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COMPARISONS OF NATIONAL PHOTOMETRIC OZONE PRIMARY STANDARDS

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Report on Results of Euromet Project 414

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Comparisons of National Photometric Ozone Primary Standards: Euromet Project 414

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COMPARISONS OF NATIONAL PRIMARY OZONE STANDARDS:

REPORT ON RESULTS OF EUROMET PROJECT 414

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COMPARISONS OF NATIONAL PRIMARY OZONE STANDARDS:

REPORT ON RESULTS OF EUROMET PROJECT 414

EXECUTIVE SUMMARY

FIELD
Amount of Substance

SUBJECT
Comparison in the field of ambient-air ozone measurement

ORGANISING BODY
Euromet METCHEM Committee

A comparison exercise has been carried out to determine the accuracy and uniformity of primary ozone calibration standards held at national measurement institutes and national reference laboratories in fifteen countries across Europe. These all use the ultraviolet photometry technique. The comparisons were carried out by employing two European national metrology institutes as pilot laboratories, and these transported photometric ozone transfer standards to all the participants. In general, the level of agreement between the 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.

Table 1: List of Participants

Country	Abbreviation	Name of Institute
Austria	UBA (A)	Umwelt Bundes Amt
Belgium	IRCEL	Interwestelijke Cel voor het Leefmilieu
Czech Republic	CHMI	Czech Hydro-Metrological Institute
Denmark	DMU	Danmarks Miljoundersogelser
EU	JRC, Ispra	European Commission, Joint Research Centre, Ispra
Finland	FMI	Finnish Meteorological Institute
France	LNE	Laboratoire National D'Essais
Germany	UBA (D)	Umwelt Bundes Amt
Germany	PTB	Physikalisch-Technischen Bundesanstalt
Hungary	IEP	Institute for Environmental Protection
Netherlands	RIVM	Rijksinstituut voor Volksgezondheid en Milieu
Norway	NILU	Norsk Instituut for Luftforskning
Slovakia	SHMI	Slovak Hydrometeorological Institute
Spain	ISCIII	Instituto de Salud Carlos III
Sweden	ITM	Institute of Applied Environmental Research
Switzerland	METAS	Metrologie und Akkreditierung Schweiz
UK	NPL	National Physical Laboratory

COMPARISONS OF NATIONAL PRIMARY OZONE STANDARDS:

REPORT ON RESULTS OF EUROMET PROJECT 414

1 INTRODUCTION

Primary ozone calibration standards, which use ultraviolet photometry, are maintained as national standards in most European countries by national measurement institutes or other national reference laboratories. A project was carried out within the framework of Euromet to carry out comparisons of these national standards. The reactive nature of gaseous ozone however, precludes its preparation and stable containment in gas cylinders or in other containers, and for that reason, standards for this species are generally measuring instruments known as ozone reference photometers. Many, but not all, of these national reference photometers were obtained from the National Institute of Standards and Technology, USA (NIST). Others were carefully-maintained commercial photometers, or European-manufactured reference photometers.

A calibrated transfer standard was transported from one of the two pilot laboratories - Physikalisch-Technischen Bundesanstalt (PTB-D) and National Physical Laboratory (NPL-GB) - to each laboratory to compare the instruments held in the Standards Laboratories. Data were obtained from fifteen national measurement institutes, related to either the PTB or NPL primary ozone standards. Measurements were also 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 comparisons. A list of the participants is given in the Executive Summary above and also, with some further information, in Appendix 1.

Each bilateral intercalibration followed a pre-prepared measurement protocol, which is attached as Appendix 2. In summary, the comparisons were carried out by determining the responses of the travelling standard and the national standard of the laboratory visited at ten different ozone concentrations between 0 ppbv and 500 ppbv. Ten successive measurements by both instruments were made at each concentration. The results of these comparisons are given in detail in Appendix 3.

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 also validated at the beginning and end of this comparison exercise. These results are given in detail in Appendix 4.

2 RESULTS OBTAINED DURING THE PTB COMPARISONS

2.1 TRACEABILITY 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 given by:

$$[\text{TE49C}] = 0.990\,[\text{SRP 19}] - 1.8\,[\text{ppb}] \qquad (1)$$

This equation was used initially to provide traceability to the PTB SRP of the results obtained of individual comparisons carried out in the participating laboratories.

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 the regression slopes of the responses to ozone

concentrations of the two primary standards was shown to be equal within their combined measurement uncertainties. However, 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 observed in the TE49C/SRP19 relationship. Therefore, in order to avoid biasing subsequent comparison results carried out by PTB, the TE49C/SRP19 relationship was amended to:

$$[\text{TE49C}] = 0.990\ [\text{SRP 19}] - 0.2\ [\text{ppb}] \qquad (2)$$

2.2 SUMMARY OF PTB RESULTS

The comparisons used equation (2) to scale the results obtained by PTB during its visits to nine national measurement institutes. These derived results are summarised in Table 2.1 below, expressed in the format:

$$\text{Participating Lab} = \text{slope}\ [\text{PTB SRP}] + \text{offset}\ [\text{ppb}]$$

The detailed results of each laboratory are given in Appendix 3.

Table 2.1: PTB Results

Laboratory Visited	Date Visited	National Photometer slope	Standard error of slope	National Photometer offset	Standard error of offset	National Standard used
CHMI (CZ)	29/09/00	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)	02/10/00	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)	06/10/00	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
SHMI (SK)	04/10/00	0.991	0.002	-6.4	0.6	TE49PS
UBA (D)	04/10/00	0.992	0.001	-0.3	0.3	UMEG

The measurement uncertainties (expressed at k=1) in the slope and offset are those obtained using a standard least-squares analysis - no generalised least-squares program was used.

As can be seen from the results, only one national ozone standard (DMU) showed a deviation from the regression slope from that of the PTB SRP of more than ±1%, and only one national standard (SMHI) showed a deviation in its offset of greater than ±1 ppb from that of the PTB SRP, when this was corrected according to equation (2).

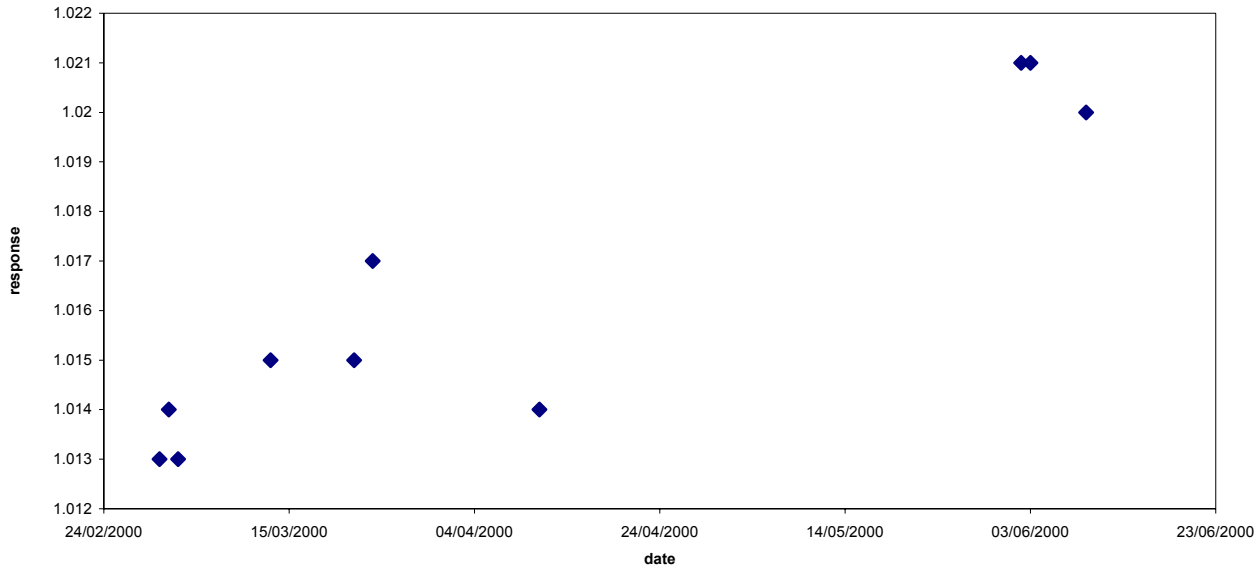
These data, along with summary results from the NPL loop are shown in Figures 4.1 and 4.2.

3 RESULTS OBTAINED DURING THE NPL COMPARISONS

3.1 TRACEABILITY OF THE NPL TRANSFER STANDARD

The NPL transfer standard (API 401) was calibrated ten times against the NPL SRP (s/n 20) over the period of the exercise. The results are given graphically below in Figure 3.1.

Figure 3.1: Slope of NPL Transfer Standard with respect to SRP 20.



As can be seen, there was an apparent drift of approximately 1% in the "span" response of the transfer standard during the exercise. Because of this, rather than simply take the mean of these results, the transfer standard response was derived for each participating laboratory visited from neighbouring calibrations against the NPL SRP.

The results of Figure 3.1, and the correction factors used, are given in Table 3.1, below:

Table 3.1: Relation of NPL Transfer Standard To SRP 20

Date	Slope of Transfer Standard to SRP	Offset (ppb)	Lab visited	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	1.014
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	1.015
04/04/00			OFMET	1.015
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 evidence, particularly near the end of the exercise, of a small drift in the zero reading of the NPL transfer standard. For these comparisons, the zero response of the NPL transfer standard was taken to be that measured at the time of each laboratory comparison using ozone-free air. The range of zero responses obtained ranged from 0 ppb to 1.2 ppb. It should be noted that such changes in the zero response do not significantly affect the slope of the regression lines obtained during the bilateral comparisons.

3.2 SUMMARY OF NPL RESULTS

The results of the comparisons carried out by NPL are given in Table 3.2 below. Detailed results from each laboratory are given in Appendix 3.

The results in the Table below are in the format:

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

Table 3.2: Results of the Ozone Comparisons (NPL)

Laboratory visited	Date visited	National Photometer Slope	Standard error of slope	National Photometer Offset	Standard error of offset	National Standard used
IRCEL (B)	07/03/00	0.988	0.001	-0.1	0.24	GPT/UMEG photometer
RIVM (NL)	09/03/00	0.981	0.001	0.6	0.16	TE49PS
ISCIII (E)	28/03/00	0.989	0.001	-0.1	0.21	SRP22
ISPRA (EU)	31/03/00	0.996	0.001	0.0	0.20	UMEG
OFMET (CH)	04/04/00	0.994	0.000	0.0	0.10	SRP14
LNE (F)	06/06/00	0.998	0.001	-0.1	0.18	SRP24

The standard errors in the derived slopes and offsets, in the above Table, are those generated by a standard least-squares fitting analysis - no generalised least-squares program was used.

From the results it can be seen that three national ozone standards (IRCEL, RIVM and ISCIII) showed deviations from that of the NPL SRP of greater than ±1% (with a maximum deviation of 1.9%), while no national standard showed an offset of greater than ± 1.0 ppb.

4 SUMMARY OF ALL RESULTS

The data obtained from both the PTB and NPL comparisons are summarised graphically below in Figures 4.1 and 4.2. As an indication of the comparability of these results, uncertainty error bars of ± 1% relative have been added to the graph showing the slope results.

Figure 4.1: Summary of Regression Slope Results.

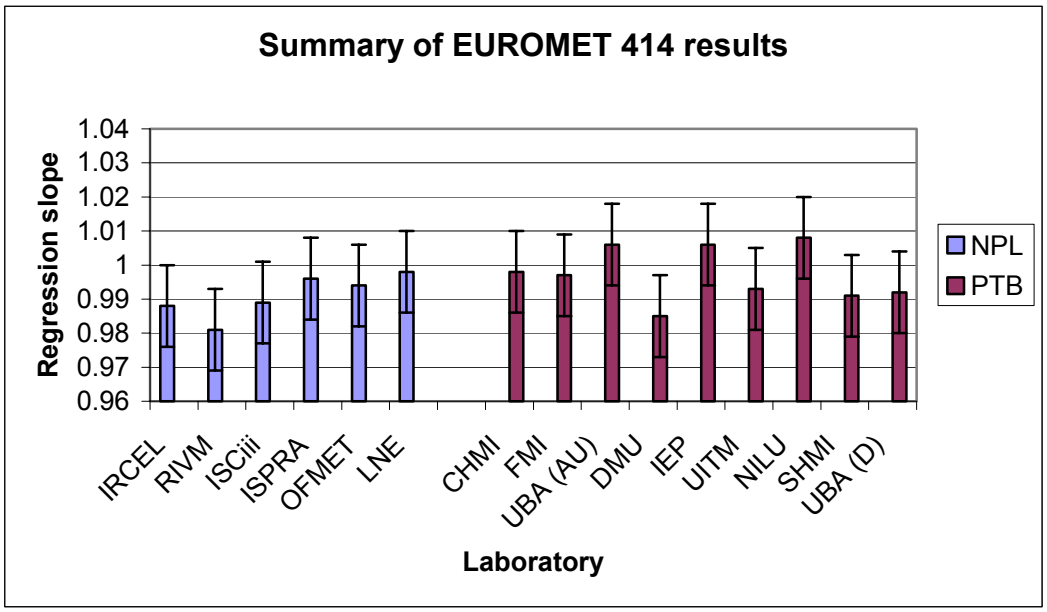
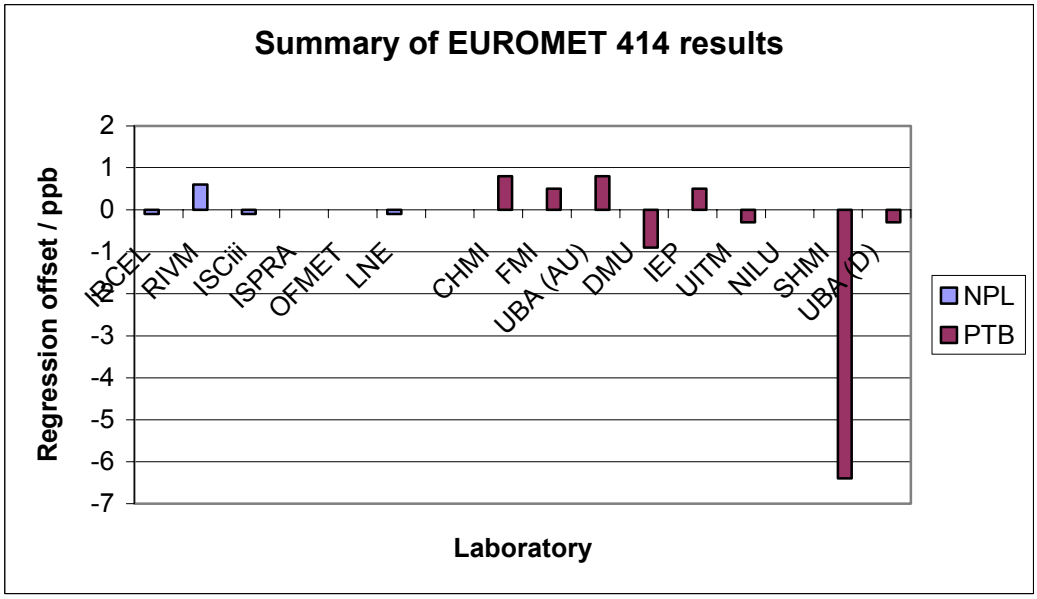


Figure 4.2: Summary of Zero Offset Results.



5 COMPARABILITY OF NPL AND PTB STANDARD REFERENCE PHOTOMETERS

The stability and comparability of the national primary ozone standards maintained by the two pilot laboratories during this comparison exercise was clearly of major importance. Several comparisons were therefore carried out during this project, alongside the results already described, to inter-relate the national ozone standards used by PTB and NPL (SRPs 19 and 20 respectively). The results obtained are presented in Appendix 4. They show that the two national ozone standards maintained a high degree of comparability and stability throughout the period of the comparison exercise, providing confidence that the individual results obtained are valid. In addition, the national ozone standard maintained by NPL was sent to the National Institute of Standards and Technology, USA in February 1998 and September 2000 for recalibrations, which showed that the NPL standard maintained good stability in its slope and offset over the period of the exercise with respect to the national ozone standard maintained by NIST.

6 ANALYSIS OF MEASUREMENT UNCERTAINTIES

6.1 SOURCES OF UNCERTAINTY IN INDIVIDUAL OZONE MEASUREMENTS

The sources of uncertainty in the result of a single ozone measurement carried out during these 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 analysers.

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

(iii) Span drift and zero drift: it is assumed that the span will not drift by more than 0.1% of the instrument full scale, 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 considered to be insignificant 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 might become significant, however, when comparing a UV photometric standard with another system, calibrated for instance using gas phase titration.

By combining the uncertainties above, at concentrations of 30, 100, 300 and 500 ppb, we have calculated the uncertainties given in Table 6.1.

Table 6.1: 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

Using this analysis, the 95% value for uncertainty in individual concentration points ranges between approximately ±5% and ±1% (at the 95% level of confidence) for concentrations between 30 ppb to 500 ppb.

6.2 UNCERTAINTY IN THE DERIVED SLOPE

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

6.2.1 Drift in the Primary Standards

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

6.2.2 Drift in the Transfer Standard

From the calibrations of the NPL transfer standard against the NPL primary standard, the worst-case situation occurred when the NPL transfer standard appeared to have drifted by 0.3% during the period 24/03/00 to 11/04/00. This was taken as the magnitude of the uncertainty of the drift of the transfer standard.

6.2.3 Repeatability

The four comparisons between the PTB and NPL primary standards presented in Appendix 4 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 results of the comparisons is 0.3% of the mean. This can be taken as indicative of the repeatability of the method which uses a transfer standard to compare two primary standards.

6.2.4 Derivation of Regression Slope

The results of these comparisons are expressed in terms of a linear regression. This regression slope will 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 results the uncertainties in the two sets of measurement data (from NPL and the participating laboratory) have been evaluated using the uncertainty budget given in Section 5.1

above. A generalised least squares computer programme developed by NPL has been used to determine the uncertainty in the regression slope.

Two laboratories, ISCIII and JRC ISPRA provided uncertainties with their data. ISCIII quoted uncertainties of ± (1.1% + 0.4 ppb) expressed with a level of confidence of about 95%. JRC ISPRA provided standard uncertainties in ppb for each of their measured points. These are shown in the ISPRA table in Appendix 3. The uncertainties supplied by these laboratories have been applied to the uncertainty determination the JRC and ISCIII instruments.

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

Table 6.2: Uncertainties in Regression Slope Calculated Using a Generalised Least Squares Method

Laboratory	Uncertainty in regression slope (%)
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 in general greater than those given by simple least squares analyses. Taking 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%.

These four components of uncertainty are combined according to the ISO Guide to the Uncertainty of Measurements (1993) in Table 6.3 below:

Table 6.3 Uncertainty Budget Assignment for the Comparisons

Source of uncertainty	Value (%)	assumed distribution	Divisor	standard error (%)
Drift in primary standard 1	0.2	rectangular	1.73	0.12
Drift in primary standard 2	0.2	rectangular	1.73	0.12
Drift in transfer standard	0.3	rectangular	1.73	0.17
repeatability of measurements	0.3	normal	1	0.3
uncertainty in derivation of gradient	0.42	normal	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 their combination in performing the comparison, the uncertainty in the results is ± 1.2% at a level of confidence of 95%.

Possible sources of uncertainty which have not been included are:

(i) 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.

(ii) Uncertainty due to pressure and temperature compensation. These on-board measurements form part of the comparisons 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.

6.3 UNCERTAINTY IN THE ZERO OFFSET

It is relatively straightforward to provide an air stream which is free of ozone since its reactivity allows it to be "scrubbed" from the air 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 the zero response of the system should have no significant effects on the final results of the comparisons.

Data in this report have been handled in slightly different ways according to the response characteristics of the individual transfer standards used. Due to some measured zero drift in the NPL transfer standard, the zero responses used at each comparison were those measured on the day of the comparisons. This is to avoid introducing apparent discrepancies in primary standard zero determination due to a drifting transfer standard.

Data from the PTB results have utilised a single common zero point for all the comparisons. This arose because consideration of the zero response of the PTB transfer showed no apparent drift. A mean value of all valid offset data was 0.1 ppb, with a standard error of the mean of 0.2 ppb.

Consideration of the system's response to zero air can be very useful in determining whether the 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 ppb and –3 ppb respectively), is an indication of contamination of the zero air, or otherwise possibly pneumatic problems, such as system leaks, pressure imbalances or insufficient sample flow rates.

APPENDIX 1

List of Participants

Country	Abbreviation	Name of Institute
Austria	UBA	Umwelt Bundes Amt
Belgium	IRCEL	Interwestelijke Cel voor het Leefmilieu
Czech Republic	CHMI	Czech Hydro Metrological Institute
Denmark	DMU	Danmarks Miljoundersogelser
EU	JRC, Ispra	European Commission, Joint Research Centre, Ispra
Finland	FMI	Finnish Meteorological Institute
France	LNE	Laboratoire National D'Essais
Germany	UBA	Umwelt Bundes Amt
Germany	PTB	Physikalisch-Technischen Bundesanstalt
Hungary	IEP	Institute for Environmental Protection
Netherlands	RIVM	Rijksinstituut voor Volksgezondheid en Milieu
Norway	NILU	Norsk Instituut for Luftforskning
Slovakia	SHMI	Slovak Hydrometeorological Institute
Spain	ISCIII	Instituto de Salud Carlos III
Sweden	ITM	Institute of Applied Environmental Research
Switzerland	METAS	Metrologie und Akkreditierung Schweiz
UK	NPL	National Physical Laboratory

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

APPENDIX 2

PROTOCOL PREPARED FOR EUROMET PROJECT 414
"COMPARISON OF OZONE PRIMARY STANDARDS"

A1 INTRODUCTION

A1.1 Objective

The objective of the 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" ozone 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 in some cases traceability may be achieved through reference to a primary standard held in other counties.

Therefore, as summarised above there are a number of means by which a national standard can be maintained. The objective of the project is therefore to determine the international comparability of the national standard as it is currently disseminated in that country as a means of establishing the overall measurement uncertainty of the primary standard as realised.

A1.2 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.ch). 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.

A1.3 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 has been selected from which that 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 sends (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).

A2 COMPARISON PROTOCOL

A2.1 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 0 ppb 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 the NPL or PTB facilities.

A2.2 PRE-COMPARISON MEASUREMENTS

A2.2.1 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.

A2.2.2 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.

A2.2.3 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.

A2.2.4 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.

A2.2.5 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.

A2.3 COMPARISON PROCEDURE

The comparability of the primary ozone photometers will be determined using 10 points in the range of 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 the photometers 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 ten points in the nominal range zero ppb 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.

A2.4 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.

A2.5 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.

A2.6 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 should be 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 will be invited to check their results for numerical errors but without being informed as to the magnitude or the sign of the apparent anomaly. If no numerical error is found the submitted result will be retained and the complete set of results will be 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 the participants or on the basis of a clear failure of the travelling standard or some other phenomenon that renders the comparison or some 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, will not be confidential, and it is likely be the subject of a publication in the scientific literature.

APPENDIX 3

DETAILED COMPARISON RESULTS

Data include 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 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 [ppb]

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

CHMI (CZ) 29/09/00

	zero	span
PTB correction	0.2	1.0101
lab correction	1.5	1.012

summary data

	lab standard				transfer 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 (DK) 24/10/2000

summary data

	lab standard				transfer 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

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	value	std_error
slope	0.985	0.001
offset	-0.897	0.373

FMI (FI) 31/10/00

summary data

	lab standard				transfer 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

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	value	std_error
slope	0.997	0.000
offset	0.473	0.092

IEP (HU) 06/10/00

summary data

PTB correction 0.2 1.0101
lab correction 0 1

	lab standard				transfer 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 (S) 28/10/00

summary data

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	lab standard				transfer 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 (N) 26/10/00

summary data

	lab standard				transfer standard		
	mean	std	%std		mean	std	%std
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

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	value	std_error
slope	1.008	0.002
offset	-0.002	0.543

SHMI (SK) 4/10/00

summary data

	lab standard				transfer standard		
	mean	std	%std		mean	std	%std
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

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

	value	std_error
slope	0.991	0.002
offset	-6.409	0.593

UBA (A) 02/10/00

summary data

	lab standard				transfer standard		
	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

	zero	span
PTB correction	0.2	1.0101
lab correction	-0.03	0.987

(SRP#15, EMPA, 19.12.2000)

UBA (D) 04/10/00

summary data

	lab standard				transfer standard		
	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

	zero	span
PTB correction	0.2	1.0101
lab correction	0	1

IRCEL (B) 07/03/00

summary data

	lab standard				transfer 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

	zero	span
NPL correction	0.5	0.9862
lab correction	0	1

	value	std_error
slope	0.988	0.001
offset	-0.079	0.244

ISCIII (ES) 28/03/00

summary data

	lab standard				transfer 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

	zero	span
NPL correction	0.8	0.9852
lab correction	0	1

	value	std_error
slope	0.989	0.001
offset	-0.134	0.156

JRC ISPRA (EU) 31/03/00

summary data

									zero	span
								NPL correction	0	0.9852
								Lab correction	0	1
	lab standard				travelling standard					
	mean	std	%std		mean	std	%std		U/c (ppb)*	
1	249	1	0		250	1	0		2.5	
2	100	1	1		100	1	1		1.7	
3	60	1	1		60	0	1		2.1	
4	199	0	0		200	0	0		1.9	
5	0	1	134		0	0	-310		3.0	
6	399	1	0		400	1	0		5.0	
7	30	1	2		30	1	2		2.5	
8	150	1	0		150	1	0		1.6	
9	499	1	0		502	1	0		6.7	
10	300		0		301	1	0		3.3	

	value	std_error
slope	0.9964	0.0008
offset	0.0474	0.214

*uncertainty (u/c) data sent by JRC Ispra 4/4/00

LNE (F) 06/06/00

summary data

								zero	span
							NPL correction	1.2	0.9794
							lab correction	0	1
	lab standard				transfer standard				
	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 (CH) 04/04/00

summary data

	lab standard			transfer 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

	zero	span
NPL correction	0.2	0.9852
lab correction	0	1

	value	std_error
Slope	0.994	0.000
Offset	0.001	0.099

RIVM (NL) 09/03/00

summary data

	lab standard				transfer 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

	zero	span
NPL correction	0.8	0.9862
lab correction	0	1

	value	std_error
slope	0.981	0.001
offset	0.575	0.184

APPENDIX 4

STANDARD REFERENCE PHOTOMETER RESULTS

A number of intercomparisons were 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 was also returned to NIST USA for recertification within this period and these results are also summarised below.

COMPARISONS BETWEEN SRPS OF PTB AND NPL

(i) February 1998

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

$$[\text{SRP 20}] = 0.995\ [\text{SRP 19}] + 1.0\ [\text{ppb}]$$

(ii) November 1999

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

$$[\text{SRP 20}] = 0.994\ [\text{SRP 19}] + 0.6\ [\text{ppb}]$$

(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

$$[\text{SRP 20}] = 1.001\ [\text{SRP 19}] - 1.6\ [\text{ppb}]$$

(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

$$[\text{SRP 20}] = 0.994\ [\text{SRP 19}] + 0.4\ [\text{ppb}]$$

(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 maintained a high level of comparability and stability throughout the period of the comparison exercise.

COMPARISONS BETWEEN NPL AND NIST

The NPL instrument was returned to NIST USA for re-certification on two occasions, in December 1998 and September 2000. Data are in the format:

NPL SRP = slope [NIST SRP] + offset [ppb]

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.