Helium 5.0
	Column	PLOT fused silica
	- Phase	Al ₂ O ₃ /KCl
	- Dimension	25 m x 0,53 mm id
	Oven	initial temp. 50 °C
	- Rise	5 min 5 deg/min
		5 min 10 deg/min
		5 min 25 deg/min
	Detector	FID
	Calibration	external standard

Sampling and analysis are done simultaneously. This instrument is used for quality assurance in laboratory. In field measurement BTX-monitors are used.

Preparation Of Benzene Calibration Gas

Benzene calibration gas mixtures are prepared using Volumetric Static Method.

A known volume of liquid benzene is added to the complementary gas in a vessel of well-defined volume and evaporated. The method is described at VDI 3490, page 14 and ISO6144.

Equipment	Glass vessel	0,11244 m ³
	Additional parts	Fan Pressure gauge Temperature gauge High-pressure valve Septum
	Operating material	Vacuum pump Microliter syringe Synthetic air

The vessel is filled with synthetic air at ambient (laboratory) pressure and temperature. After injection the benzene concentration is about 4 mg/m³.

$$\text{calculation : Benzene in } \mu\text{g/m}^3 = V_B \times r_B \times T_v \times p_0 / (V_v \times T_0 \times p_v)$$

where : V_B = injected volume benzene (20 °C) in μl
 r_B = density of benzene = 878 $\mu\text{g} / \mu\text{l}$
 T_v = temperature in the vessel in K
 p_0 = standard pressure = 1013 hPa
 T_0 = standard temperature = 273 K
 V_v = defined volume of the vessel = 0,11244 m³
 p_v = ambient pressure = pressure in the vessel in hPa

Dilution can be done in two ways

1. Static dilution

The vessel pressure is reduced to ~ 100 hPa by vacuum pump and filled again with synthetic air to 1000 hPa. This reduction is repeated and the pressure is set to 1500 hPa at the end.

Then there are ~ 50 l calibration gas available.

$$\text{calculation : } c_{\text{benzene}} = (\text{benzene}_{\text{vessel}} \times p_1 \times p_{1,1}) / (p_2 \times p_{2,1})$$

where p_1 = Pressure in the vessel after reduction
 p_2 = Pressure in the vessel after refilling

2. Dynamic dilution

After injection the pressure in the vessel is set to 1500 hPa.

The concentration of benzene is about 3 mg/m³.

Automatic dilution is performed using mass flow controllers and a mixing chamber.

$$\text{calculation : } c_{\text{benzene}} = (\text{benzene}_{\text{vessel}} \times \text{flow}_{\text{vessel}}) / (\text{dilution flow} + \text{flow}_{\text{vessel}})$$

Performance parameter

injection 0,5 μl benzene (p.a.) 20 °C
 evaporation with fan 2 min at ambient temperature

Static dilution

p_1 and $p_{1,1}$ ~ 100 hPa
 p_2 ~ 1000 hPa
 $p_{2,1}$ ~ 1500 hPa

Dynamic dilution

$\text{flow}_{\text{vessel}}$ 2 ml/min
 $\text{dilution flow}_{(\text{synth. air})}$ 200 ml/min

c_{benzene} ~ 30 $\mu\text{g/m}^3$

(vi) Summary Of Results Obtained in the Benzene Intercomparison

The results obtained for the benzene intercomparison so far, are given below:

Circulation cylinder :	5700527	result NMI = (20,8 ± 0,4) × 10 ⁻⁹ mol/mol
		result NPL = (21,4 ± 0,8) × 10 ⁻⁹ mol/mol
Cylinder nr. :	5701214	result NMI = (20,7 ± 0,4) × 10 ⁻⁹ mol/mol
		result NPL = (21,2 ± 0,8) × 10 ⁻⁹ mol/mol

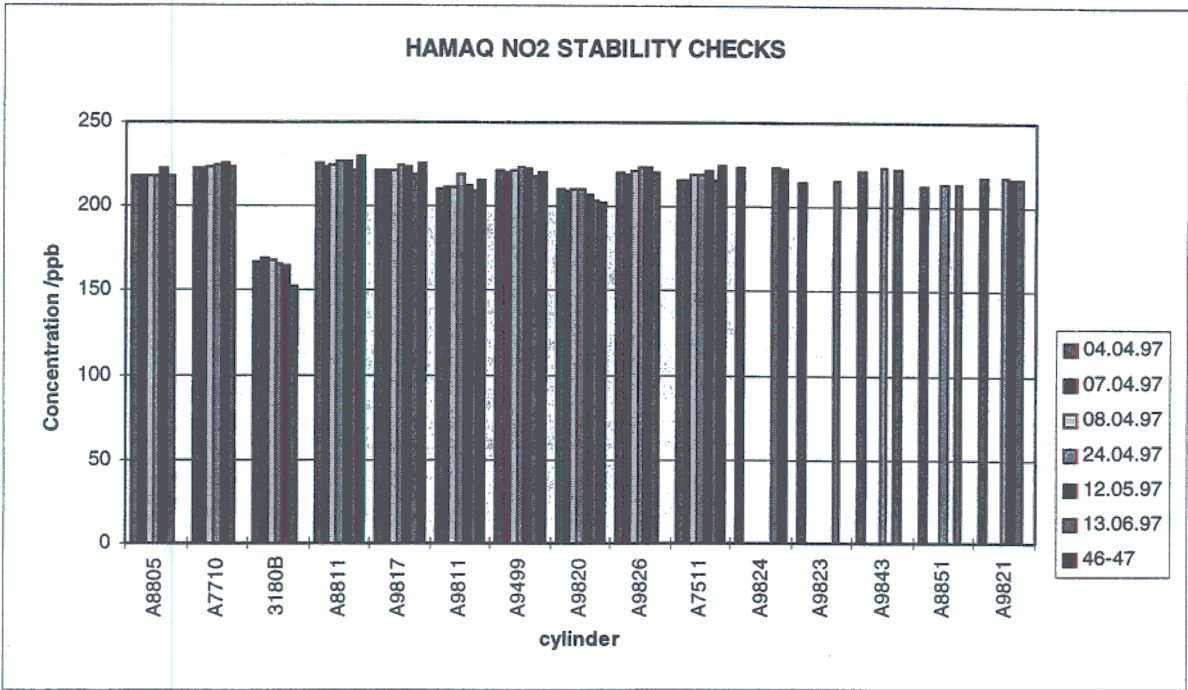
3.2.5 NO₂ intercomparison

(i) UBA measurements and stability tests

Following delivery of fifteen NO₂ cylinders an analysis of all cylinders was conducted during April 1997. A chemiluminescence analyser was calibrated using three independantly prepared NO primary standards generated using a static volumetric method at UBA. Before analysis of the NO₂/Air mixtures the converter efficiency was determined six times, yielding values between 98.7 and 99.5%. An average value of 99% was taken. A batch of ten cylinders were analysed during the period 4th April - 13th June 1997. The remaining cylinders were measured twice at the beginning of the intercomparison. With these cylinders further experiments were conducted to investigate the effects of rolling. The results are shown in table 21 and the figure below.

Table 21: UBA NO₂ stability tests

NO2 cylinder no	04.04.97	07.04.97	08.04.97	24.04.97	12.05.97	13.06.97	46-47	mean	std
1 A8805	217.8	217.8	217.8	218.1	222	218.4		218.65	1.658614
2 A7710	222.8	222.7	223.3	225.1	226	223.5		223.9	1.343131
3 3180B	167.3	169.3	168.3	165.8	165	152.4		164.6833	6.220423
4 A8811	225.7	223.7	224.7	227.1	226.5	221.5	230.1	225.6143	2.052965
5 A9817	221.7	221.7	221.7	225.1	224	219	225.5	222.6714	2.12791
6 A9811	210	210.8	211.8	219.1	212	209.3	215.8	212.6857	3.550023
7 A9499	221.7	219.7	221.7	223.1	222	218.4	220.6	221.0286	1.719302
8 A9820	209.8	208.8	209.8	210	206.5	203.2	202.5	207.2286	2.698456
9 A9826	219.7	218.7	221.7	223.1	224	220.4		221.2667	2.040261
10 A7511	215.8	215.7	218.6	219.1	221	215.4	225.1	218.6714	2.302173
11 A9824	223.7					223.5	222	223.0667	0.141421
12 A9823	214.8					215.4		215.1	0.424264
13 A9843	220.7			224		222.5		222.4	1.652271
14 A8851	212.9			214		213.3		213.4	0.556776
15 A9821	217.8			218	217	216.4		217.3	0.739369



With the exception of cylinder 3180B, which was measured at a concentration of 164.7ppb, the concentration range at the beginning of the stability tests was relatively small, with average measurements ranging from 207 - 225 ppb. The standard deviation of these measurements ranged from 0.1 - 2.3%, giving a relative uncertainty of generally less than 2% and mostly less than 1%. In comparison with previous measurements on other cylinders these cylinders show good stability and are therefore suitable for use as transfer standards.

As defined in the workprogramme, following stability testing two cylinders were sent to JRC, Ispra. An additional cylinder was sent to LNE. The cylinder A7710 was initially measured at UBA to give a concentration of 223.9 ppb. The JRC measurements yielded a value of 229.1ppb. The reanalysis upon return of the cylinder to UBA gave a value of 230.1 ppb. The results of the intercomparison are given in table 22 below.

Table 22: Summary of results of NO₂ intercomparison

NO2 INTERCOMPARISON				
Cylinder No.	UBA	LNE	ERLAP	UBA
	13.06.97	24-26.09.97	13-17.11.97	46-47.KW
A7710	223.9		229.1	230.1
A8805	218.7		230.6	
A8811	224.9			

The circulation cylinder (A8811) measurements are not yet complete, but so far good agreement has been shown between UBA and LNE (discrepancy < 1%).

Uncertainty Estimate

As in the case of NO, The uncertainty of analyser and primary calibration gas the dominating factor is the non linearity of the instrument and the reproducibility of the preparation of the primary NO standard (~2ppb). A further 0.5ppb is added to allow for converter efficiency. This gives an overall uncertainty of 2.5 ppb. This is in agreement with the initial stability tests but not in agreement with the intercomparison measurements. The observed discrepancies will be investigated in the second intercomparison.

(ii) LNE measurements.

The LNE results for the individual cylinder are summarised in Table 21 below.

Table 23: Results for Cylinder number A8811

measurement N°	date	result (ppb)	number of sub measurements
1	97-9-24	224	1
2	97-9-25	224	1
3	97-9-26	223	1

Result (assigned value) : 223.7 ppb
Assigned overall uncertainty (*) : 2.5 ppb for 95 % confidence level

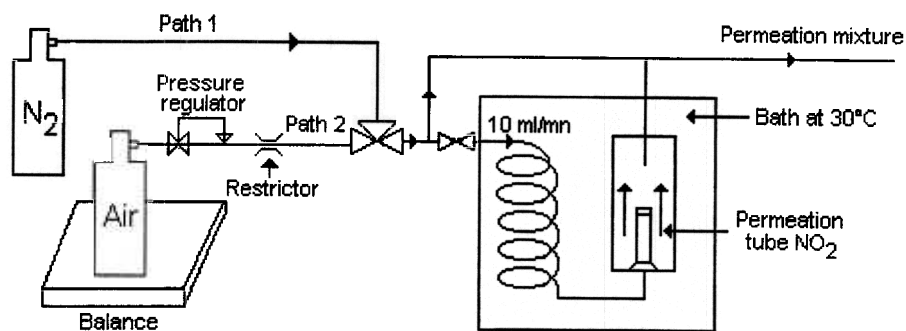
1. Calibration Standards :

1.1 LNE PERMEATION BENCH

1.1.1. Description

This permeation bench based on permeation method consists in :

- a water bath whose temperature is regulated at (30.0±0.1)°C by a thermostatic immersion heater (HAAKE E8) and a refrigeration unit (HUBER),
- a permeation tube within a stainless steel casing,
- a platinum sensor 100 ohms at 0°C (AOIP) in accordance with DIN 43760, version 1/10 DIN in a stainless steel sheath to monitor the stability of the bath temperature (stability of the order of 0.02°C), a nitrogen cylinder to provide a continuous flow of dry gas over the permeation tube (path 1 on diagram).



LNE permeation bench for generating primary NO₂ mixtures in air

1.1.2. Determining the permeation tube flow

The NO₂ permeation tube is removed from the permeation bath at regular intervals (every month) and is left for half an hour at ambient temperature.

It is then weighed on a METTLER AT 201 balance accurate to 0.01 mg. The measured mass is corrected for ambient hygrometry, pressure and temperature. The slope of the permeation tube mass vs. time curve is then calculated using the last three mass measurements only, because the permeation rate decreases in the time: this gives the permeation tube rate.

1.2 GENERATING THE PRIMARY NO₂ GAS MIXTURE

The LNE permeation bench generates primary gas mixtures of NO₂ in air at different concentrations. A primary gas mixture is obtained by passing synthetic air from a cylinder on a 15 kg balance over an NO₂ permeation tube. The balance is connected to a computer which allows the flow to be measured directly by loss of mass vs. time (path 2 of diagram). As the permeation tube rate is fixed, the air flow must be varied to obtain gas mixtures with different NO₂ concentrations.

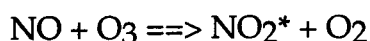
The NO₂ concentration of the primary gas mixture is given by the permeation rate divided by the permeation rate plus the air flow rate.

LNE does not maintain primary standards of NO₂, because of the method which consists in generating primary standards of NO₂ by the permeation bench. But, the traceability of the measurements is ensuring by weighing the permeation tubes every month.

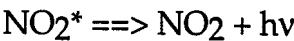
2. Reference method :

An Environnement SA AC31M analyser is used to measure the NO₂. This uses chemiluminescence. It is used exclusively for this procedure.

The oxidation of NO by ozone causes chemiluminescence.



When the excited NO₂* molecules return to their ground state, radiation is produced in the range 600 to 1200 nanometers.



3. Instrument calibration :

The unknown gas mixture is passed into the NO₂ analyser. The concentration displayed by this analyser (C_{read}) is recorded and taken as the reference value.

A primary gas mixture (NO₂ in air) is then generated from the LNE permeation bench. This mixture is obtained by passing synthetic air from a cylinder on a balance over an NO₂ permeation tube (path 2 of the diagram). As the permeation tube rate is fixed, the synthetic air flow is regulated to obtain the same concentration reading (C_{read}) as given for the gas mixture to be analysed. The NO₂ concentration (C_{NO2}) of the primary gas mixture is the permeation tube rate divided by the permeation tube rate plus the air flow rate.

Using this procedure, the NO₂ concentration of the unknown gas mixture is the same as the NO₂ concentration of the primary gas mixture (C_{NO2}).

This procedure is carried out three times.

4. Sample Handling :

Cylinders were maintained inside a laboratory at a nominal temperature of 20 °C for all the period. Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

5. Uncertainty :

The uncertainty analysis used to derive the uncertainties given above is summarised in table 22 below :

Table 24: Uncertainty analysis for LNE NO₂ measurements

Variable	Source of uncertainty	Uncertainty (U in ppb)	Variance
Primary gas mixture	Concentration of the primary gas mixture (1)	1.87	0.87
Analyser	Repeatability for the primary gas mixture (2)	1.15	0.33
	Repeatability for the analysed gas mixture (2)	1.15	0.33

Notes : 1. The uncertainty on the primary gas mixture concentration is derived from an uncertainty analysis of the primary NO₂ mixture prepared by permeation method (uncertainty on the purity of used pure gases, uncertainty on the weighing process, uncertainty on the molar masses, uncertainty on the dilution...).

2. The repeatability of the NO₂ analyser (± 1 ppb, rectangular distribution) is estimated by injecting a gas mixture in the NO₂ analyser within short intervals of time in the same day, with the same method, in the same laboratory by the same operator.

(iii) ERLAP Measurements

The ERLAP measurements for both individual and circulation cylinders are given in Tables 25 and 26 below.

Table 25: ERLAP results for cylinder number A7710

measurement No.	date	result (mol/mol)	number of sub-measurements
1	97-11-13	226.1	1
2	97-11-14	230.7	1
3	97-11-17	230.5	1

Result (assigned value) : 229.1
Assigned overall uncertainty (*) : 3.1 ppb

Table 26: ERLAP results for cylinder number A8805 (CIRCULATION CYLINDER)

measurement No.	date	result (mol/mol)	number of sub-measurements
1	97-11-13	228.3	1
2	97-11-14	233.0	1
3	97-11-17	230.4	1

Result (assigned value) : 230.6 ppb
Assigned overall uncertainty : 3.1 ppb

Calibration Standards:

A permeation tube with NO_2 is maintained in a thermostated system with a continuous flow of nitrogen over the permeation system. At regular intervals the tube is removed from the permeation system, left for 90 min at ambient conditions (20 °C, 50 % r.H.) and weighed on a Mettler AT201 balance.

Calibration standards are made by dilution with cleaned air. The total flow NO_2 in N_2 and air is measured with a calibrated mercury sealed piston flow meter.

The NO_2 fraction in the mixture is then calculated by dividing the permeation rate by the total flow.

ERLAP maintains three permeation systems for NO_2 with different permeation rates. Through dilution concentrations in a range from 50 to 800 ppb NO_2 can be generated.

2. Reference Method:

Monitor: Environmental Instruments Inc. Model 42 C, Chemiluminescence analyzer

Nitric oxide and ozone react to produce a characteristic luminescence. Nitrogen dioxide must be transformed into NO (Mo converter) before it can be measured using the chemiluminescent reaction. A valve routes the sample either straight to the reaction chamber (NO mode) or through the converter and then to the reaction chamber (NO_x mode).

3. Instrument Calibration:

A calibration curve (linear regression) is made with three or four standards

4. Sample Handling:

The cylinders were maintained inside the laboratory at about 20 °C all the time. The sample were transferred to the analyzer by using a pressure regulator and an overflow valve

5. Uncertainty

The uncertainty analysis used to derive the uncertainties given in above is summarised in table 27 below :

Table 27: Uncertainty, analysis for ERLAP NO₂ measurements

Variable	Source of uncertainty	Uncertainty (U in ppb)	Variance
Preparation of span gas	Concentration of the gas mixture obtained by permeation (1)	2	1
Zero gas	Concentration of zero gas (2)	0.58	0.083
Analyzer	Repeatability (3)	1	0.25
	Non-linearity (4)	2	1

Notes :

1. The uncertainty on the span gas concentration is derived from an uncertainty analysis of the NO₂ mixtures prepared by permeation method. It is described in detail in Report EUR 16432 EN (1996) Study of the Long Term Stability of NO₂ Permeation Sources – Annex 1: Uncertainty calculation
2. The concentration of zero gas is estimated to be between 0 and 1 ppb.
3. The uncertainty of repeatability is estimated at ± 1 ppb.
4. The uncertainty of linearity is estimated to be 1% in 200 ppb scale.

4. OBJECTIVES FOR THE FOLLOWING PERIOD (1/12/95-30/11/98)

The second HAMAQ intercomparison (WP3) will be conducted during the period January-October 1998. The objectives of this intercomparison will be to demonstrate consistency between the partners involved in the first intercomparison, employing a range of primary methods. The target level of agreement is 1%. In addition, the remaining partners and participants (VTT, ISCIII and the Greek Ministry of the Environment) will become involved in this intercomparison. In this intercomparison each partner will measure, where possible, all of the gases by whichever method they have available. This contrasts with the first intercomparison in which only three or four of the partners were involved for each gas. As in the final intercomparison, one cylinder will be sent to each partner and a single cylinder (or two in the case of SO₂ and NO₂) will be circulated. The agreed timetable for the circulation of this cylinder is indicated in tables 28 and 29 below. Additional European institutes responsible for quality assurance activities within national air quality monitoring networks will be invited to participate in the intercomparison and the final HAMAQ workshop.

Each pilot laboratory will be responsible for the smooth and efficient running of their intercomparisons. The results of the second intercomparison will be discussed at an annual progress meeting to be held during the week of 26th October 1998 at ERLAP, JRC, Ispra.

In parallel with the second intercomparison a number of technical investigations will be conducted which aim to explain the largest of the discrepancies identified from the first intercomparison. Specifically, they are:

- (i) To investigate the response of NDIR analysers to CO calibration mixtures prepared in air and nitrogen, in order to explain the 2.5% discrepancy in the CO intercomparison. This investigation will be conducted at NPL.
- (ii) To remeasure the SO₂ circulation cylinder 6991 at ERLAP in order to determine whether the apparent upward trend in the concentration is real (given the good agreement with the individual cylinders).
- (iii) Further measurements will be made on NO₂ cylinders A8805 and A7710 to determine whether the upward trend in concentration is real.

Table 28: Timetable for the Second Intercomparison

	CO	NO	C ₆ H ₆
Pilot Lab	NPL	LNE	NMi
January	LNE	VTT	NPL
February	NMi	JRC	JRC
March	VTT	ISCI	
April	UBA	NPL	UBA
May	ISCI	UBA	VTT
June	JRC	NMi	LNE
July	NPL	LNE	NMi
August	Completed	Completed	Completed
September			

	NO ₂ Cylinder 1	NO ₂ Cylinder 2
Pilot Lab	UBA	UBA
January / February	VTT	VTT
March	LNE	JRC
April	ISCI	NPL
May	NMI	
June	UBA	UBA
July	Completed	Completed
August		
September		

	SO ₂ Cylinder 1	SO ₂ Cylinder 2
Pilot Lab	JRC	JRC
January	NPL	LNE
February / March	NMI	NMI
April	VTT	UBA
May	ISCI	
June	JRC	JRC
July	Completed	Completed
August		
September		

Table 29: Individual partner timetables for second intercomparison

	VTT	ISCIH	NMi	NPL	JRC	LNE	UBA
December			C₆H₆ Pilot Lab	CO Pilot Lab	SO₂ Pilot Lab	NO Pilot Lab	NO₂ Pilot Lab
January	NO NO ₂ (2)	x		SO ₂ C ₆ H ₆	x	CO SO ₂	x
February		x	CO SO ₂ (2)		NO C ₆ H ₆		x
March	CO	NO			NO ₂ (C ₆ H ₆)	NO ₂	x
April	SO ₂	NO ₂		NO NO ₂			CO SO ₂ C ₆ H ₆
May	C ₆ H ₆	CO SO ₂	NO ₂				NO
June			NO		CO SO ₂ Pilot Lab	C ₆ H ₆	NO₂ Pilot Lab
July	x		C₆H₆ Pilot Lab	CO Pilot Lab		NO Pilot Lab	

5. CONCLUSIONS

The first two workpackages of the HAMAQ programme have been completed successfully. As part of workpackage 1 the commercial gas companies, Scott Gases and Messer, produced fifteen mixtures of CO, NO, SO₂, NO₂ and C₆H₆. Stability tests on a subset of these batches for the SO₂, NO₂ and C₆H₆ mixtures took place during the period February-October 1997. The findings of these stability tests so far have been:

1. SO₂: no significant decay was detected in the sample of six cylinders measured over the period 28th February-23rd October 1999. The standard deviation of the measurements on individual cylinders ranged from ± 0.8 to $\pm 1.3\%$.
2. NO₂: one cylinder from the batch of fifteen showed evidence of decay (of $\sim 2.5\%$ per month). The remaining cylinders in the batch appeared stable over the period 4th April-13th June. The measurements showed standard deviations of ± 0.1 to $\pm 2.3\%$.

3. C_6H_6 : stability measurements on all fifteen cylinders during the period April-October showed no sign of decay with measurements of individual cylinders showing standard deviations of ± 0.8 to $\pm 1.2\%$.

We have therefore demonstrated that compressed gas mixtures in cylinders are sufficiently stable over timescales of 6 months to be used as transfer standards to assess the comparability of various primary methods to a level of 1% to 2 %, if careful initial stability checks are conducted.

With a few exceptions (eg the SO_2 and NO_2 circulation cylinder schedules not the complete for logistic reasons, and the benzene intercomparison not completed due to extended stability tests at NMi) all measurements were completed in accordance with a measurement protocol formulated by the partners and in the order determined by the agreed measurement schedule.

The intercomparison has so far shown maximum discrepancies of 2.1%, 2.4%, 7.1%, 5.4% and 3.0% for CO , NO , SO_2 , NO_2 and C_6H_6 respectively. In the case of NO this discrepancy is not significant given the measurement uncertainties of the participating laboratories.

As a result of discussions at the annual progress meeting held in Madrid on 3rd and 4th November 1997, a number of possible causes of these discrepancies were identified and technical investigations were planned to eliminate these. They were:

- (i) The investigation of the response of NDIR analysers to CO standards prepared in air compared to those prepared in nitrogen.
- (ii) The investigation of a possible upward trend in the concentration of some of the SO_2 and NO_2 gas mixtures were in the intercomparison possibly due to unusual conditions encountered during handling.

The results of these investigations, together with the four remaining measurements of the SO_2 and NO_2 circulation cylinders in addition to additional benzene measurements will be included in the mid term review report.

The issues identified in the first intercomparisons need to be resolved in order to achieve the target level of agreement of 1% within the second intercomparison. In addition, in some cases it is important that measurement uncertainties are reduced further in order to ascertain whether observed differences are statistically significant (eg whether the NO discrepancies of 2.4% are significant) or not.