V1.6

INTERCOMPARISON OF NATIONAL OZONE PRIMARY STANDARDS

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Report on Results of Euromet Project 414

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Intercomparison of National Ozone Primary Standards
Euromet Project 414

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REPORT ON RESULTS OF EUROMET PROJECT 414: INTERCOMPARISONS OF NATIONAL PRIMARY OZONE STANDARDS

EXECUTIVE SUMMARY

An intercomparison exercise has been carried out to determine the accuracy and uniformity of primary ozone calibration standards which use ultraviolet photometry held at national measurement institutes in fifteen countries across Europe. This was carried out using two European national metrology institutes who acted as pilot laboratories and transported ozone transfer standards to all participants. In general, the level of agreement between these nationally-held primary standards was good with only two laboratories showing deviations of greater than ±1.2% from the primary standards operated by the pilot laboratories.

1 INTRODUCTION

To determine the level of agreement between National Standards Laboratories ozone primary standards a project has been set up to carry out an intercomparison of these standards. The reactive nature of ozone precludes its preparation and containment in gas cylinders or other containers, and for that reason, standards for this species are generally measuring instruments.

To compare the instruments held in the Standards Laboratories, a calibrated transfer standard was transported from one of the two pilot laboratories Physikalisch (PTB-D) and National Physical Laboratory (NPL-GB), to each laboratory. Data were obtained from fifteen national measurement institutes, related to either the PTB or NPL primary ozone standards. Measurements were carried out in two other national measurement institutes – which, due to their ozone measurement systems not being fully mature, have not been included in the final results of the comparison. A list of the participants is given in Appendix 1.

Each bilateral intercalibration followed a pre-prepared measurement protocol, which is attached as Appendix 2. This report details how each intercomparison was to proceed. In summary, the intercomparisons were carried out by noting the response of the travelling standard and the laboratory standard, at ten different ozone concentrations between 0 ppbv and 500 ppbv. Ten successive measurements were made at each concentration generated by both instruments.

The comparability of the primary Standard Reference Photometers (SRP) 19 and 20, obtained from the National Institute of Standards and Technology (NIST) USA, and held as national standards by PTB and NPL respectively, was checked at the start and end of this exercise.

2 RESULTS OBTAINED DURING THE PTB INTERCOMPARISONS

2.1 STABILITY OF THE PTB TRANSFER STANDARD

The transfer standard used by PTB was a Thermo Electron TE49C s/n 57024. This was calibrated initially against the PTB primary standard (NIST SRP s/n 19) and found to have a response, relative to the SRP, given by:

[TE49C] = 0.990 [SRP 19] – 1.8 [ppb]

This equation was initially used to provide traceability of individual comparison results back to the PTB SRP.

2.2 PERFORMANCE OF THE PTB SRP

At the beginning of the exercise reported here in February 2001, the NPL travelling standard was taken to PTB to determine the consistency of the PTB and NPL primary standards. During four separate calibrations carried out over two days it was noted that the PTB SRP had a response to zero air of 1.4, 1.6, 1.6 and 1.9 ppb. The magnitude of this measured offset is consistent with the intercept of –1.8 ppb seen in the TE49C/SRP19 relationship. Therefore, in order to avoid biasing subsequent intercalibration results carried out by PTB the offset of this transfer standard, the TE49C/SRP19 relationship was amended to:

[TE49C] = 0.990 [SRP 19] – 0.2 [ppb]

2.3 RESULTS OF THE INTERCOMPARISONS (PTB LOOP) (2)

Using this equation to scale the intercomparison results obtained by PTB during its visits to nine national measurement institutes, the results derived are summarised in Table 2.2 below. The results in the Table below are expressed in the format:

Participating Lab = slope [PTB SRP] + offset [ppb]

The detailed results of each laboratory are given in Appendix 2.

Table 2.2: Results of the Ozone Intercomparison (PTB Loop)

Laboratory Visited	Date Visited	National Photometer slope	Standard error of slope	National Photometer offset	Standard error of offset	National Standard used
CHMI (CZ)	29/9/00	0.998	0.001	0.8	0.2	SRP17
FMI (FIN)	31/10/00	0.997	0.000	0.5	0.1	SRP15
UBA (AU)	2/10/00	1.006	0.001	0.8	0.3	SRP15
DMU (DK)	24/10/00	0.985	0.001	-0.9	0.4	UMEG
IEP (H)	6/10/00	1.006	0.003	0.5	0.9	ENV O341M
ITM (S)	28/10/00	0.993	0.001	-0.3	0.4	SRP 11
NILU (N)	26/10/00	1.008	0.002	0.0	0.5	ML9811
SMHI (SK)	4/10/00	0.991	0.002	-6.4	0.6	TE49PS
UBA (D)	4/10/00	0.992	0.001	-0.3	0.3	UMEG

† Appendix 1 provides details of the national measurement institutes abbreviated in this Table.

The standard errors in the slope and offset are those generated by a least - squares analysis

As can be seen from the results, only one national ozone standard showed a deviation from the regression slope, of the PTB SRP of more than ±1%, and only one standard showed a deviation in its offset of greater than ±1 ppb from that of the PTB SRP is corrected as given in equation (2).

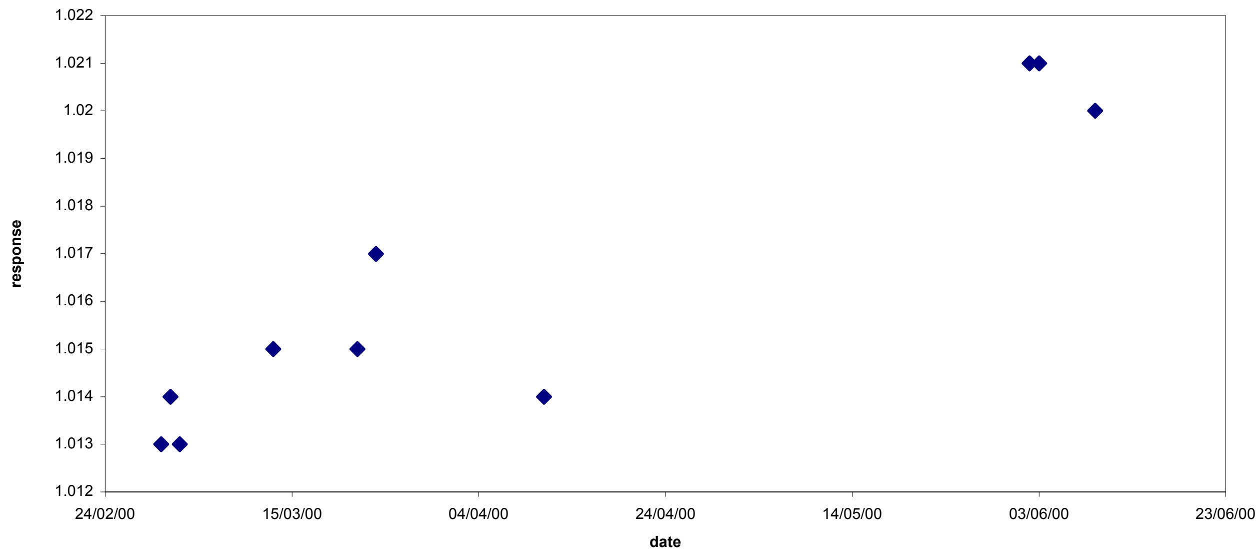
These data, along with summary results from the NPL loop are shown graphically in Figures 3.2 and 3.3.

3 RESULTS OBTAINED DURING THE NPL INTERCOMPARISONS

3.1 STABILITY OF NPL TRAVELLING STANDARD

The NPL travelling standard was calibrated ten times against the NPL SRP (s/n 20) during the Euromet Intercalibration. The results are given below, graphically (Fig 3.1) and in tabular form (Table 3.1).

Figure 3.1: Ratio of Slope of NPL Travelling Standard with respect to that of SRP 20, the UK national ozone standard.



As can be seen from the above data, there is a "drift" of approximately 1% in the "span" response of the travelling standard during the exercise. Because of this rather than simply mean these results, which would introduce a large uncertainty due to this measured drift, the travelling photometer response was derived, for each participating laboratory visited, from the most relevant calibrations against the NPL SRP.

Thus the correction factors used to express concentrations measured by the travelling photometer in terms of those as would be measured by the NPL primary standard are as given below:

Table 3.1: Results of Calibrations of NPL Travelling Standard Against SRP 20

Date	Ratio of Slope /Travelling /SRP	Offset (ppb)	Lab visited	Response Slope factor used
01/03/00	1.013	-1		
02/03/00	1.014	-2		
03/03/00	1.013	-1		
07/03/00			IRCEL	1.014
09/03/00			RIVM	
13/03/00	1.015	-1		
22/03/00	1.015	-1		
24/03/00	1.017	-1		
28/03/00			ISCIII	1.015
31/03/00			ISPRA	
04/04/00			OFMET	
11/04/00	1.014	-1		
02/06/00	1.021	1		
03/06/00	1.021	1		
06/06/00			LNE	1.021
09/06/00	1.020	4		

There was also evidence, particularly near the end of the exercise, of zero drift in the NPL travelling standard. To account for this, the zero response of the transfer standard used at each laboratory was that measured at each laboratory. This range of zero responses was 0 ppb to 1.2 ppb. It is worth noting that changing the zero response in this manner will not affect significantly the slope of the intercomparison regression line obtained during bilateral intercomparisons.

3.2 RESULTS OF THE INTERCOMPARISONS (NPL LOOP)

The results of the intercomparisons carried out by NPL are given in Table 3.2 below. Detailed results from each laboratory are given in Appendix 2.

The results in the Table below are in the format:

Participating Lab = slope [NPL SRP] + offset

Table 3.2: Results of the Ozone Intercomparison (NPL Loop)

Laboratory visited†	Date visited	National Photometer Slope	Standard error of slope	National Photometer Offset	Standard error of offset	National Standard used
IRCEL (B)	7/3/00	0.988	0.001	-0.1	0.24	GPT/uMEG photometer
RIVM (NL)	9/3/00	0.981	0.001	0.6	0.16	TE49PS
ISCIII (E)	28/3/00	0.989	0.001	-0.1	0.21	SRP22
ISPRA (EU)	31/3/00	0.996	0.001	0.0	0.20	UMEG
OFMET (CH)	4/4/00	0.994	0.000	0.0	0.10	SRP14
LNE (F)	6/6/00	0.998	0.001	-0.1	0.18	SRP24

†Appendix 1 provides details of the national measurement institutes which are abbreviated in this Table.

The standard errors in the derived slopes and offsets, in the above Table, are those generated by a least squares analysis

As can be seen from the results three national ozone standards showed a deviation from the NPL SRP of more than ±1% in the regression slope, and one national standard showed an offset of greater than ± 0.5 ppb.

4. SUMMARY OF THE RESULTS OF ALL INTERCOMPARISON

The data obtained from both the PTB and NPL intercomparisons are summarised graphically below in Figures 3.2 and 3.3. As an indication of the comparability of these results, an uncertainty error bars of ± 1% relative have been added to the graph showing the slope results.

Figure 3.2:

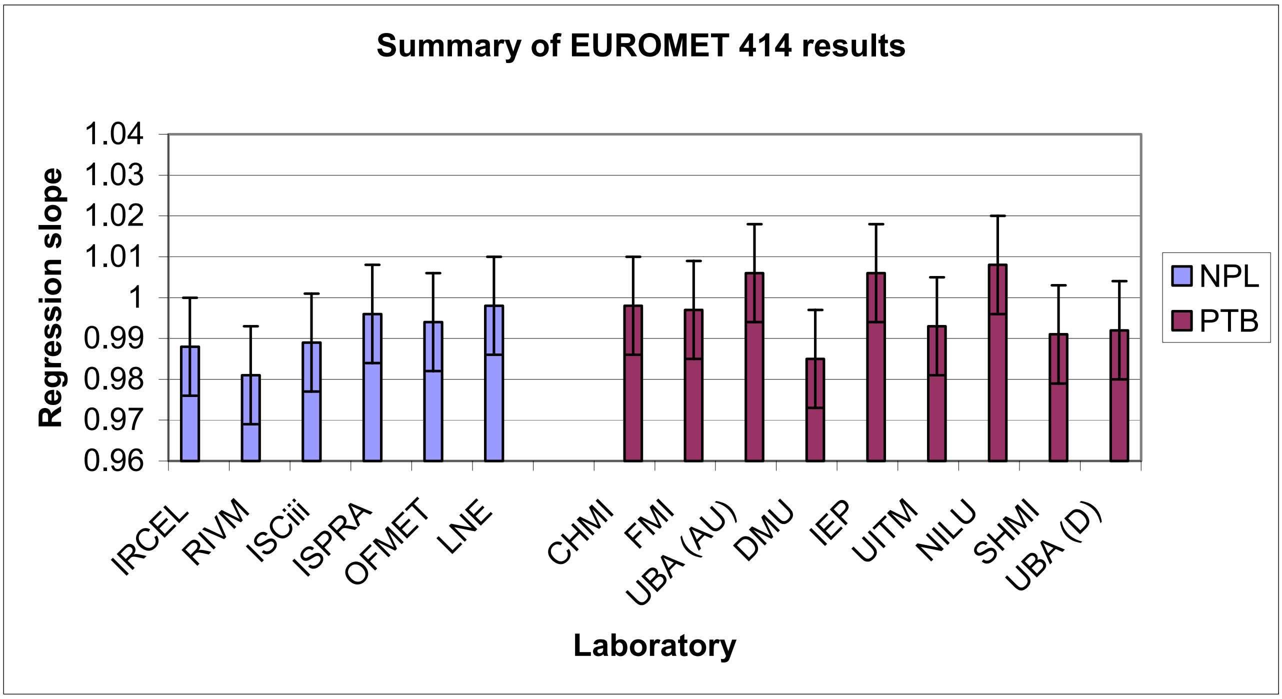
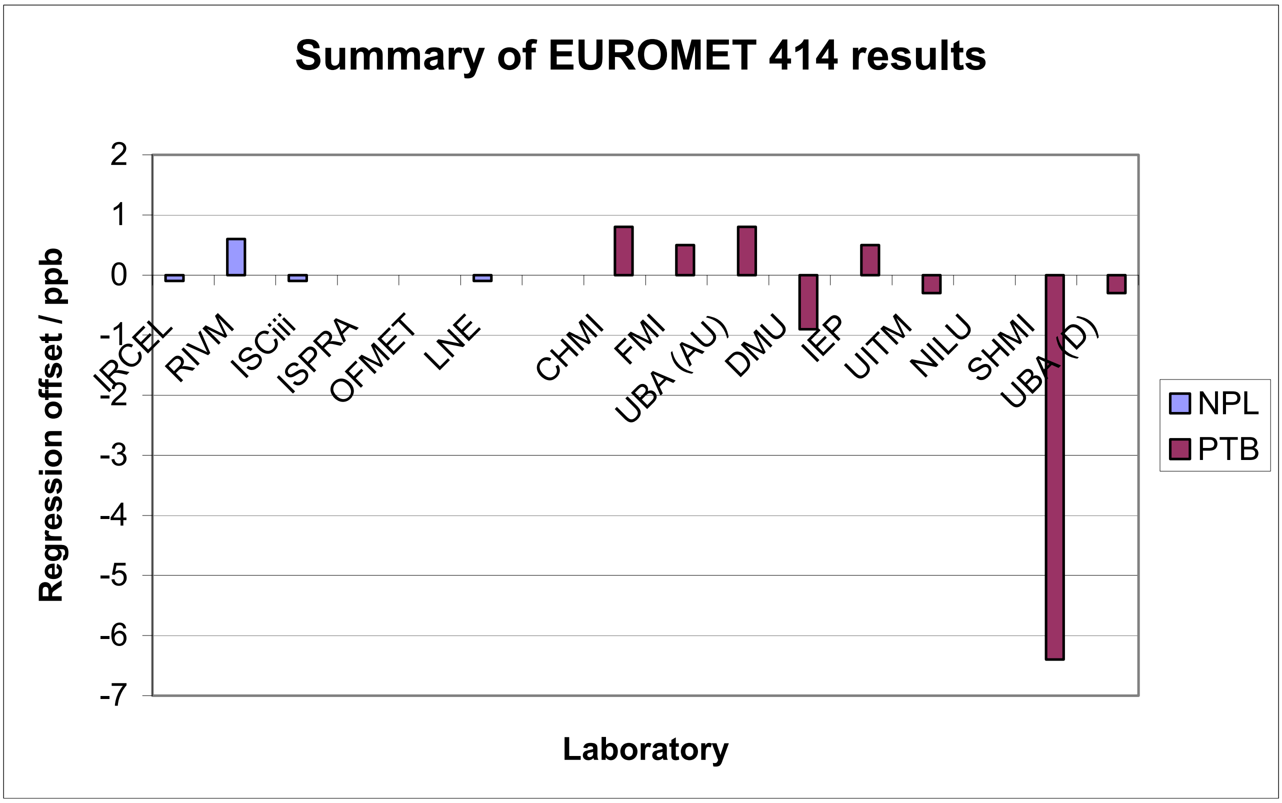


Figure 3.3:


Summary of EUROMET 414 results
Regression offset / ppb
2
1
0
-1
-2
-3
-4
-5
-6
-7
JRCEL
RIVM
ISCiii
ISPRA
OFMET
LNE
CHMI
FMI
UBA (AU)
DMU
IEP
UITM
NILU
SHMI
UBA (D)
Laboratory
NPL
PTB

4 THE COMPARABILITY AND STABILITY OF NPL AND PTB NATIONAL OZONE PRIMARY STANDARDS

Of paramount importance in this intercalibration exercise was the stability and comparability of the standards held by the pilot laboratories. To ensure their comparability, a number of calibrations were carried out to inter-relate the primary standards used by PTB and NPL (SRPs 19 and 20 respectively)

5 ANALYSIS OF MEASUREMENT UNCERTAINTIES IN THE INTERCOMPARISONS

5.1 SOURCES OF UNCERTAINTY IN INDIVIDUAL OZONE MEASUREMENTS

The sources of uncertainty in the result of a single ozone measurement carried out during these inter-comparisons repeated ten times, will include the following components:

(i) Analyser repeatability. - a value of 0.5% relative of value has been assigned to this based on previous experience of these analyses.

(ii) Analyser noise, is taken to be the standard deviation of the ten successive measurements comprising each point.

(iii) Span drift and zero drift. It is assumed that the span will not drift by more than 0.1% of FSD (and hence of value) and the zero will not drift by more than 0.5 ppb during the time taken to carry out the measurements.

The uncertainty due to temperature and pressure measurement and in the determination of optical path length are all negligible in well-characterised primary standard systems. No account has been taken of the ozone cross-section at 254 nm because all measurement systems use the same value for this. This may become significant, though, when comparing a UV photometric system with another system calibrated using GPT for instance.

Combining the uncertainties shown in 5.1.1 to 5.1.3 we have at concentrations of 30, 100, 300 and 500 ppb we have

Table 5.1: Determination of the Uncertainty of Individual Measurements

	ppb	%		30 ppb	100 ppb	300 ppb	500 ppb
zero drift	0.50			1.67	0.50	0.17	0.10
span drift		0.10		0.10	0.10	0.10	0.10
repeatability		0.50		0.50	0.50	0.50	0.50
signal noise	0.60			2.00	0.60	0.20	0.12
		uc(%)		2.65	0.93	0.57	0.53
		Uc(k=2) (%)		5.31	1.87	1.15	1.07

Thus, using this analysis, the 95% value for uncertainty in individual concentration points in this intercomparison range between approximately 5% and 1% of value for corresponding concentrations of 30 ppb to 500 ppb.

5.2 SOURCES OF UNCERTAINTY IN THE UTILISATION OF A TRANSFER STANDARD TO INTERCOMPARE THE TWO PRIMARY STANDARDS

When using a transfer standard to intercompare two primary standards, likely sources of uncertainty are as follows:

5.2.1 Drift in either of the primary standards being compared.

From the data given above, the NPL standard appears to have drifted by 0.2% compared to the NIST standard. This can be taken, therefore, as indicative of the drift which may be expected for a single well-maintained primary standard.

5.2.2 Drift in Transfer Standard

From the calibrations of the NPL transfer standard against the NPL primary standard, the worst case situation was where the NPL transfer standard appeared to have drifted by 0.3% in the period 24/034/00 to 11/04/00. This can be taken as the magnitude of the uncertainty of the drift of the transfer standard.

5.2.3 Repeatability

The 4 comparisons between the PTB and NPL primary standards were carried out using transfer standard instruments. Considering these data, and assuming no relative drift in either of the primary standards, the standard deviation of the comparison results is 0.3% of the mean. This can be taken as indicative of the repeatability of the method of using a transfer standard to compare two primary standards.

5.2.4 Derivation of regression slope

The results of this intercomparison are given in terms of a linear regression. The regression slope will itself have uncertainty limits due to the scatter of points around the best fit line and also due to the uncertainty of each individual data point.

For the NPL loop the uncertainties in the two series of measurement data (NPL and the participating Laboratory) have been evaluated using the uncertainty budget given in section 5.1 above. These have been input, along with the mean values, to a generalised least squares calculation package to generate the uncertainties in the regression slope.

Two laboratories, ISCIII and JRC ISPRA provided uncertainties with their data. ISC111 quoted uncertainties of ± (1.1% + 0.4 ppb) (k=2). JRC ISPRA provided standard uncertainties in ppb for each of their measured points. These are shown in the ISPRA table in Appendix 2). The uncertainties supplied by these laboratories have been used for the JRC and ISCIII instruments.

The uncertainties in the regression slope, calculated for all of the NPL loop comparisons, are shown below:

Table 5.2: Uncertainties in Regression Slope Calculated Using Generalised Least Squares Method

Laboratory	Uncertainty in regression slope using method of generalised least squares (%)
ISCIII	0.40
ISPRA	0.83
IRCEL	0.40
RIVM	0.45
LNE	0.39
OFMET	0.42

Note that these values for the uncertainty in the slope are many times greater than those given by simple least squares analyses. Taking a typical value, the median, of these values as generally representative of the uncertainty in the gradient due to fitting a straight line through the comparison data sets, the uncertainty is some 0.42%.

Combining these four components of uncertainty according to the Guide to The Uncertainty of Measurements (1993).

Source of uncertainty	value	assumed distribution	divisor	standard error (%)
Drift in primary standard 1	0.2	r	1.73	0.12
Drift in primary standard 2	0.2	r	1.73	0.12
Drift in transfer standard	0.3	r	1.73	0.17
repeatability of measurements	0.3	n	1	0.3
uncertainty in derivation of gradient	0.42	n	1	0.42
combined uncertainty				0.6
95% confidence level (k=2)				1.2

Thus, from a consideration of the uncertainties in both individual measurements and in performing this sort of intercomparison, the uncertainty in the intercalibration results is quoted as ± 1.2% at a level of confidence of 95%.

Possible sources of uncertainty which have not been included are:

1. Uncertainty in ozone optical absorption cross-section at 254 nm. This has been ignored as all instruments tested derived their traceability from UV measurements, using the same value for ozone absorption cross section.

2. Uncertainty due to pressure and temperature compensation. These on-board measurements form part of the intercomparisons and as such any uncertainties associated with these should be reflected in the results. Any drifts in these measurements will, however, be included in the uncertainties due to drifts noted above.

5.3 UNCERTAINTIES IN THE ZERO OFFSETS GENERATED

It is relatively straightforward to provide an air stream which is free of ozone since its reactivity allows it to be "scrubbed" very efficiently. Given this, it is easy to determine the instrument response at zero concentration, and to use this response to act as a reliable zero point in the determination of ozone concentrations. For well-maintained primary standard measurement systems drifts and other uncertainties in zero response have no significant effect on the * of the intercomparison.

Data in this report have been manipulated in slightly different ways according to the response characteristics of the individual <u>transfer</u> standards used. Due to some measured zero drift in the NPL transfer standard, the zero responses used at each comparison was that which was measured on the day of the comparison. This is to avoid introducing apparent discrepancies in primary standard zero determination due to drifting transfer standard.

Data from the PTB loop have used a single common zero point to carry out the intercomparison. Consideration of the zero response of the PTB transfer standard has shown a mean value over all valid intercomparison data of 0.1 ppb with a standard error of the mean of 0.2 ppb.

Consideration of the system response to zero air can be very useful in determining that correct pneumatic and flow conditions are being met. For instance, the relatively large offset observed in the results obtained at national institute in Slovakia, where both the lab and PTB standards produced negative readings with zero air (-9 and –3 ppb respectively), is an indication of some contamination of zero air, or possibly pneumatic problems, such as system leaks, pressure imbalances or insufficient sample flow rates.

APPENDIX 1

List of Participants in the Intercomparison Exercise

Country	Abbreviation	Name of Institute
Austria	UBA (AU)	
Belgium	IRCEL	
Czech Republic	CHMI	
Denmark	DMU	
EU	JRC ISPRA	
Finland	FMI	
France	LNE	
Germany	UBA (D)	
Hungary	IEP	
Netherlands	RIVM	
Norway	NILU	
Slovakia	SMHI	
Spain	ISC111	
Sweden	ITM	
Switzerland	OFMET	

National Reference Laboratories were also visited in Ireland (EPA) and Poland (GUM). Data from these countries have not been included in the report as their ozone measurements systems are relatively new and of unknown stability and for measurement uncertainty. Calibrations were, however, carried out at these laboratories, and it is hoped that this will facilitate in the establishment of accurate and traceable results in these countries.

APPENDIX 2

PROTOCOL FOR EUROMET PROJECT 414
“COMPARISON OF OZONE PRIMARY STANDARDS”

1 INTRODUCTION

1.1 Objective

The objective of this project is to determine the extent of comparability of “national standards” of ozone in countries within the European Union.

In some countries, the “national standard” is a “primary” photometer, which justifies its primary status on the basis of the quality of its design and maintenance. In other countries, the national standard is a “commercial” photometer and traceability may be achieved through reference to a primary standard held in other counties.

Since there are many possible means by which a national standard can be maintained, the objective of the project is to determine the comparability of the national standard as disseminated in that country.

1.2 Background

This project is being operated within the framework of EUROMET under the coordination of NPL and PTB which are acting as pilot laboratories (an overview of EUROMET is available at www.euromet.org*). The objectives and implementation of the project are consistent with the requirements of the European Union to standardise measurements of ozone required by the Ambient Air Framework Directive 96/62 EC, and the relevant Daughter Directive.

This project is complementary to those comparisons organised by the EC Central Laboratory for Air Pollution at the Joint Research Centre at Ispra, Italy.

1.3 Identification of Participants and Facilities

As far as possible, the pilot laboratories have identified one participating organisation from each country. In each case either the designated “national reference” laboratory has been chosen or the laboratory from which the country derives traceability for ozone measurements. Each participating organisation will be visited by one of the two pilot laboratories to compare a travelling reference standard with that country’s national standard.

Prior to being visited each participant shall send (e-mail or fax) the following information to both pilot laboratories. This information shall be as below:

Information to be communicated to the pilot laboratories before the comparison visit
Manufacturer and type of standard photometer to be used in the comparison
Flow rate required through measurement cell.
Flow rate generated by ozone generator (if applicable)

2 INTERCOMPARISON PROTOCOL

2.1 COMPARISON METHOD

The following procedure will be used:

A direct comparison will be made between the travelling comparison photometer and the participating standard over 10 concentrations in the range zero to 500 ppb.

The ozone concentrations used to carry out the comparison will be delivered, where possible, by the participating laboratory. In the event that it is not possible for the participating laboratory to produce stable ozone concentrations at the required flow rate, these will be generated by NPL/PTB.

2.2 PRE-COMPARISON MEASUREMENTS

2.2.1 Stabilisation of instrumentation

Prior to the arrival of the travelling comparison standard, all instrumentation that will be used for the comparison shall be switched on and allowed to stabilise for at least eight hours.

2.2.2 Temperature and Pressure

Checks will be made of the pressure and temperature measurement systems of the standards. If any adjustments from the "as found" state are required, they will be noted. The participating laboratory will be required to provide evidence for the traceability of these measurements.

2.2.3 Conditioning of pneumatic lines

Interconnecting PTFE lines will be conditioned at a concentration of approximately 500 ppb for at least one hour. NPL /PTB will provide an ozone generator to facilitate this. However, other than the normal operating procedures used by the participating laboratory, sample cells and pneumatic components within the standard ozone instruments of the participating institutes will not be conditioned.

2.2.4 Calibration of the Travelling Analyser (NPL visits only)

To verify that the travelling comparison standard has retained its calibration during transport, NPL will calibrate a travelling analyser on arrival at the participating laboratory, prior to the comparison of standards. This verification will take the form of a ten point check between the travelling analyser and travelling photometer.

This analyser will be calibrated by NPL, using the on-board ozone generation facility of the NPL travelling standard. The zero air required by the NPL system for generating ozone and for the reference measurements will be supplied by the participating laboratory, and will be from an identical source as that used by the participating laboratory ozone generation and measurement system.

Each of the 10 measurement points will be sampled for at least ten minutes, simultaneously by the travelling analyser and NPL travelling transfer standard. Following this, 10 concentration outputs, at the same concentration, from each instrument will be noted at 30 second intervals.

If the standard deviation of either set of results is greater than 3 ppb or 1.5% of concentration (which ever is larger), the point will be retaken following a further 5 minute stabilisation time.

The points will be sampled in the order specified in 2.5, such as to take account of potential hysteresis effects.

A regression will be performed to characterise the response of the analyser in terms of the NPL primary standard.

2.2.5 Test on Zero Air

After calibration, the travelling analyser will be used to verify that the ozone concentration of the zero air used in the photometer tests is less than 1 ppb.

2.3 INTERCOMPARISON PROCEDURE

The comparison of ozone instruments will take place over 10 points in the range zero ppb to 500 ppb.

Sample gas for the comparison with a stable concentration of ozone in air will be supplied by the participating laboratory. The ozone concentrations required will be 30 ppb to 500 ppb at flow rates of up to 5 standard litres per minute.

To avoid pressurisation effects, the excess gas will be vented directly into the laboratory.

Zero air for the generation of ozone and for both photometer's reference measurements, will be supplied from a common source, by the participating laboratory.

Each of the 10 measurement points will be sampled for at least ten minutes simultaneously by each photometer according to paragraph 2.4. Following this, the output from each instrument will be recorded at 10 second intervals for 5 minutes, i.e. 30 values from each instrument will be noted at each concentration.

The mean and standard deviation of the recorded values for each instrument will be evaluated. If the standard deviation of either set of results is greater than 2 ppb or 1.5% of concentration (which ever is larger), the point will be retaken following a further 5 minute stabilisation time. Repeated instances of unacceptable values in the standard deviation of the results would indicate that there are instabilities in the generation or measurement systems. The reasons for these will be examined and documented prior to the comparison continuing.

As stated above, the comparison will be carried out at 10 points in the nominal range zero to 500 ppb.

The points will be sampled in the following sequence:

250, 100, 60, 200, zero, 400, 30, 150, 500, 300

The concentrations given above are nominal values - it is anticipated that the actual delivered values will be within +/- 15 ppb of those given above.

2.4 DATA ACQUISITION AND HANDLING

Average values and standard deviations will be calculated for each system for each of the ten points.

Data from the NPL/PTB travelling standard will then be scaled according to the previous calibration against the primary standard, carried out at NPL. or PTB as appropriate.

Scaled NPL/PTB data will then be combined with those of the participating laboratory to form a linear regression with data from the participating laboratory as the dependant variable. Thus, the inter-calibration will relate the participating laboratory standard to the NPL or PTB primary standard in each case.

2.5 POST-COMPARISON VERIFICATION

Upon return to the pilot laboratory, the travelling transfer standard (and if appropriate, the travelling analyser) will be calibrated against the NPL/PTB ozone standard to demonstrate that no significant drift has occurred in either instrument during the exercise.

2.6 DISSEMINATION OF RESULTS

NPL/PTB are responsible for the preparation of a report of the comparisons. The report passes through a number of stages before publication and these are referred to here as drafts A and B.

The first draft, draft A, is prepared when results are available from all of the comparisons. It includes the results from each participant, identified by name. It is confidential to the participants. The second draft, draft B, is subsequently prepared for wider dissemination and is not confidential.

In more detail, the procedure is as follows:

- During the comparison, as the results are received by the pilot institute, they are kept confidential by the pilot institute until all the participants have completed their measurements and all the results have been received, or until the date limit, set by the pilot laboratory, for the comparison has passed.

- The results from a participant are not considered complete without associated uncertainties, and is not included in the draft report unless it is accompanied by an uncertainty supported by a complete uncertainty budget.

- If, on examination of the complete set of results, the pilot laboratory finds results that appear to be anomalous, the corresponding institutes are invited to check their results for numerical errors but without being informed as to the magnitude or sign of the apparent anomaly. If no numerical error is found the result stands and the complete set of results is sent to all participants. (Note that once all participants have been informed of the results, individual values and uncertainties may be changed or removed, or the complete comparison abandoned, only with the agreement of all participants or on the basis of a clear failure of the travelling standard or some other phenomenon that renders the comparison or part of it invalid.)

- Draft A of the report is sent, as soon as possible after completion of the comparison, to all the participants for comment, with a reasonable deadline for replies.

- If any controversial or contradictory comments are received by the pilot laboratory, they are circulated to all participants and discussion continues until a consensus is reached.

- Draft A is considered as confidential to the participants. Copies are not given to non participants, and graphs or other parts of the draft are not used in oral presentations at an outside Conference without the specific agreement of all the participants.

- On receipt of final comments from participants, the second draft, draft B, is prepared.

- Draft B, which supersedes draft A, is not considered confidential, and is likely be the subject of a publication in the scientific literature.

APPENDIX 3

A number of interaction inter-comparisons have been carried out during the period February 1998 to February 2000 to demonstrate the stability and the comparability of the PTB and NPL SRPs. These are summarised below. The NPL SRP has also been returned to NIST USA for recertification within this period and these results are also summarised below.

A3.1 INTERCOMPARISONS BETWEEN PTB AND NPL SRPS

(i) February 1998

Using NPL TE49PS as a transfer standard, the relationship between SRP 20 and SRP 19 was found to be

[SRP 20] = 0.995 [SRP 19] + 1.0 [ppb]

(ii) November 1999

Using PTB TE49C as a transfer standard, the relationship between SRP 20 and SRP 19 was found to be

[SRP 20] = 0.994 [SRP 19] + 0.6 [ppb]

(iii) February 2001.

Using NPL API 401 as a transfer standard in a visit to PTB, the relationship between SRP 20 and SRP 19 was found to be

[SRP 20] = 1.001 [SRP 19] – 1.6 [ppb]

(iv) February 2001

Using PTB TE49C as a transfer standard in a visit to NPL, the relationship between SRP 20 and SRP 19 was found to be

[SRP 20] = 0.994 [SRP 19] + 0.4 [ppb]

(v) Average of the Above Results

The mean slope of the above results February 1998 to February 2001 is 0.996, with a standard deviation of the mean of 0.0015. Therefore, the two national ozone standards had shown a high level of comparability and stability throughout the period of the intercomparison exercise.

A3.2 INTERCOMPARISONS BETWEEN NPL AND NIST SRPS

The NPL instrument has been returned to NIST USA for recertification on two occasions - September 2000 and December 1998. Data are in the format

$$\text{NPL SRP} = \text{slope [NIST SRP]} + \text{offset}$$

The "as-received" calibration data are tabulated below

Date	slope	offset
December 1998	0.996	-0.1
August 2000	0.998	0.2

From these data it can be seen that, compared to an independent standard (NIST SRP 2 in both cases) the NPL instrument has retained satisfactory stability in both its slope and offset over the period of this exercise.

APPENDIX 3

Detailed results from the Intercomparison Exercise

Data in this section are as follows:

The zero and span corrections (top right) are the multiplier and offset used to scale raw data from transfer standards to primary standards. The summary data for the lab and PTB/NPL standards are the concentrations measured by the transfer standards which have been scaled, using the multiplier and offsets shown, and are therefore consistent with lab and PTB or NPL primary standards. The standard deviations (std and %std) shown are the standard deviations of the 10 measurements taken at each concentration generated for each of the instruments.

These data are then reduced, by simple linear regression, to form a relationship between the laboratory's national primary standard and the PTB or NPL primary standard in the form

national primary standard = slope [PTB (or NPL)] primary standard + offset

Also shown are the standard error in the slope and the offset.

CHMI 29/09/00

	zero	span
PTB correction	0.2	1.0101
lab correction	1.5	1.012

summary data

	lab standard				PTB travelling standard		
	mean	std	%std		mean	std	%std
1	254	2	1		254	2	1
2	104	1	1		103	0	0
3	66	1	2		65	0	0
4	198	1	0		198	0	0
5	1	1	76		0	0	105
6	396	1	0		397	1	0
7	35	1	4		34	0	1
8	156	1	1		156	0	0
9	507	2	0		507	1	0
10	306	1	0		305	1	0

	value	std_error
slope	0.998	0.001
offset	0.786	0.182

DMU 24/10/2000

summary data

			zoom	span
	PTB correction		0.2	1.0101
	lab correction		0	1

	lab standard				ptb travelling standard		
	mean	std	%std		mean	std	%std
1	251	1	0		254	0	0
2	99	1	1		102	0	0
3	59	1	1		61	0	0
4	200	1	0		204	0	0
5	1	1	66		1	0	10
6	402	1	0		408	0	0
7	29	1	2		30	0	1
8	149	1	1		152	0	0
9	500	2	0		509	1	0
10	300	1	0		306	1	0

	value	std_error
slope	0.985	0.001
offset	-0.897	0.373

FMI 31/10/00

summary data

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	lab standard				ptb travelling standard		
	mean	std	%std		mean	std	%std
1	256	n/a	n/a		256	n/a	n/a
2	105	n/a	n/a		104	n/a	n/a
3	64	n/a	n/a		64	n/a	n/a
4	205	n/a	n/a		205	n/a	n/a
5	0	n/a	n/a		0	n/a	n/a
6	406	n/a	n/a		407	n/a	n/a
7	34	n/a	n/a		34	n/a	n/a
8	155	n/a	n/a		155	n/a	n/a
9	491	n/a	n/a		492	n/a	n/a
10	306	n/a	n/a		307	n/a	n/a

	value	std_error
slope	0.997	0.000
offset	0.473	0.092

IEP 06/10/00

summary data

PTB correction	0.2	1.0101
lab correction	0	1

	lab standard				ptb travelling standard		
	mean	std	%std		mean	std	%std
1	266	n/a	n/a		265	n/a	n/a
2	100	n/a	n/a		100	n/a	n/a
3	64	n/a	n/a		64	n/a	n/a
4	212	n/a	n/a		208	n/a	n/a
5	0	n/a	n/a		0	n/a	n/a
6	414	n/a	n/a		409	n/a	n/a
7	32	n/a	n/a		32	n/a	n/a
8	153	n/a	n/a		150	n/a	n/a
9	500	n/a	n/a		499	n/a	n/a
10	312	n/a	n/a		308	n/a	n/a

	value	std_error
slope	1.006	0.003
offset	0.475	0.887

ITM 28/10/00

summary data

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	lab standard				ptb travelling standard		
	mean	std	%std		mean	std	%std
1	243	0	0		246	0	0
2	100	0	0		101	0	0
3	57	0	0		58	0	0
4	200	0	0		201	0	0
5	0	0	0		0	0	19
6	400	0	0		402	1	0
7	32	0	0		33	0	0
8	151	0	0		152	0	0
9	502	0	0		507	1	0
10	299	0	0		302	0	0

	value	std_error
slope	0.993	0.001
offset	-0.333	0.378

NILU 26/10/00

summary data

								zero	span
	lab standard				ptb			PTB correction 0.2	1.0101
	mean	std	%std		mean	std	%std	lab correction 0	1
1	249	0	0		249	0	0		
2	101	0	0		101	1	1		
3	60	0	1		59	0	1		
4	200	0	0		198	0	0		
5	1	0	22		1	0	16		
6	399	1	0		396	1	0		
7	31	0	1		30	0	1		
8	150	0	0		148	0	0		
9	499	0	0		495	0	0		
10	299	0	0		297	1	0		

	value	std_error
slope	1.008	0.002
offset	-0.002	0.543

SHMI 4/10/00

summary data

								zero	span
	lab standard				npl travelling standard			PTB correction 0.2	1.0101
	mean	std	%std		mean	std	%std	lab correction 0	1
1	250	1	1		257	1	0		
2	100	1	1		106	1	1		
3	60	1	1		67	1	1		
4	199	1	0		207	1	0		
5	-9	0	-5		-3	0	-7		
6	399	2	0		409	2	0		
7	30	1	2		38	0	1		
8	149	1	1		158	1	1		
9	499	2	0		511	2	0		
10	300	1	0		309	1	0		

	value	std_error
slope	0.991	0.002
offset	-6.409	0.593

UBA (AU) 02/10/00

summary data

	zero	span
PTB correction	0.2	1.0101
lab correction	-0.03	0.987

(SRP#15, EMPA, 19.12.2000)

	lab standard				ptb		
	mean	std	%std		mean	std	%std
1	247	1	0		244	1	0
2	99	0	0		98	0	0
3	59	0	0		58	0	0
4	197	0	0		194	1	0
5	0	0	-332		0	0	-87
6	395	0	0		392	0	0
7	30	0	1		29	0	1
8	148	0	0		146	0	0
9	493	0	0		490	1	0
10	296	0	0		294	0	0

	value	std_error
slope	1.006	0.001
offset	0.824	0.259

UBA (D) 04/10/00

summary data

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	lab standard				ptb		
	mean	std	%std		mean	std	%std
1	245	2	1		247	1	0
2	99	0	0		100	0	0
3	60	1	2		60	0	0
4	196	1	1		198	1	0
5	0	1	-876		0	0	15
6	393	1	0		396	1	0
7	30	1	3		30	0	1
8	146	1	1		149	0	0
9	501	1	0		505	1	0
10	295	1	0		297	1	0

	value	std_error
slope	0.992	0.001
offset	-0.298	0.278

IRCEL 07/03/00

			zero	span
summary data		NPL correction	0.5	0.986
		lab correction	0	1

	lab standard				npl travelling standard		
	mean	std	%std		mean	std	%std
1	253	0	0		255	0	0
2	98	0	0		100	0	0
3	58	0	0		59	0	0
4	202	0	0		204	0	0
5	0	0	-99		0	0	65358
6	397	0	0		402	1	0
7	39	0	0		40	0	1
8	150	0	0		152	1	0
9	495	0	0		501	0	0
10	299	0	0		304	0	0

	value	std_error
slope	0.988	0.001
offset	-0.079	0.244

ISCiii 28/03/00

			zero	span
summary data		NPL correction	0.8	0.9852
		lab correction	0	1

	lab standard				npl travelling standard		
	mean	std	%std		mean	std	%std
1	248	0	0		251	0	0
2	98	0	0		100	1	1
3	62	0	0		63	0	0
4	198	0	0		200	0	0
5	0	0	-324		0	0	-257
6	397	0	0		401	1	0
7	34	1	2		34	0	1
8	149	0	0		151	0	0
9	493	1	0		499	0	0
10	296	0	0		299	0	0

	value	std_error
slope	0.989	0.001
offset	-0.134	0.156

JRC ISPRA 31/03/00

								zero	span
summary data							NPL correction	0	0.9852
	lab standard			npl travelling standard			lab correction	0	1
	mean	std	%std	mean	std	%std			
1	249	1	0	250	1	0			
2	100	1	1	100	1	1			
3	60	0	1	60	0	1			
4	199	1	0	200	0	0			
5	0	0	134	0	0	-310			
6	399	1	0	400	1	0			
7	30	1	2	30	1	2			
8	150	1	0	150	1	0			
9	499	1	0	502	1	0			
10	300	1	0	301	1	0			

	value	std_error
slope	0.996	0.001
offset	0.047	0.214

LNE 06/06/00

									zero	span
summary data								NPL correction	1.2	0.9794
	lab standard				npl travelling standard			lab correction	0	1
	mean	std	%std		mean	std	%std			
1	117	1	1		117	0	0			
2	299	0	0		299	0	0			
3	150	0	0		150	0	0			
4	250	0	0		251	0	0			
5	190	0	0		191	0	0			
6	63	0	0		63	0	0			
7	0	0	-53		0	0	1323			
8	409	0	0		410	0	0			
9	25	0	1		25	0	1			
10	495	0	0		496	0	0			

	value	std_error
slope	0.998	0.001
offset	-0.051	0.204

OFMET 04/04/00

summary data

			zero	span
	NPL correction		0.2	0.98522
	lab correction		0	1

	lab standard			npl travelling standard		
	mean	std	%std	mean	std	%std
1	243	0	0	245	0	0
2	97	0	1	97	0	1
3	61	0	0	61	0	0
4	195	0	0	196	0	0
5	0	0	n/a	0	1	2051
6	394	0	0	396	0	0
7	29	0	1	29	0	1
8	146	0	0	147	1	0
9	483	0	0	486	1	0
10	287	0	0	289	0	0

	value	std_error
slope	0.994	0.000
offset	0.001	0.099

RIVM 09/03/00

summary data

			zero	span
	NPL correction		0.8	0.9862
	lab correction		0	1

	lab standard				npl travelling standard		
	mean	std	%std		mean	std	%std
1	249	1	0		253	1	0
2	100	1	1		101	1	1
3	60	0	1		61	0	1
4	199	1	0		203	1	0
5	1	0	61		0	0	-1298
6	397	1	0		404	0	0
7	30	1	2		30	0	1
8	148	1	1		149	0	0
9	446	2	0		454	0	0
10	298	1	0		303	0	0

	value	std_error
slope	0.981	0.001
offset	0.575	0.184