

**WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL**

**at the
FEDERAL ENVIRONMENTAL AGENCY
GERMANY**

**EUROPEAN INTERCOMPARISON
WORKSHOP ON
AIR QUALITY MONITORING**

Vol. 5

– MEASURING OF NO, NO₂, SO₂ AND O₃ –

**Hans-Guido Mücke, Manfred Kratz,
Gisbert Sukale and Volker Stummer**

REPORT 15

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**WHO Collaborating Centre
for Air Quality Management and Air Pollution Control
in co-operation with UBA Pilotstation
– Federal Environmental Agency –**

Air Hygiene Report 15

Hans-Guido Mücke*, Manfred Kratz**,
Gisbert Sukale ** and Volker Stummer **

European Intercomparison Workshops on Air Quality Monitoring
Vol. 5
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See also: www.umweltbundesamt.de/whocc/titel/titel21.htm

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PREFACE

The World Health Organization has been concerned with air pollution and its impact on human health for almost 50 years. The WHO/Europe programme on air quality and health contributes to the ongoing struggle to protect health from harm caused by air pollution. As one main product, the WHO Air Quality Guidelines for Europe have provided a uniform basis for the development of strategies for the control of air pollution, and have contributed to the maintenance and improvement of public health in several countries. In providing pollutant levels below which lifetime exposure or exposure for a given averaging time does not constitute a health risk, they form a basis for setting national standards for air pollution.

Further, to assess and evaluate the impacts of air pollution on human health air quality measurements and data must be harmonized to be comparable and applicable e.g. for an international health impact assessment and in an environment and health information system, which covers 51 Member States of the WHO European Region. Acting within the WHO/Europe programme on air quality and health of the WHO European Centre for Environment and Health, Bonn Office, the WHO Collaborating Centre for Air Quality Management and Air Pollution Control - German Federal Environmental Agency (UBA) in Berlin, supports the efforts being made in line with the process of harmonizing air quality measurements by international programmes on quality assurance and control in the WHO European Region. During the past nine years international quality assurance and control actions on air quality monitoring have been implemented by the WHO Collaborating Centre - as reported within the AIR HYGIENE REPORT series. In May 2002, this programme was continued by conducting the eleventh WHO European Intercomparison Workshop on Air Quality Monitoring. This publication is the fifth volume on intercomparisons and reports on the Workshop of May 2002, which focused on the components oxides of nitrogen, sulphur dioxide and ozone (NO, NO₂, SO₂ and O₃).

The Workshop was granted by the German Ministry for the Environment, Nature Conservation and Nuclear Safety, Berlin/Bonn, which is gratefully acknowledged.

WHO Collaborating Centre for
Air Quality Management and Air Pollution Control
Berlin, Germany, May 2003

ABSTRACT

This report presents the results of a WHO European Intercomparison Workshop on Air Quality Monitoring (NO, NO₂, SO₂ and O₃) conducted in May 2002 by the WHO Collaborating Centre for Air Quality Management and Air Pollution Control in co-operation with the national reference laboratory of UBA Pilotstation in Langen, Germany. The Workshop was a contribution to on-going quality assurance and control activities on air quality measurements for Member States of the WHO European Region. Eleven laboratories mainly from Central and Eastern Europe used the opportunity to compare their measurement methods (14 manual methods and 20 monitors) and standards.

Summing up all intercomparison measurements of nitrogen oxides, sulphur dioxide and ozone, one main conclusion is that the different analytical methods applied (manual and automatic techniques) provide suitable and reliable results. Very good results were obtained for NO/NO₂ measurements: more than 90% of the results agreed within a tolerance of +/- 10% and more than 70% within a tolerance of +/- 5%. Furthermore, the intercomparison results showed good agreement for different analytical methods for sulphur dioxide and ozone at both tolerance levels. However, it has been noticed that the participating laboratories systematically recorded lower SO₂ values using automatic methods. No clear reasons were found. Nevertheless, a technical problem of the test gas generating unit cannot be excluded.

Some specific measurement problems were found to be associated with the use of automatic methods, and others for manual methods. Thus, there is a need to routinely continue intercomparisons to check and to verify the causes of problems. It is recommended, that in future intercomparisons, manual methods and monitors should be calibrated and controlled by gaseous transfer standards.

(Key words: Air quality monitoring, quality assurance, quality control, intercomparisons, calibrations)

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1 INTRODUCTION

Former quality assurance activities have shown a questionable comparability of air quality data in Europe, mostly because of important variations due to implemented calibration practices, maintenance and handling of instrumentation. Comparable measurement methods are fundamental for a harmonised air quality assessment.

For several years efforts have been strengthened in the process of harmonising air quality measurements in Europe. Activities were supported and conducted e.g. by the European Reference Laboratory of Air Pollution (ERLAP, Ispra) at the EC Joint Research Centre for Member States of the European Union in line with the Council Directive 96/92/EC on Ambient Air Quality Assessment and Management which sets up a framework for a harmonized air quality assessment in Europe (Borowiak et al. 2000).

Since 1994, the WHO Collaborating Centre for Air Quality Management and Air Pollution Control (WHO CC) - German Federal Environmental Agency (UBA), Berlin, supports the process of harmonizing air quality measurements by international quality assurance and control actions (QA/QC) in the WHO European Region (Mücke et al. 1995, 1996, 1999 and 2000). Such activities form the basis for comparability and facilitate the compatibility of air quality data of country networks within the 51 WHO European Member States in order to assess and to evaluate health impacts of air pollution.

Continuing the series of European Intercomparisons on Air Quality Monitoring, the WHO CC conducted a one week Workshop from 13 to 17 May 2002, which took place at the national reference laboratory for air quality of the German Federal Environmental Agency (UBA Pilotstation, Langen). Laboratories responsible for QA/QC in national and international ambient air quality monitoring networks from Albania, Bulgaria, Croatia, Czech Republic, Estonia, Lithuania, Romania, Russian Federation, Slovenia, Republic of Uzbekistan and Germany were invited with the objective to compare measurements methods and calibration procedures and to assess the repeatability of these measurements (see Annex I). The Workshop focused on such components as oxides of nitrogen, sulphur dioxide and ozone (NO, NO₂, SO₂ and O₃). Test gas mixtures had to be generated continuously during day and night-time. All test gases were dry gases; the relative humidity was below 10%.

The timetable and working programme is given in Annex II. Tables and graphs of the intercomparison measurements are compiled in Annex III.

The report presents and works up the results of the intercomparison measurements of this Workshop. To simplify terminology in this report 'secondary standard calibration gas' is replaced by 'test gas'. The outcome of the intercomparisons are not subject to judgement on the quality of the participants' work. For the evaluation of the results of these intercomparisons the anonymity of the participating laboratories is ensured by using codes.

2 PURPOSE

The purpose of the WHO CC Intercomparison Workshop series on air quality monitoring is to assist and help laboratories to check, compare and improve the quality of their ambient air quality measurements during measuring test periods (so-called runs) for day and night-time. Furthermore, these are good opportunities to compare different kinds of measurement systems, to check calibration procedures and standards and to share acquired experiences and know-how among expert laboratories. The tasks of UBA Pilotstation laboratory, the construction of the sample air manifold as well as the generation procedure of test gas have been comprehensively reported (Mücke et al. 1996). The sample air manifold is appropriate for measurements with automated, semi-automated or manual devices under harmonized conditions. Therefore, it is essential that the expert teams bring their own and complete equipments to UBA Pilotstation, including all devices, reagents, test standards, control and computer systems, which are normally used for routine calibration and measurements. During this Workshop, not all participants could transfer the respective primary calibration standard to UBA Pilotstation. In these cases, the traceability to the primary calibration standard was contrived with a high quality transfer standard.

3 MEASUREMENT METHODS AND DEVICES

Eleven laboratories participated in this Intercomparison Workshop (Annex I). Individual codes were given, because few laboratories applied more than one single measurement method and/or device per component.

Manual Methods

Laboratory A measured NO, NO₂, SO₂ and O₃ with manual spectrophotometric methods (NO/NO₂: modified Griess-Saltzman; SO₂: modified pararosaniline; O₃: neutral kalium iodide), which are national standards.

Laboratory B measured NO₂ and SO₂ with manual spectrophotometric methods (NO₂: modified Griess-Saltzman; SO₂: modified pararosaniline), and O₃ automatically (O₃: Chemiluminescence solid phase, Fa. Optec).

Laboratory C measured NO₂ and SO₂ with manual spectrophotometric methods (NO₂: Saltzman; SO₂: pararosaniline), which are national standards.

Laboratory D measured NO, NO₂, SO₂ and O₃ with manual spectrophotometric methods (NO/NO₂: Modified Saltzman; SO₂: Thorin).

Laboratory E measured NO, NO₂, SO₂ and O₃ with manual spectrophotometric methods (NO/NO₂: Griess-Saltzman; SO₂: TCM pararosaniline; O₃: neutral kalium iodide), which are national standards.

Laboratory UBA (M) measured NO₂ and SO₂ with manual methods (NO₂: Saltzman, VDI 2453-1; SO₂: TCM method, VDI 2451-3).

Automatic Methods

Laboratory F measured NO, NO₂, SO₂ and O₃ with automatic methods (NO/NO₂: Chemiluminescence, Fa. Monitor Labs MLU 200A; SO₂: UV Fluorescence, Fa. Monitor Labs MLU 100A; O₃: UV Absorption, Fa. Monitor Labs MLU 400).

Laboratory G measured NO, NO₂, SO₂ and O₃ with automatic methods (NO/NO₂: Chemiluminescence, Fa. Environment AC 31M; SO₂: UV Fluorescence, Fa. Environment AC 21M; O₃: UV Photometry, Fa. Environment S.A. AC 41M), which are the national reference methods.

Laboratory H measured NO, NO₂, SO₂ and O₃ with automatic methods (NO/NO₂: Chemiluminescence, Fa. Horiba APNA 360CE; SO₂: UV Fluorescence, Fa. Horiba APSA 360CE; O₃: UV Absorption, Fa. Horiba APOA 360CE).

Laboratory J measured NO, NO₂, SO₂ and O₃ with automatic methods (NO/NO₂: Chemiluminescence, Fa. Horiba APNA 360CE; SO₂: UV Fluorescence, Fa. Horiba APSA 350E; O₃: UV Absorption, Fa. Horiba APOA 350E).

Laboratory K measured NO, NO₂, SO₂ and O₃ with automatic methods (NO/NO₂: Chemiluminescence, Fa. Environnement S.A. AC 30M; SO₂: UV Fluorescence, Fa. Environnement S.A. AC 21M; O₃: UV Photometry, Fa. Environnement S.A. AC 43M).

Laboratory L measured SO₂ automatically (UV Fluorescence; Fa. Horiba APSA-350E).

Laboratory UBA (A) measured NO, NO₂, SO₂ and O₃ with automatic methods (NO/NO₂: Chemiluminescence, Fa. Horiba APNA 360; SO₂: UV Fluorescence, Fa. Horiba APSA 360; O₃: UV Absorption, Fa. Thermo Electron 49C).

4 METHODS OF EVALUATION

Measurement results are given in volume to volume ratios, as parts per billion (ppb). They can be converted into accurate SI-units if temperature and air pressure are defined. The following table shows volume to volume conversions into SI-units ($\mu\text{g}/\text{m}^3$) at defined temperatures and at a constant air pressure of 101.3 kPa.

Table 1: Conversion factors for NO, NO₂, SO₂ and O₃

	0° C	20° C	25° C
NO	1.34	1.25	1.23
NO ₂	2.05	1.91	1.88
SO ₂	2.86	2.66	2.58
O ₃	2.14	2.00	1.96

- Daytime Samplings

In the tables of Annex III each result represents a 30 minute mean value (**columns 1 to 4**) of each participating unit (column with laboratory **code**). Column **stdev** is the calculated standard deviation, **average** shows the calculated average of each unit, while **xAv** is the average of participating laboratory averages. Column **av+st** presents the average plus the standard deviation, and **av-st** shows the average minus the standard deviation. Column **n** presents the number of values, column **T%** presents the percentage deviation of the target value (target value = 100%). The definition of the target value is given in chapter 5. Finally, the **Median** of all 30 minute mean values is given.

The results are also shown in form of error bar charts. For each participating laboratory the measurement averages are depicted together with the standard deviation (**av+st**; **av-st**) in one error bar chart (black dots represent manual methods, white ones automatic methods). There are three lines running parallel to the abscisse. The bold line represents the target value, whereas the two dotted lines mark the +/-10% tolerance from the target value.

- Night-time Samplings

Tables and graphs for each night-time sampling are also presented in a comprehensive form in Annex III.

In these tables each result represents the mean value of each laboratory (**Codes**) and for each run (**Runs**) per test gas concentration. The first column gives the **Target Value** for each run.

The results are also shown in form of bar charts, one bar for each laboratory per run and each group of bars corresponds to a set of runs (a, b, c, d) per night. The first column of each bar graph collection depict the target value with a tolerance of +/- 10% from the target value.

5 RESULTS

During the Workshop the volume to volume ratios of the test gases were generated by the UBA Pilotstation laboratory. In order to give a point of reference the results of UBA monitors - UBA (A) were defined and used as the target value in the tables and in the error bar charts of each test gas run. A target value is not necessarily a true value, but it is considered to be the most accurate means for comparison purposes.

To compare the measurements of NO, NO₂, SO₂ and O₃ under laboratory conditions, the working programme offered constant concentration steps for the same period of time (Annex II).

For the intercomparisons of NO, NO₂, SO₂ and O₃ (manual as well as automatic methods) all measuring units were used in daytime samplings. Night-time measurements were performed for NO, NO₂, SO₂ and O₃ by monitors only. The results of all measurements are shown for each run and for each test gas as a table/graph combination (one page per run) in the Annex III. Daytime intercomparison results will be presented in the following.

Nitrogen Monoxide

For two generated NO test gas runs (20 and 200 ppb) altogether 16 intercomparison measurement results were recorded. 94% of these results agreed with the target value within a tolerance of +/- 10%, and 75% agreed within a tolerance of +/- 5%.

Nitrogen Dioxide

For the intercomparison of NO₂ four test gas runs (20, 60, 100 and 250 ppb) were generated. Altogether 44 measurement results were recorded. 95% of these results agreed with the target value within a tolerance of +/- 10%, and 82% agreed within a tolerance of +/- 5%.

Sulphur Dioxide

Four test gas runs (5, 20, 45 and 130 ppb) were generated for the SO₂ intercomparisons. Altogether 44 measurement results were recorded. 61% of these results agreed with the target value within a tolerance of +/- 10%, and 39% agreed within a tolerance of +/- 5%.

Ozone

Also four test gas runs (20, 60, 100 and 200 ppb) were generated for the O₃ intercomparisons. Altogether 32 measurement results were recorded. 66% of these results agreed with the target value within a tolerance of +/- 10%, and 44% agreed within a tolerance of +/- 5%.

Table 2 gives an overview of the percentage of daytime measurements obtained by different analytical methods (automatic and manual techniques) within a tolerance of +/- 5 and +/- 10%.

Table 2: Percentage of Automatic and Manual Daytime Measurements within the Tolerances of +/- 10% and +/- 5%

	<u>Automatic Methods</u>	<u>Manual Methods</u>
NO	100%: n=10	100%: n=6
+/- 10%	90%	100%
+/- 5%	70%	83%
NO₂	100%: n=20	100%: n=24
+/- 10%	95%	96%
+/- 5%	70%	92%
SO₂	100%: n=20	100%: n=24
+/- 10%	50%	71%
+/- 5%	20%	54%
O₃	100%: n=24	100%: n=8
+/- 10%	67%	63%
+/- 5%	42%	50%

To illustrate these results, figures 1 to 4 show the ratio between the value measured by the participating laboratories and the target value given by UBA (A) as point of reference. Therefore, UBA (A) results are not depicted in these figures. The range of +/- 10 % tolerance is indicated by bold lines at 0.90 to 1.10. Additionally, the pattern of the measurement results could give hints on systematical and statistical errors of a measurement technique through various concentration steps for each participating laboratory.

Figure 1: NO Intercomparisons – Ratio of Participant Value to Target Value

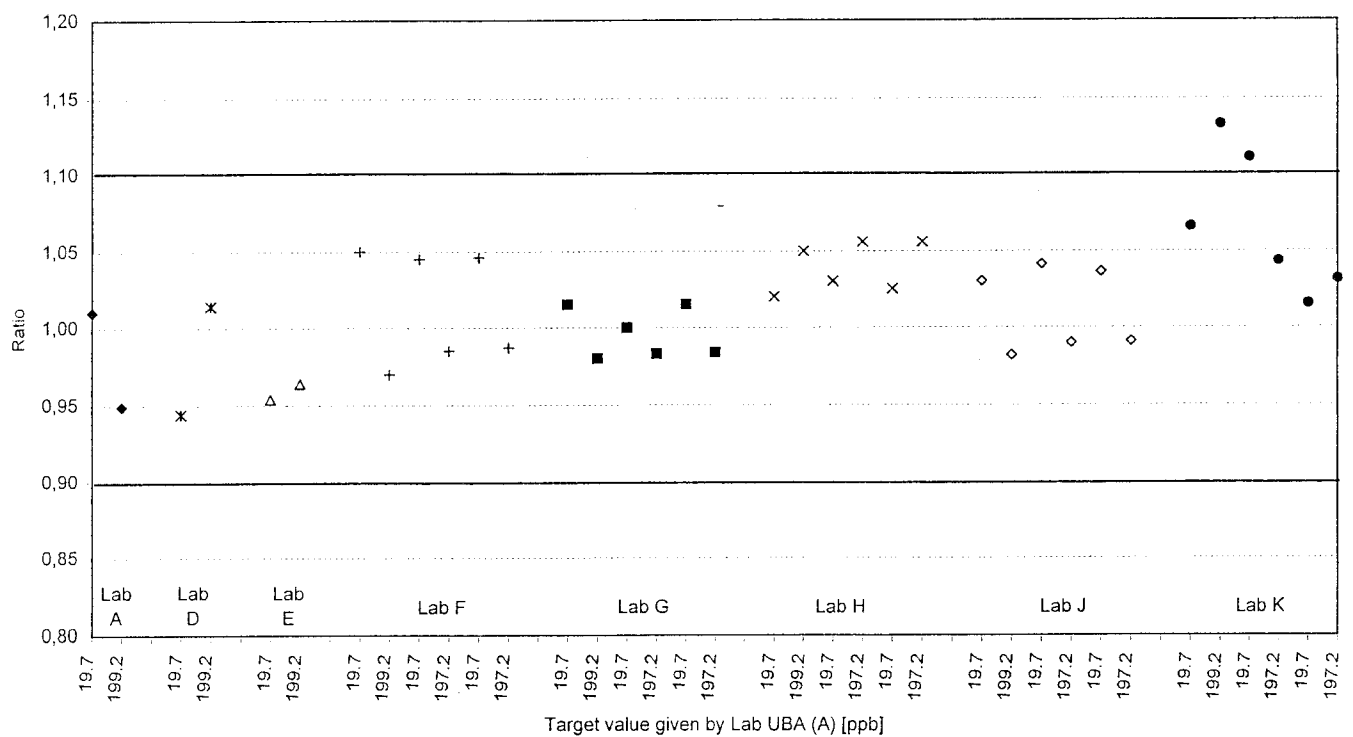


Figure 2: NO₂ Intercomparisons – Ratio of Participant Value to Target Value, manual methods (on top), automatic methods (on bottom)

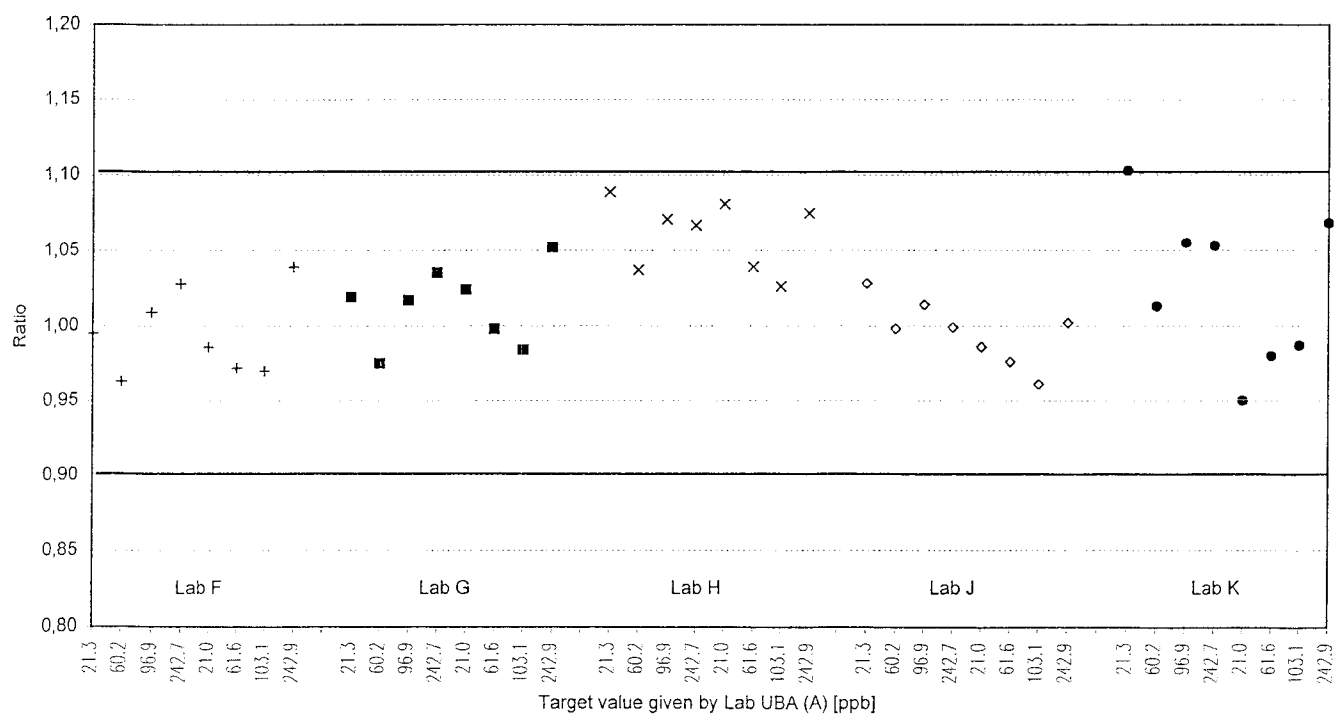
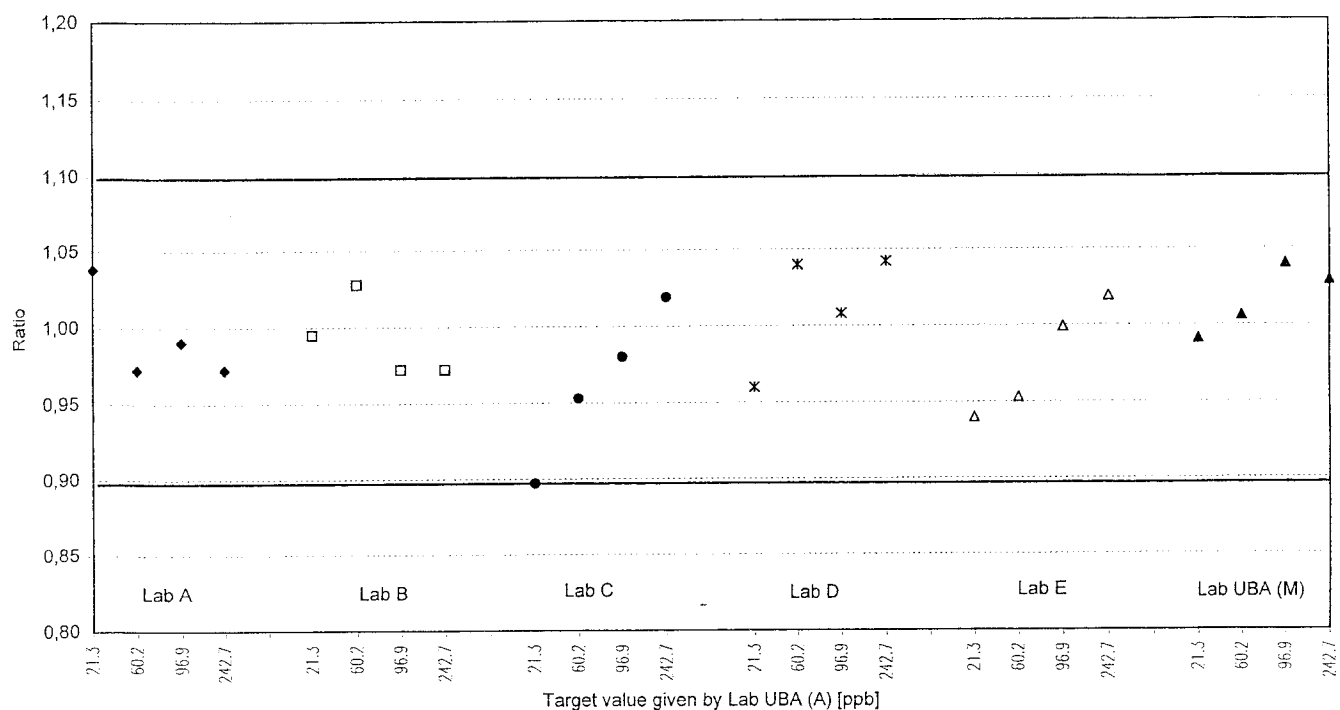


Figure 3: SO₂ Intercomparisons – Ratio of Participant Value to Target Value, manual methods (on top), automatic methods (on bottom)

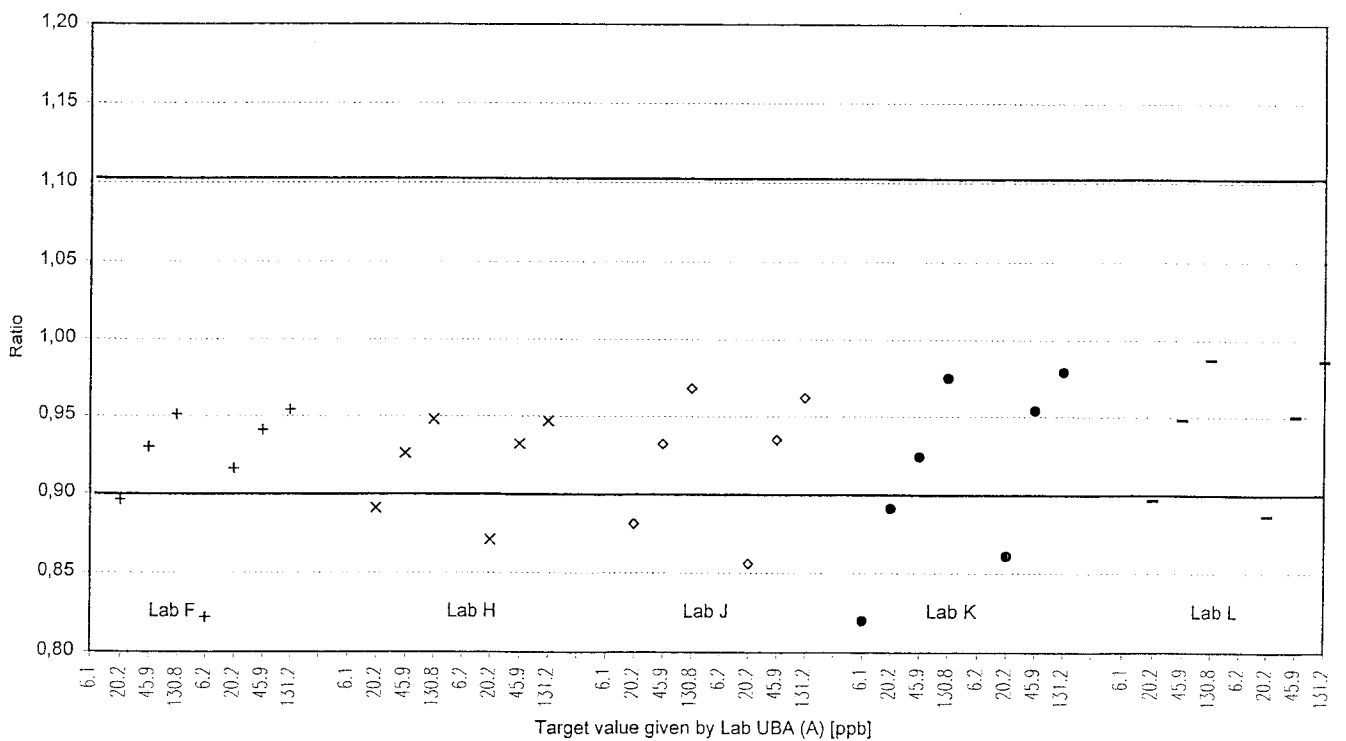
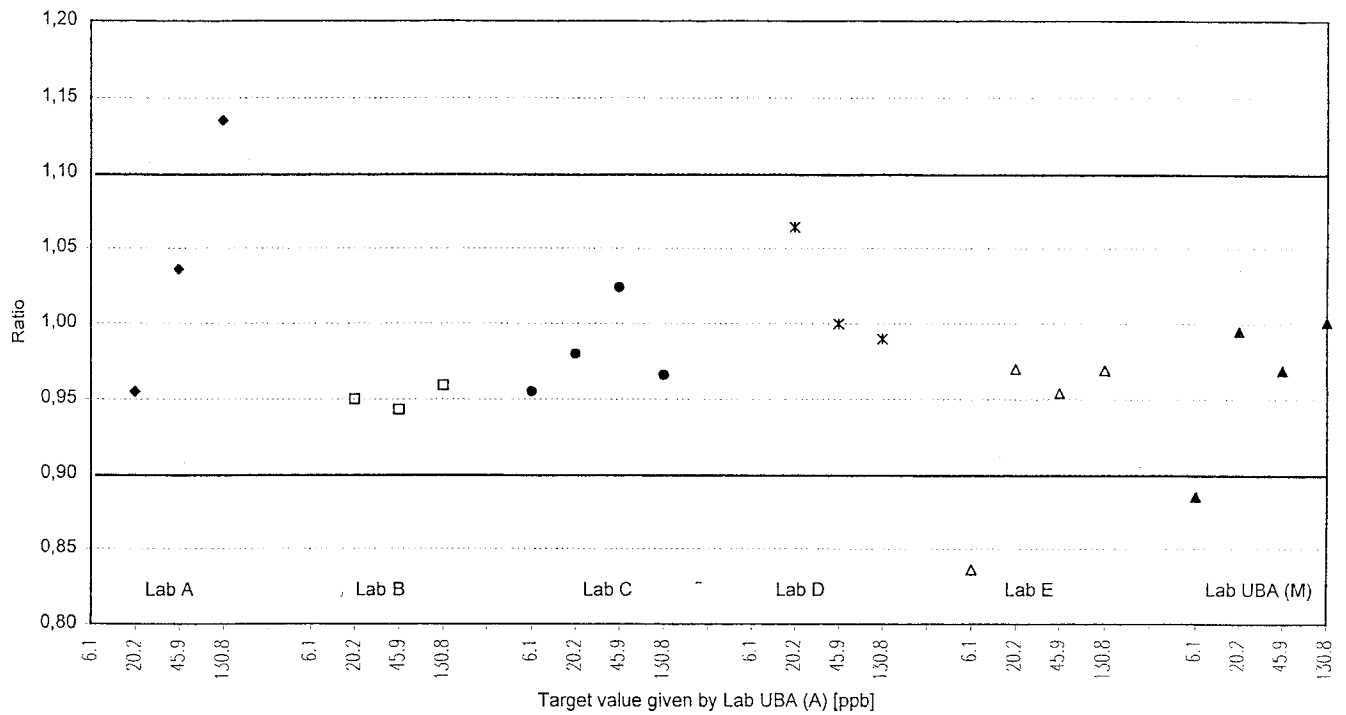
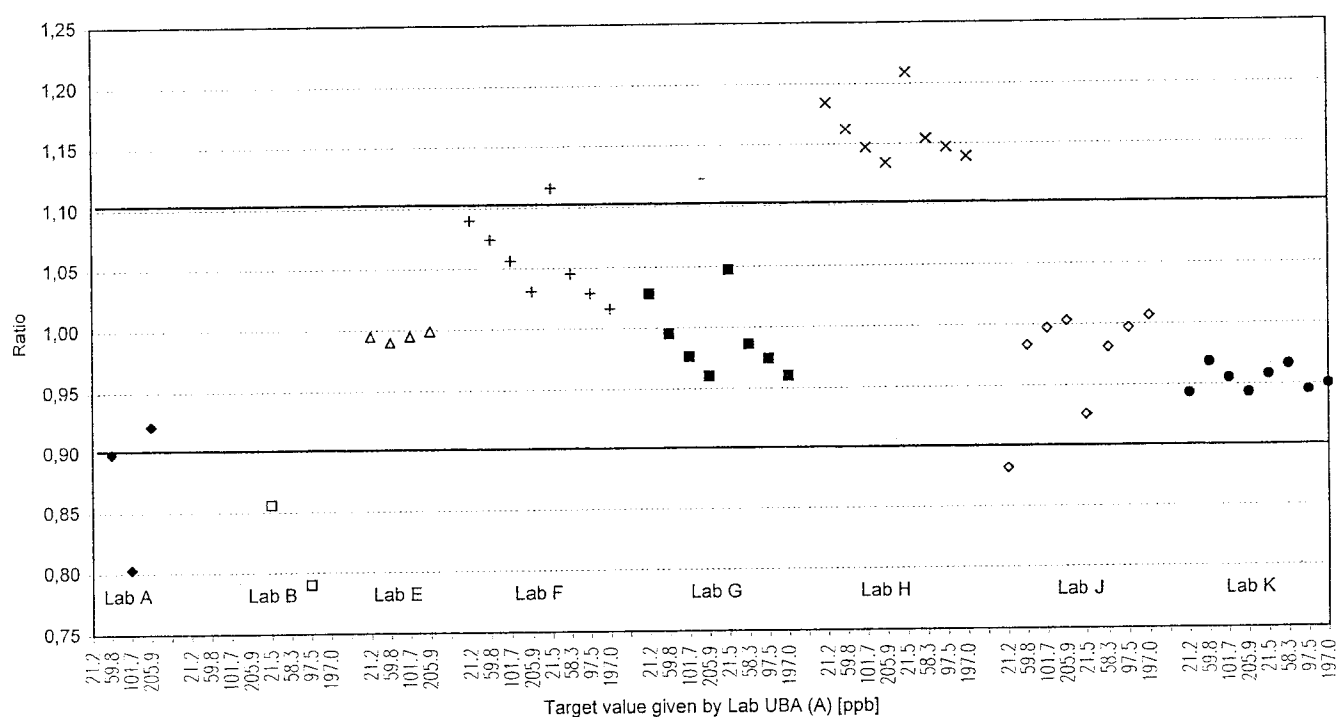


Figure 4: O₃ Intercomparisons – Ratio of Participant Value to Target Value



6 DISCUSSION AND CONCLUSION

Eleven laboratories took the opportunity to compare their measuring methods and equipment during the WHO European Intercomparison Workshop on Air Quality Monitoring (NO, NO₂, SO₂ and O₃) conducted in May 2002 at the UBA Pilotstation laboratory in Langen, Germany. The revised and updated WHO Air Quality Guidelines for Europe (WHO 2000) and the recent EC Intercomparison Exercises (Borowiak et al. 2000) oriented the steps to generate concentration levels.

The results of the nitrogen monoxide (NO) intercomparison measurements showed very good agreement for the different analytical methods (automatic and manual) employed during the Workshop. Nevertheless, some systematic deviations of measurement results were observed. Individual systematic performance of monitors is often observed, especially at different concentration levels. Many of the applied monitors are commonly used and have been tested. They have shown linear calibration curves (+/- 2%) over the whole range. Measurements close to the detection limit lead sometimes to non-linearity.

Specific problems occurred during NO test gas runs at the NO_x monitor of laboratory K. Transportation was identified as being responsible for unstable measurements which resulted in systematically higher results. The monitor was checked and re-calibrated, but some problems remained unsolved.

Comparing the results of these and the previous intercomparisons, the important conclusion that can be drawn is that measurements of nitrogen monoxide for both automatic and manual methods have improved and became more reliable over the last years.

The nitrogen dioxide (NO₂) intercomparisons of automatic and manual methods showed satisfactory results. Historically, NO₂ is the most difficult compound to measure. Different calibration methods are available and implemented when performing automatic measurements. The converter efficiency can cause additional problems. Individual systematic performance of NO₂ monitors was observed again during various concentration steps. As described above, the monitoring unit of laboratory K identified certain problems, which influenced the NO₂ intercomparison measurements too.

As observed in previous Intercomparison Workshops uncertainties and problems were recognised at low concentrations (~ 10 to 20 ppb) for manual methods in particular. Some of the applied manual methods for NO₂ are defined for a sampling time up to 24 hours (e.g. laboratory C). For such methods, the flowrate

and the concentration of the reagent might be too low for the measurement duration of 30 minutes.

In addition to the described individual problems, the comparison of results obtained by different analytical methods during this workshop showed a very good agreement. One main conclusion is that the results of nitrogen dioxide intercomparison measurements for both automatic and manual methods have improved over the last years. Most of the methods could show their suitability and reliability for measuring NO₂ concentrations. However, from the described impediments for measurements at particularly low concentrations it can be concluded that there is still a need for further intercomparisons to check and to improve the reliability of manual NO₂ measurement methods.

The results of the sulphur dioxide (SO₂) intercomparison measurements showed a different picture. Considering that SO₂ measurements have been undertaken since many years, which provided experts a lot of experience with these measurements it is surprising that the agreement between these results is not as good as those of NO₂. On the one hand, problems occurred in general especially during measurements of low concentrations (step 6 ppb) at both automatic and manual methods. Furthermore specific technical problems occurred, e.g. laboratory A identified problems within all SO₂ measurements, which was caused by an increasing flow rate of the aspirator. On the other hand, another problem was identified during the test gas runs of 6 and 20 ppb (runs 12 and 13). The results of laboratories B, E, UBA (M), F, H, J, K and L are in good accordance and vary in comparison to each other within the range of +/- 10%, but they measured systematically lower concentrations compared to the given target value of UBA (A). No clear reasons were identified for this phenomenon, a technical problem or/and an offset at the SO₂ monitor of UBA (A) can not be excluded. This example showed once again that during an Intercomparison Workshop technical problems can occur, even at the test gas generating laboratory unit. As mentioned earlier in the previous chapter, the given target value is not necessarily to be seen as the 'true' value. From the described results the conclusion can be drawn that there is still a need for further intercomparisons to check and improve the reliability of SO₂ measurements, especially at low concentrations.

The intercomparison measurements of ozone (O₃) showed partly satisfactory results. Most measurements of laboratories E, F, G, J and K range within the tolerance of +/- 10%. Automatic methods recorded small drifts in their monitors,

and laboratory F identified an offset, which was probably due to interferences e.g. with vapour, organic compounds or even mercury in the zero filter.

Some problems were evident for laboratories A, B and H. Again, laboratory A found an increasing flow rate of the aspirator, which influenced all O₃ measurements too. Laboratory B used the Workshop as an opportunity to test a recently developed automatic device, which was at this stage obviously not appropriate to measure reliable results. After returning back home, laboratory H observed that they measured O₃ with an offset of ~ 12% compared to their primary standard, which was explained as an influence of transportation. A continuation of quality assurance and control activities to check the suitability of O₃ measurement methods to obtain reliable ozone data is necessary for the future.

As an overall conclusion, it can be stated that this workshop produced satisfactory results, even no WHO intercomparisons took place for two years. All monitors were well checked and maintained during the workshop. Decisive technical differences between the applied methods were only occasionally obtained. However, none of the used manual or automated measurement methods could however claim to measure the "true" value. Furthermore, one must keep in mind that intercomparison tests can only record a momentary measuring situation under laboratory conditions. This and the negative impacts resulting from the transport of equipment and devices has to be taken into account when intercomparisons are evaluated.

A continuous necessity of further intercomparisons was recognized, especially when measuring low concentrations in ambient air. Concerning the data quality objectives and compilation of results of air quality assessment it has to be considered that intercomparisons regard only one part of the Council Directive 1999/30/EC provisions. Annex VIII of this Directive sets the required total accuracy for continuous air quality measurements (SO₂, NO₂ and NO_x) to 15%. Under routine operations more sources of uncertainty such as ambient air conditions, sampling, drift and maintenance status will probably give a higher deviation than the reported intercomparison results.

The WHO Intercomparison Workshop Series on Air Quality Monitoring (Measuring of NO, NO₂, SO₂ and O₃) is to be seen as an important step to improved quality assurance and control measures to provide reliable data for health impact assessment in the WHO European Region. Therefore, the WHO Regional Office for Europe highly recommends the Member States to take into account the benefit of such Workshop experiences and results, and to transfer it to their air quality monitoring networks measuring concentrations with automated and/or manual methods at the national, regional and local level.

Recently the WHO Regional Office for Europe and the European Commission strengthened their intention to intensify the cooperation in the broad field of environment and health. Because of the increasing number of EU Member States, which are actually already Member States of the WHO European Region, the EC JRC-European Reference Laboratory of Air Pollution (ERLAP, Ispra) and the WHO Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin, are discussing on the practical level to harmonize in the future their quality assurance and control activities on air quality monitoring, such as joint intercomparisons.

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ANNEX I

LIST OF PARTICIPATING LABORATORIES

LIST OF PARTICIPATING LABORATORIES

Institute of Hydrometeorology, Tirana, ALBANIA

National Centre of Hygiene, Medical Ecology and Nutrition, Sofia, BULGARIA

Institute for Medical Research and Occupational Health, Zagreb, CROATIA

National Institute of Public Health, Prague, CZECH REPUBLIC

Estonian Environmental Research Centre, Tallinn, ESTONIA

Federal Environmental Agency - UBA Pilotstation, Langen, GERMANY

Environmental Protection Ministry - Joint Research Centre, Vilnius,
LITHUANIA

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Environmental Agency of Slovenia, Ljubljana, SLOVENIA

Central Asian Research Hydrometeorological Institute, Tashkent,
UZBEKISTAN

ANNEX II

WORKING PROGRAMME

WORKING PROGRAMME

Sunday - 12 May 2002

13:00 - 15:00	Registration at the Workshop Office
15:00 - 18:00	Installation of devices at the laboratories

Monday - 13 May 2002

08:45 - 09:00	Calibrations, checks, etc.
09:00 - 11:30	Test gas 1 – NO Zero gas
11:45 - 13:15	Test gas 2 – NO 20 ppb
12:00 - 13:00	<i>Lunchtime</i>
13:30 - 15:00	Test gas 3 – NO 200 ppb
15:30 -	Test gas 4 – NO, overnight measurement

Tuesday – 14 May 2002

08:45 - 09:00	Evaluation
08:45 - 09:45	Test gas 5 – NO ₂ Zero gas
10:00 - 11:30	Test gas 6 – NO ₂ 20 ppb
11:45 - 13:15	Test gas 7 – NO ₂ 60 ppb
12:00 - 13:00	<i>Lunchtime</i>
13:30 - 15:00	Test gas 8 – NO ₂ 100 ppb
15:15 - 16:45	Test gas 9 – NO ₂ 250 ppb
17:00 -	Test gas 10 – NO ₂ , overnight measurement

Wednesday – 15 May 2002

08:45 - 09:00	Evaluation	
08:45 - 09:45	Test gas 11 – SO ₂	Zero gas
10:00 - 11:30	Test gas 12 – SO ₂	5 ppb
11:45 - 13:15	Test gas 13 – SO ₂	20 ppb
12:00 - 13:00	<i>Lunchtime</i>	
13:30 - 15:00	Test gas 14 - SO ₂	45 ppb
15:15 - 16:45	Test gas 15 - SO ₂	130 ppb
17:00 -	Test gas 16 - SO ₂ , overnight measurement	

Thursday - 16 May 2002

08:45 - 09:00	Evaluation	
08:45 - 09:45	Test gas 17 - O ₃	Zero gas
10:00 - 11:30	Test gas 18 - O ₃	20 ppb
11:45 - 13:15	Test gas 19 - O ₃	60 ppb
12:00 - 13:00	<i>Lunchtime</i>	
13:30 - 15:00	Test gas 20 - O ₃	100 ppb
15:15 - 16:45	Test gas 20 - O ₃	300 ppb
17:00 -	Test gas 22 - O ₃ , overnight measurement	

Friday - 17 May 2002

08:45 - 09:00	Evaluation
09:00 - 12:00	Dismantling of the devices or optional Test gas for NO/NO ₂ SO ₂ and/or O ₃ (at disposal for suggestions of the participants)
10:00 - 11:00	Final Discussion
13:00 - 14:00	<i>Lunchtime</i>
14:00 - 15:00	At disposal for suggestions of the participants
15:00	Disassembly and transportation of the devices

ANNEX III

TABLES AND GRAPHS OF THE INTERCOMPARISON MEASUREMENTS (NO, NO₂, SO₂ AND O₃)

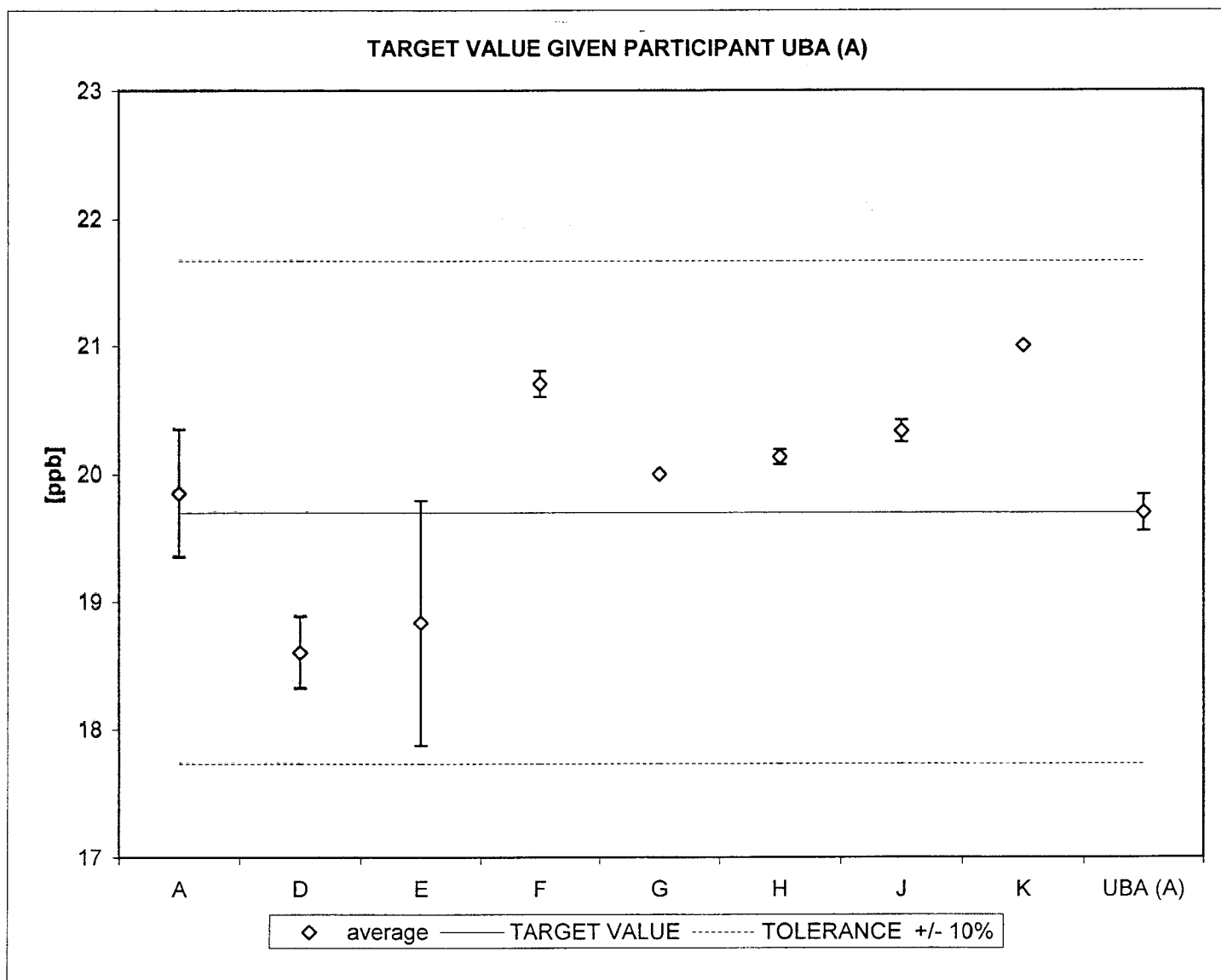
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO Run No.: 2

TARGET VALUE GIVEN PARTICIPANT UBA (A)

19.7 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
	19.5	20.2		A	0.495	19.9	20.3	19.4	2	0.76
18.4	18.8			D	0.283	18.6	18.9	18.3	2	-5.58
19.7	17.8	19.0		E	0.961	18.8	19.8	17.9	3	-4.40
20.8	20.7	20.6		F	0.100	20.7	20.8	20.6	3	5.08
20.0	20.0	20.0		G	0.000	20.0	20.0	20.0	3	1.52
20.2	20.1	20.1		H	0.058	20.1	20.2	20.1	3	2.20
20.3	20.3	20.4		J	0.085	20.3	20.4	20.2	3	3.21
21.0	21.0			K	0.000	21.0	21.0	21.0	2	6.60
19.8	19.6			UBA (A)	0.141	19.7	19.8	19.6	2	0.00
					xAv	19.9	20.1	19.7		
20.1					Median					



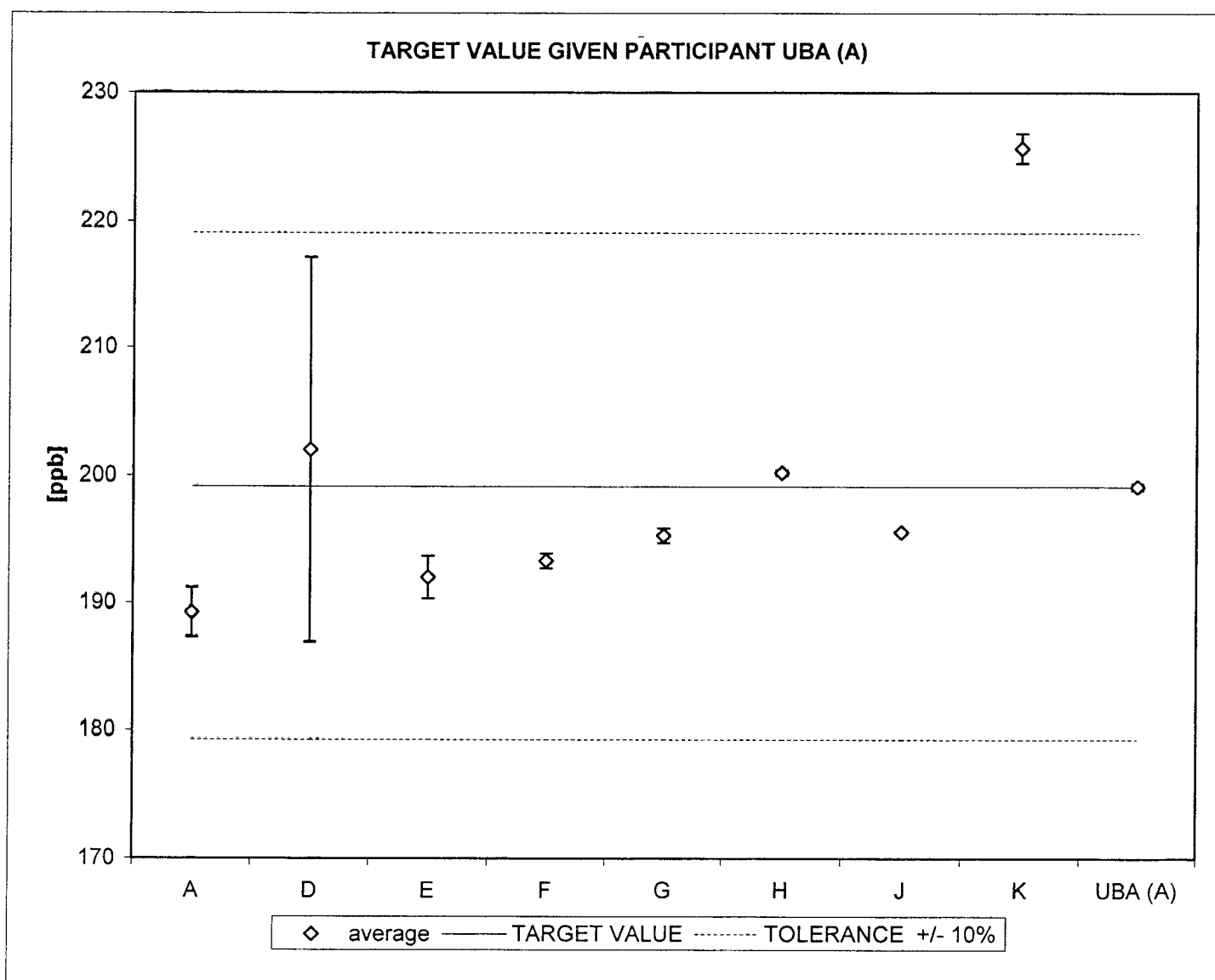
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO Run No.: 3

TARGET VALUE GIVEN PARTICIPANT UBA (A)

199.2 ppb

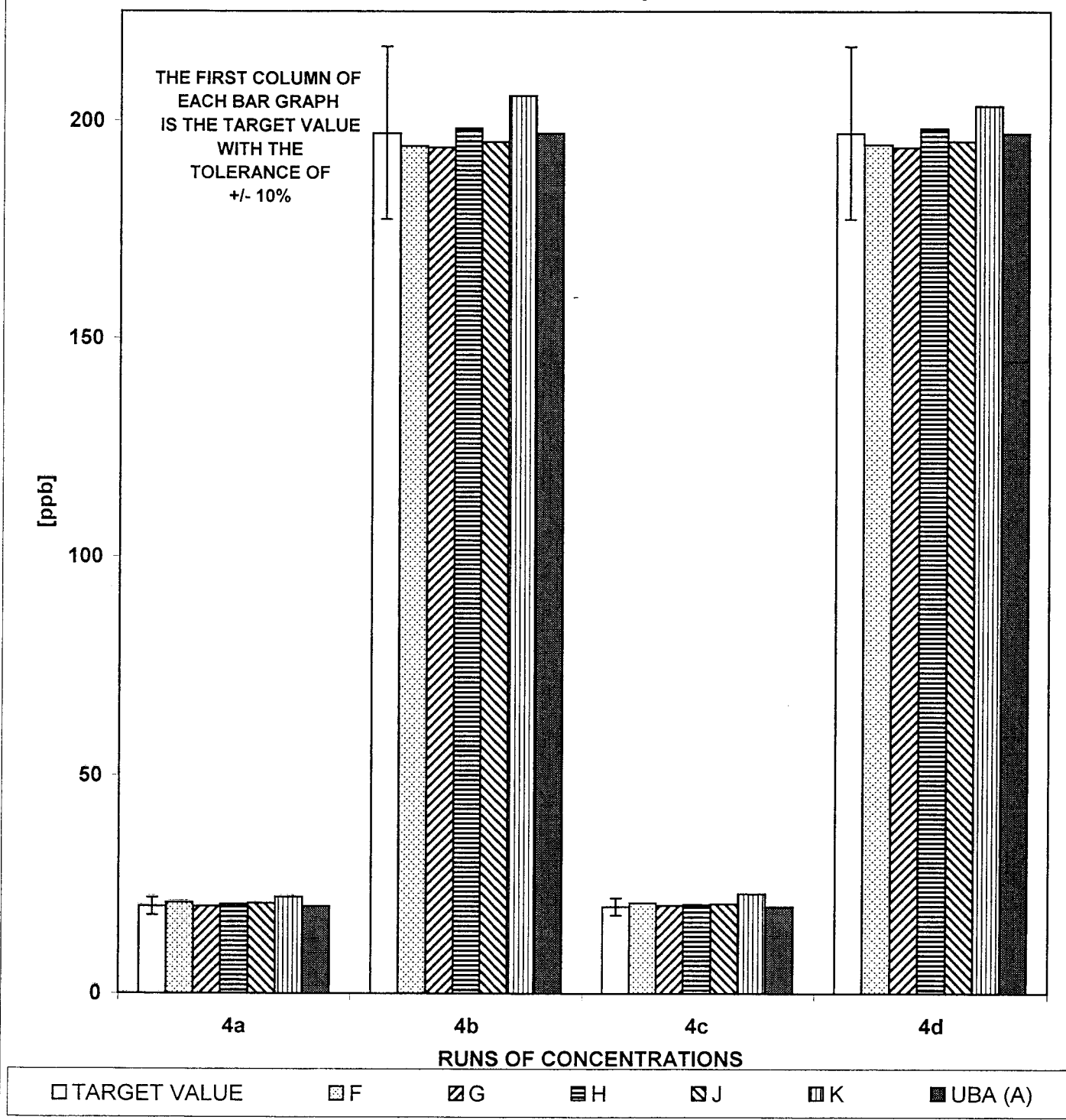
1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
187.0	190.0	190.7		A	1.966	189.2	191.2	187.3	3	-4.99
191.3	212.7			D	15.132	202.0	217.1	186.9	2	1.42
190.1	192.7	193.3		E	1.701	192.0	193.7	190.3	3	-3.58
194.0	193.0	193.0		F	0.577	193.3	193.9	192.8	3	-2.93
195.0	195.0	196.0		G	0.577	195.3	195.9	194.8	3	-1.92
200.0	200.3	200.4		H	0.208	200.2	200.4	200.0	3	0.54
195.7	195.6	195.5		J	0.100	195.6	195.7	195.5	3	-1.79
227.0	225.0	225.0		K	1.155	225.7	226.8	224.5	3	13.31
199.4	198.9	199.2		UBA (A)	0.252	199.2	199.4	198.9	3	0.00
					xAv	199.2	201.6	196.8		
195.6					Median					



NO RUN No.: 4

Runs	TARGET VALUE	F	G	H	J	K	UBA (A)
4a	19.8	20.7	19.8	20.3	20.5	22.0	19.8
4b	197.2	194.3	194.0	198.3	195.3	205.7	197.2
4c	19.7	20.6	20.0	20.2	20.4	22.7	19.7
4d	197.2	194.7	194.0	198.3	195.4	203.4	197.2

OVERNIGHT RUN 13 - 14 May 2002



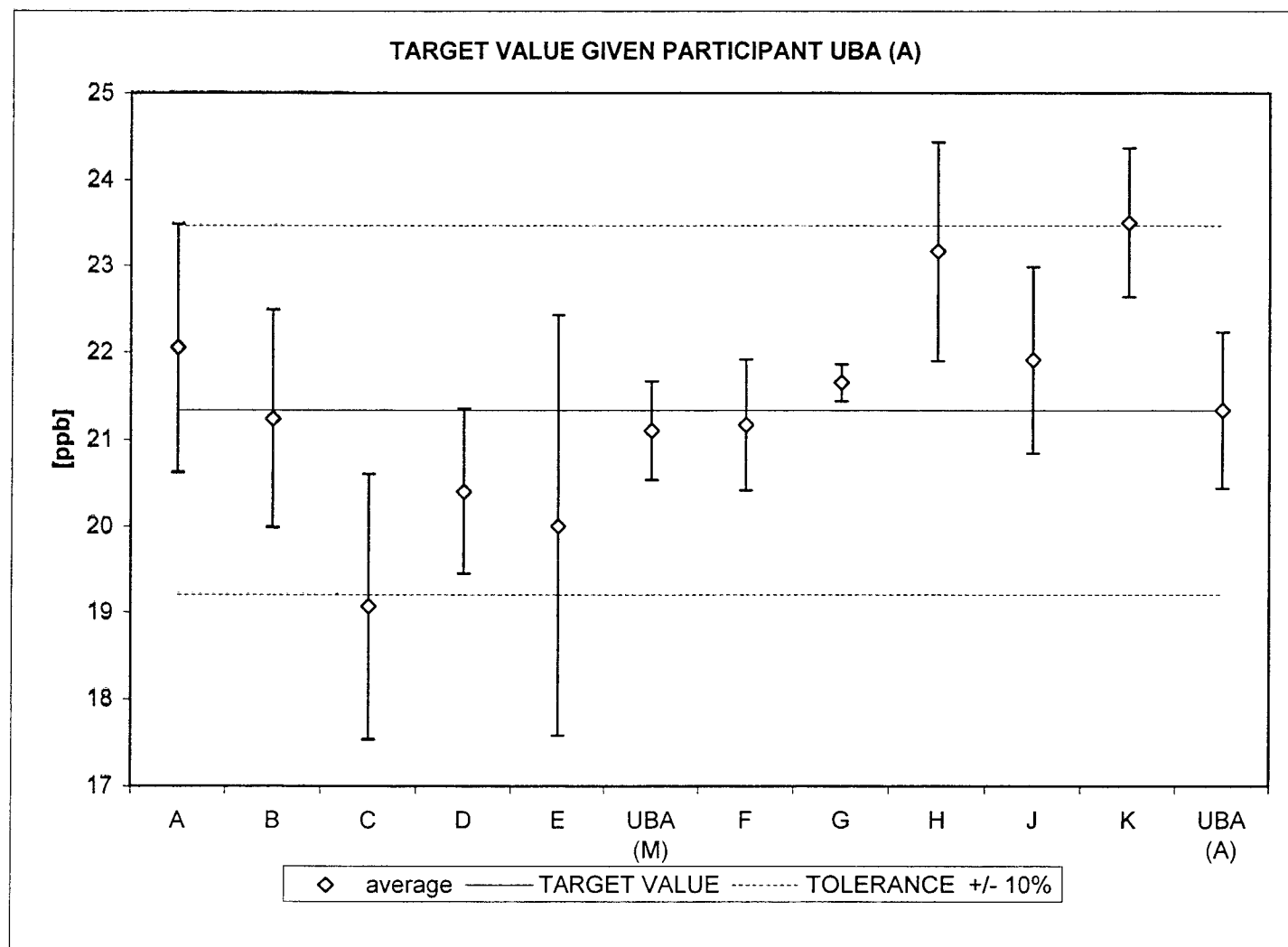
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO₂ Run No.: 6

TARGET VALUE GIVEN PARTICIPANT UBA (A)

21.3 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
20.4	23.2	22.6		A	1.435	22.1	23.5	20.6	3	3.36
21.8	22.1	19.8		B	1.250	21.2	22.5	20.0	3	-0.47
18.5	20.9	17.3	19.7	C	1.536	19.1	20.6	17.5	4	-10.63
21.3	19.4	20.5		D	0.954	20.4	21.4	19.4	3	-4.37
17.4	20.4	22.2		E	2.425	20.0	22.4	17.6	3	-6.25
20.7	21.5			UBA (M)	0.566	21.1	21.7	20.5	2	-1.09
20.3	21.6	21.6		F	0.751	21.2	21.9	20.4	3	-0.78
21.5	21.8			G	0.212	21.7	21.9	21.4	2	1.48
21.7	23.9	23.9		H	1.270	23.2	24.4	21.9	3	8.59
20.7	22.4	22.6		J	1.069	21.9	23.0	20.8	3	2.70
22.5	24.0	24.0		K	0.866	23.5	24.4	22.6	3	10.16
20.3	21.8	21.9		UBA (A)	0.896	21.3	22.2	20.4	3	0.00
					xAv	21.4	22.5	20.3		
21.6					Median					



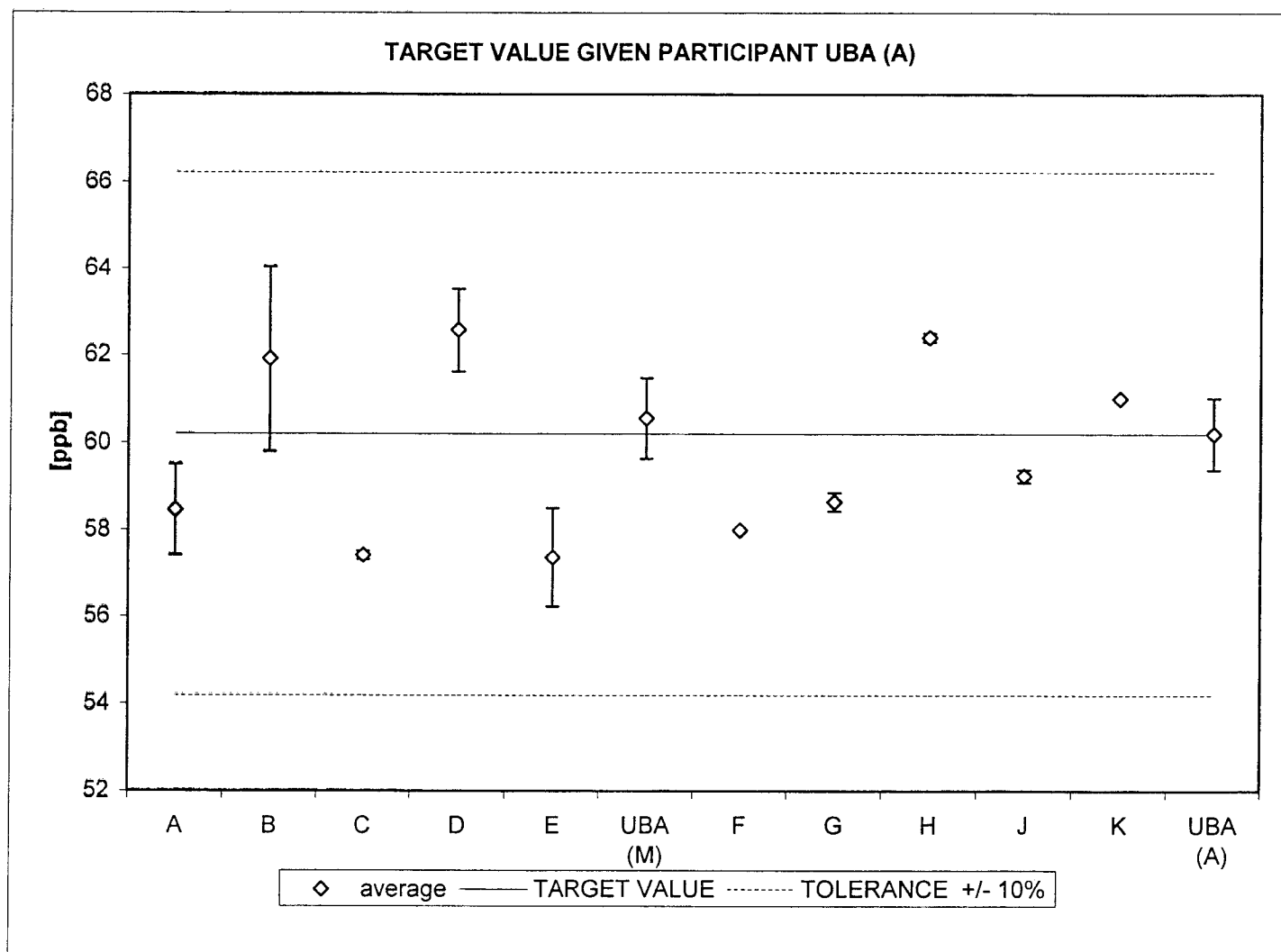
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO₂ Run No.: 7

TARGET VALUE GIVEN PARTICIPANT UBA (A)

60.2 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
58.9	57.3	59.2		A	1.045	58.5	59.5	57.4	3	-2.90
59.7	63.9	62.2		B	2.121	61.9	64.0	59.8	3	2.85
57.5	57.4			C	0.099	57.4	57.5	57.3	2	-4.62
63.5	61.6	62.6		D	0.950	62.6	63.5	61.6	3	3.93
56.1	57.7	58.3		E	1.137	57.4	58.5	56.2	3	-4.71
61.2	59.9			UBA (M)	0.919	60.6	61.5	59.6	2	0.58
58.0	58.0	58.0		F	0.000	58.0	58.0	58.0	3	-3.65
58.5	58.8			G	0.212	58.7	58.9	58.4	2	-2.57
62.3	62.4	62.5		H	0.100	62.4	62.5	62.3	3	3.65
59.4	59.1	59.3		J	0.149	59.2	59.4	59.1	3	-1.59
61.0	61.0	61.0		K	0.000	61.0	61.0	61.0	3	1.33
59.3	60.4	60.9		UBA (A)	0.819	60.2	61.0	59.4	3	0.00
					xAv	59.8	60.4	59.2		
59.4					Median					



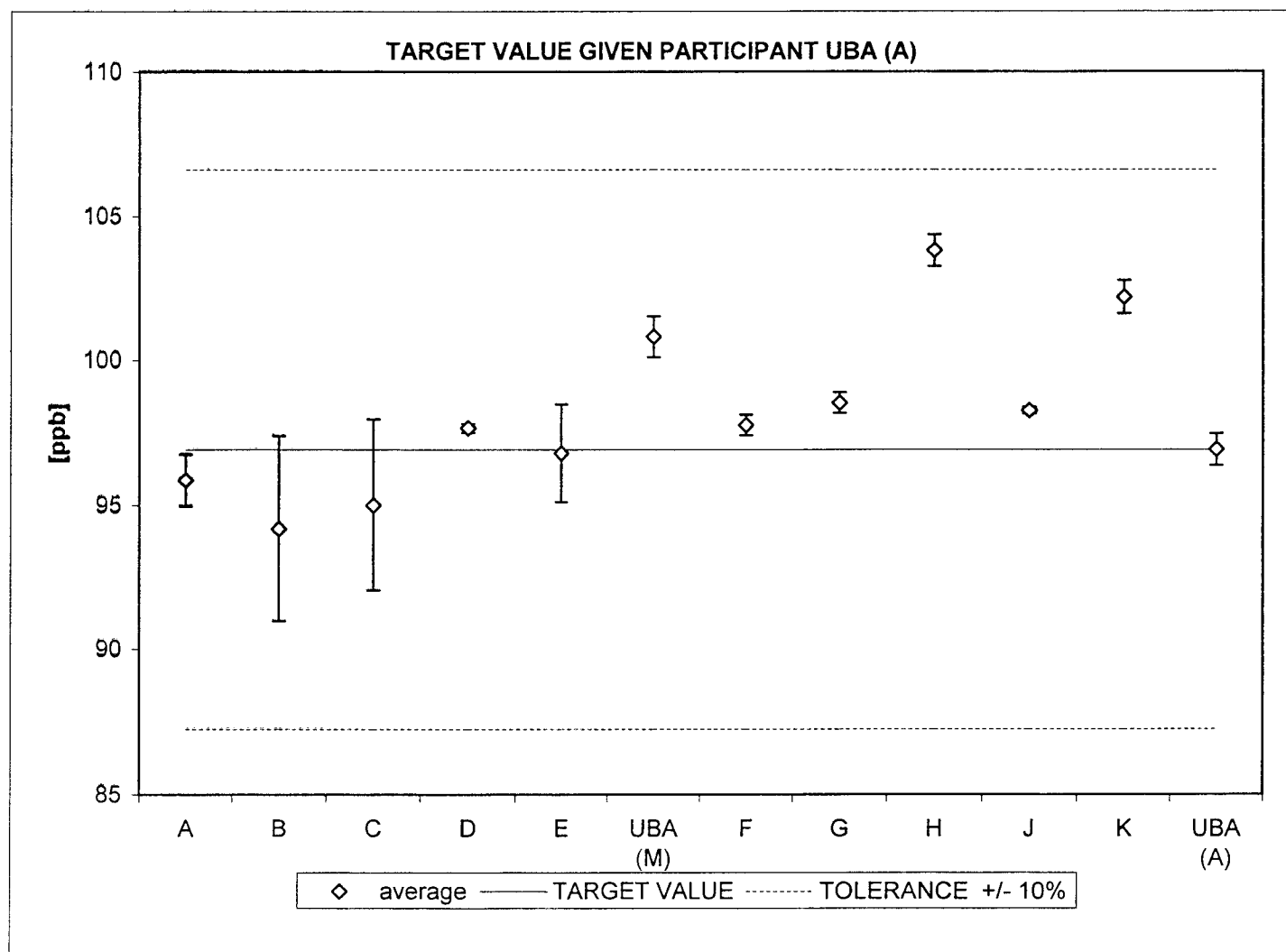
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO₂ Run No.: 8

TARGET VALUE GIVEN PARTICIPANT UBA (A)

96.9 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
96.5	95.2			A	0.891	95.9	96.8	95.0	2	-1.11
91.9	96.5			B	3.224	94.2	97.4	91.0	2	-2.84
97.1	92.9			C	2.963	95.0	98.0	92.0	2	-1.99
97.7	97.8	97.5		D	0.153	97.7	97.8	97.5	3	0.76
94.9	97.4	98.1		E	1.682	96.8	98.5	95.1	3	-0.14
100.3	101.3			UBA (M)	0.707	100.8	101.5	100.1	2	3.99
97.4	97.8	98.1		F	0.351	97.8	98.1	97.4	3	0.86
98.2	98.5	98.9		G	0.351	98.5	98.9	98.2	3	1.65
103.2	103.9	104.3		H	0.557	103.8	104.4	103.2	3	7.08
98.2	98.4	98.2		J	0.119	98.3	98.4	98.2	3	1.38
101.5	102.5	102.5		K	0.577	102.2	102.7	101.6	3	5.40
96.4	96.9	97.5		UBA (A)	0.551	96.9	97.5	96.4	3	0.00
					xAv	98.1	99.2	97.1		
98.0					Median					



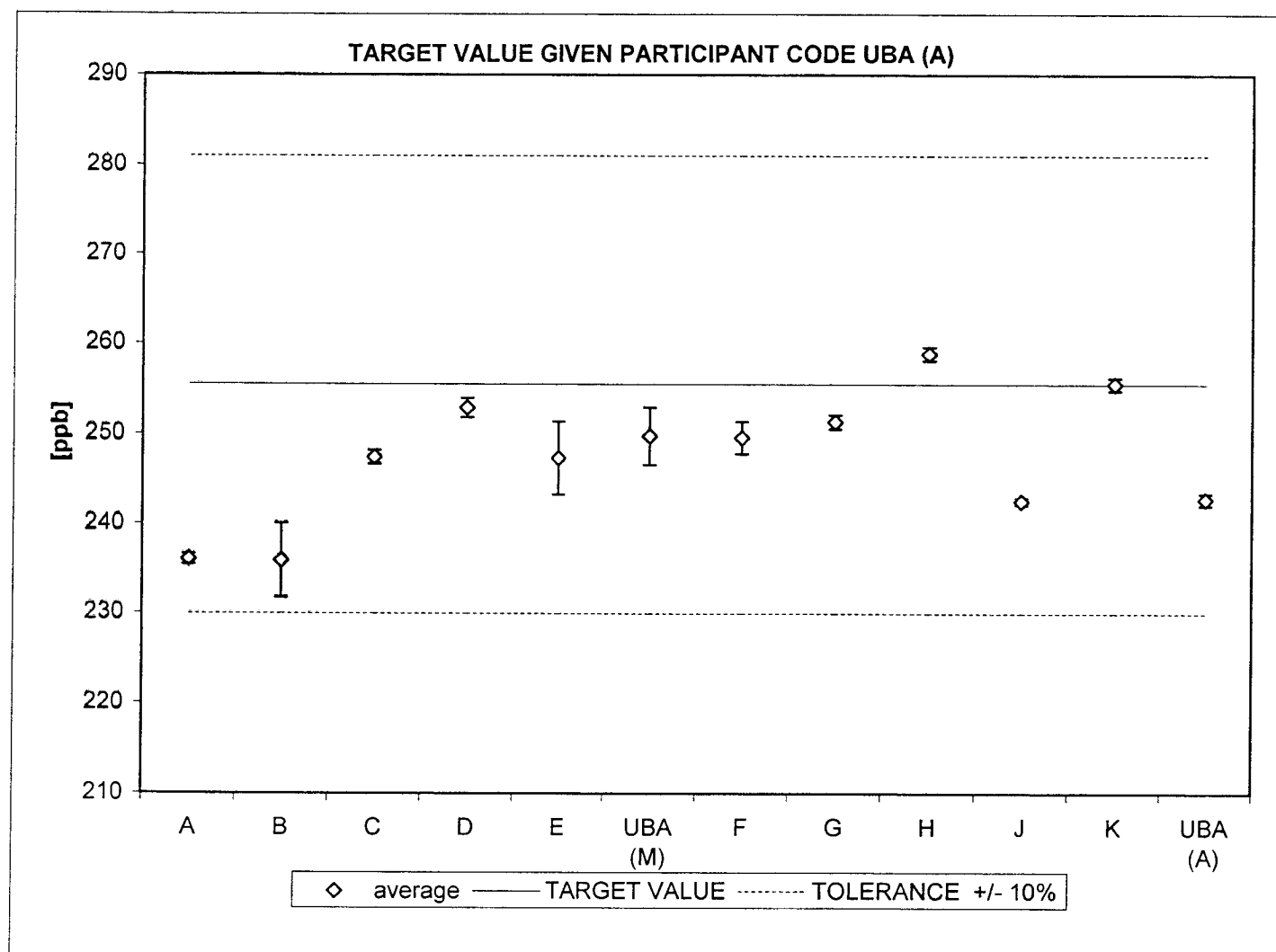
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO₂ Run No.: 9

TARGET VALUE GIVEN PARTICIPANT CODE UBA (A)

242.7 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
235.6	236.4			A	0.573	236.0	236.6	235.4	2	-7.63
238.8	232.9			B	4.172	235.9	240.0	231.7	2	-7.69
246.8	247.9			C	0.764	247.4	248.1	246.6	2	-3.18
253.9	251.8	252.9		D	1.050	252.9	253.9	251.8	3	-1.03
247.2	243.3	251.4		E	4.051	247.3	251.4	243.2	3	-3.21
247.5	252.0			UBA (M)	3.182	249.8	252.9	246.6	2	-2.25
247.5	250.4	250.8		F	1.801	249.6	251.4	247.8	3	-2.32
250.5	251.5	252.0		G	0.764	251.3	252.1	250.6	3	-1.63
258.0	259.2	259.4		H	0.757	258.9	259.6	258.1	3	1.32
242.1	242.6	242.8		J	0.377	242.5	242.9	242.1	3	-5.08
255.0		256.0		K	0.707	255.5	256.2	254.8	2	0.00
242.0	243.0	243.2		UBA (A)	0.643	242.7	243.4	242.1	3	-5.00
					xAv	247.5	249.0	245.9		
247.9					Median					

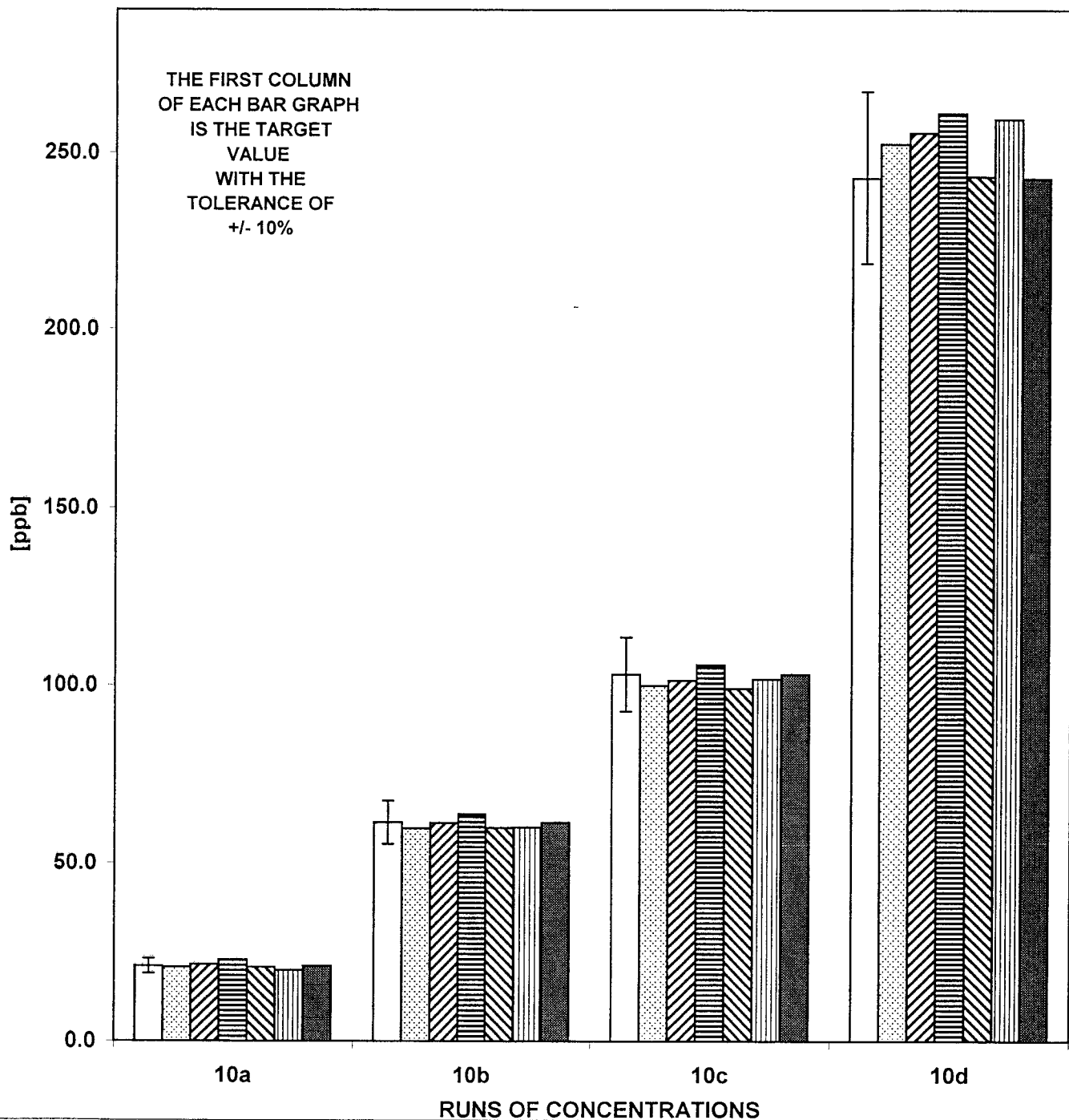


WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

NO₂ RUN No.: 10

Runs	TARGET VALUE	F	G	H	J	K	UBA (A)
10a	21.0	20.7	21.5	22.7	20.7	19.9	21.0
10b	61.6	59.9	61.5	64.0	60.1	60.3	61.6
10c	103.1	100.0	101.4	105.8	99.1	101.8	103.1
10d	242.9	252.5	255.6	261.1	243.4	259.5	242.9

OVERNIGHT RUN 14 - 15 May 2002



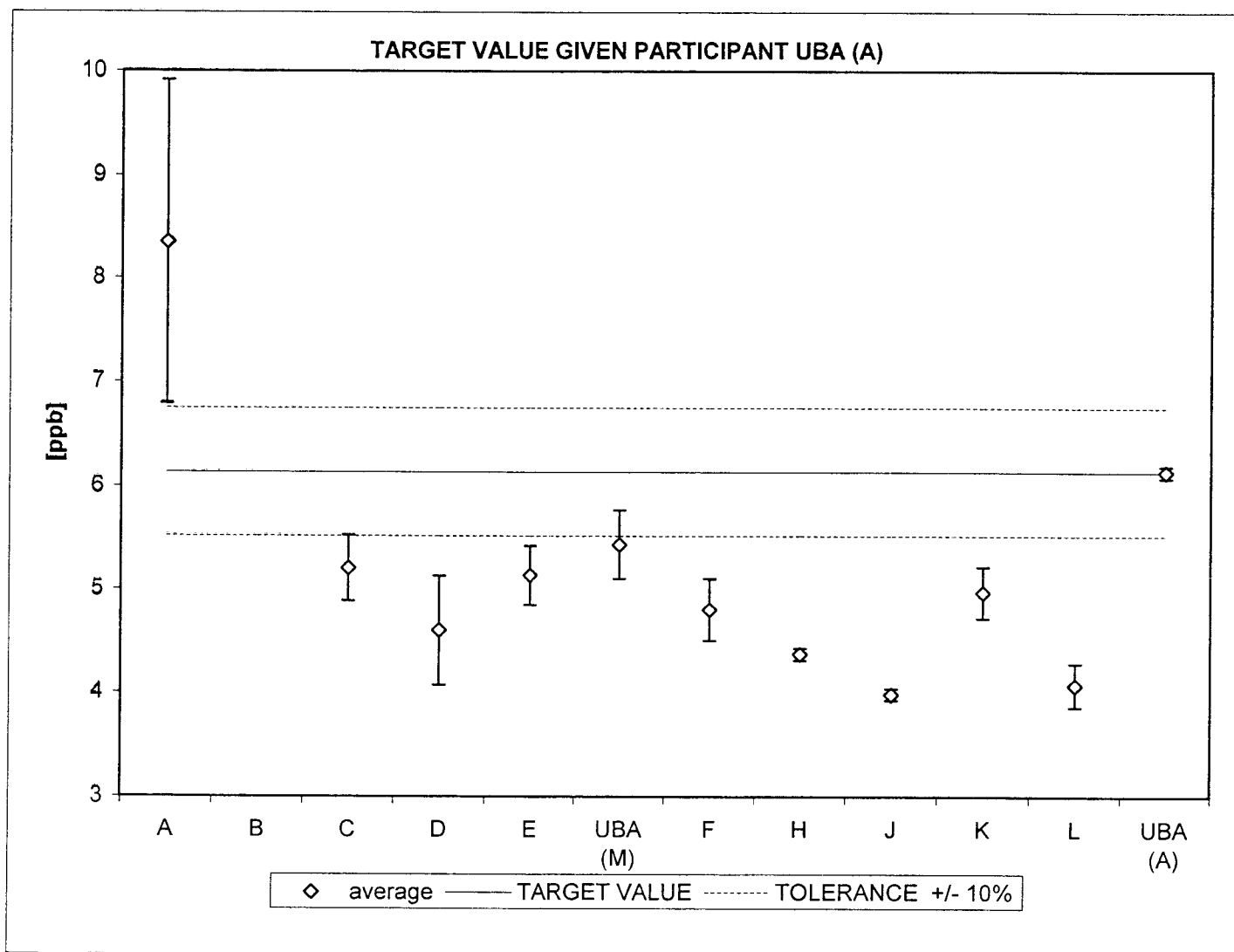
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

SO₂ Run No.: 12

TARGET VALUE GIVEN PARTICIPANT UBA (A)

6.1 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
10.0	6.9	8.2		A	1.563	8.4	9.9	6.8	3	36.14
0.0	0.0	0.0		B	0.000	0.0	0.0	0.0	3	-100.00
5.6	5.4	4.9	4.9	C	0.323	5.2	5.5	4.9	4	-15.14
4.4	5.2	4.2		D	0.529	4.6	5.1	4.1	3	-25.00
4.8	5.3	5.3		E	0.289	5.1	5.4	4.8	3	-16.30
5.2	5.8	5.2		UBA (M)	0.335	5.4	5.8	5.1	3	-11.41
5.1	4.8	4.5		F	0.300	4.8	5.1	4.5	3	-21.74
4.4	4.4	4.3		H	0.058	4.4	4.4	4.3	3	-28.80
3.9	4.0	4.0		J	0.056	4.0	4.0	3.9	3	-35.11
5.2	5.0	4.7		K	0.252	5.0	5.2	4.7	3	-19.02
4.3	3.9	4.0		L	0.208	4.1	4.3	3.9	3	-33.70
6.1	6.2	6.1		UBA (A)	0.058	6.1	6.2	6.1	3	0.00
					xAv	4.8	5.1	4.4		
4.9					Median					



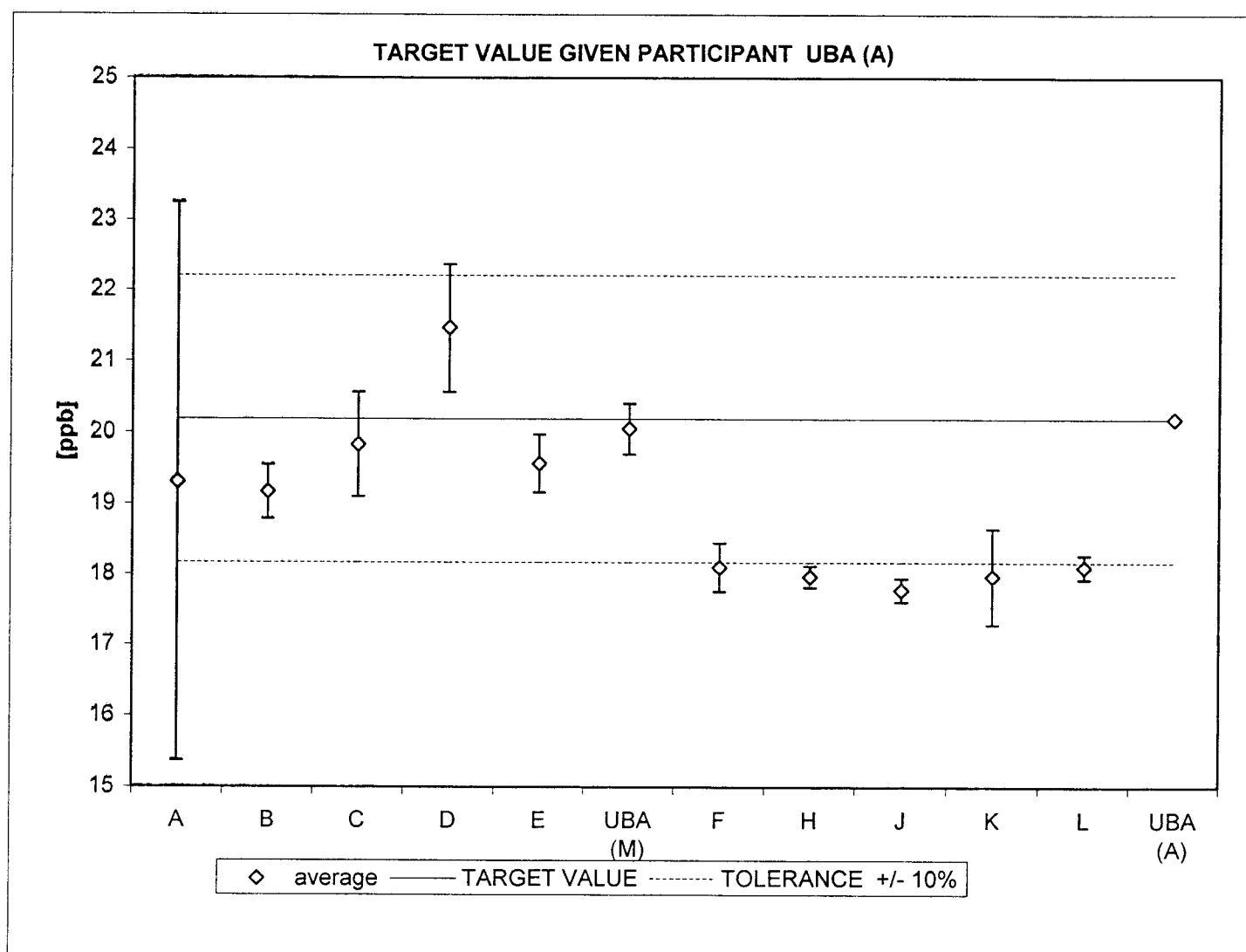
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

SO₂ Run No.: 13

TARGET VALUE GIVEN PARTICIPANT UBA (A)

20.2 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
19.2	15.4	23.3		A	3.940	19.3	23.2	15.4	3	-4.38
18.9	19.0	19.6		B	0.379	19.2	19.5	18.8	3	-5.07
19.4	19.8	20.9	19.3	C	0.733	19.8	20.6	19.1	4	-1.78
22.4	21.4	20.6		D	0.902	21.5	22.4	20.6	3	6.32
19.1	19.8	19.8		E	0.404	19.6	20.0	19.2	3	-3.09
19.8	20.3			UBA (M)	0.354	20.1	20.4	19.7	2	-0.69
17.7	18.3	18.3		F	0.346	18.1	18.4	17.8	3	-10.35
17.8	18.1	18.0		H	0.153	18.0	18.1	17.8	3	-11.01
17.8	17.9	17.6		J	0.165	17.8	17.9	17.6	3	-11.97
18.5	18.2	17.2		K	0.681	18.0	18.6	17.3	3	-11.01
18.3	18.0	18.0		L	0.173	18.1	18.3	17.9	3	-10.35
20.2	20.2	20.2		UBA (A)	0.017	20.2	20.2	20.2	3	0.00
					xAv	19.1	19.8	18.4		
19.1					Median					



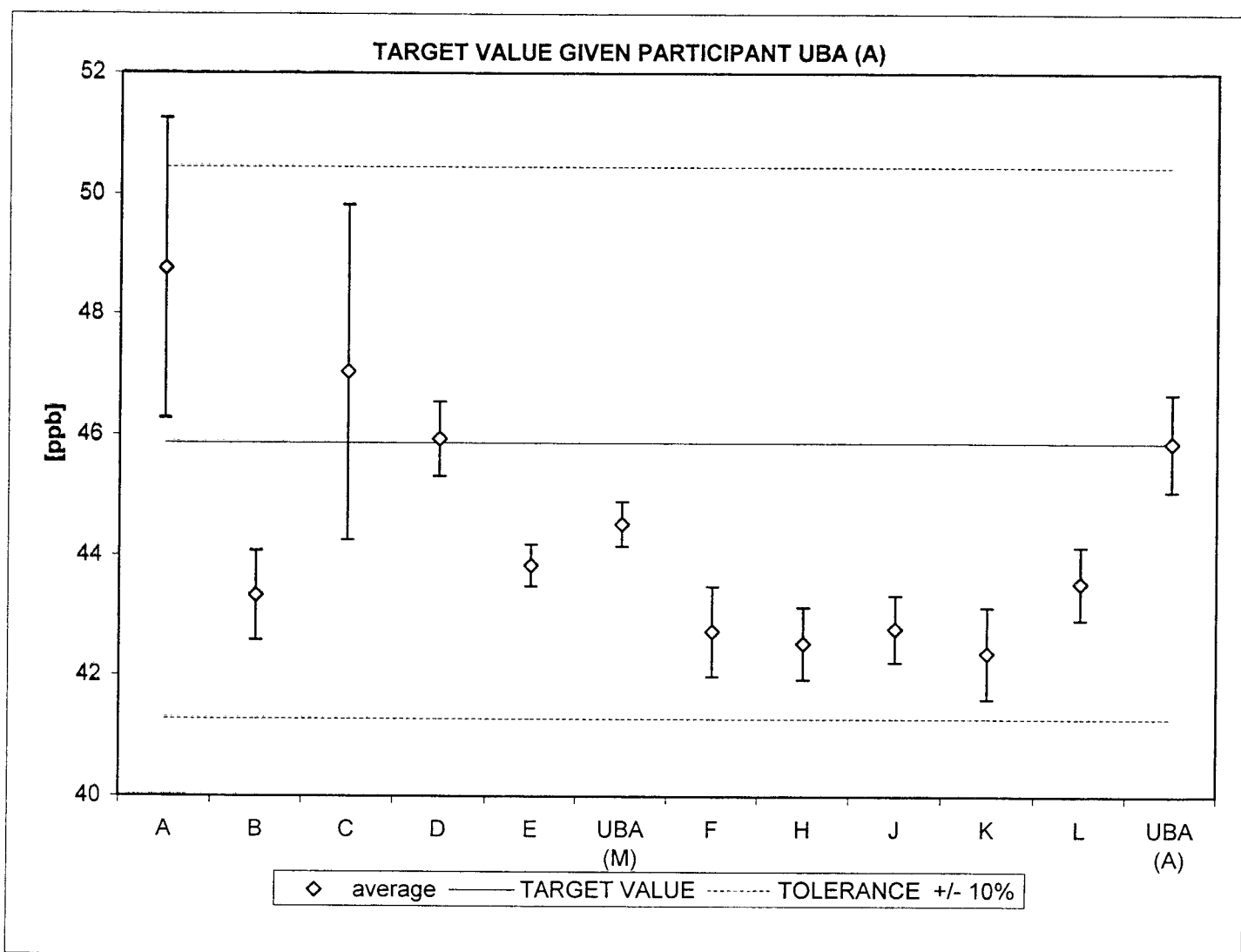
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

SO₂ Run No.: 14

TARGET VALUE GIVEN PARTICIPANT UBA (A)

45.9 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
49.2	46.1	51.0		A	2.494	48.8	51.3	46.3	3	6.31
42.8	43.9			B	0.750	43.3	44.1	42.6	2	-5.53
44.6	44.7	49.4	49.5	C	2.778	47.0	49.8	44.3	4	2.56
46.6	45.8	45.4		D	0.611	45.9	46.5	45.3	3	0.15
43.5	44.2	43.8		E	0.351	43.8	44.2	43.5	3	-4.43
44.4	44.3	45.0		UBA (M)	0.372	44.5	44.9	44.2	3	-2.92
43.5	42.0	42.7		F	0.751	42.7	43.5	42.0	3	-6.83
43.1	41.9	42.6		H	0.603	42.5	43.1	41.9	3	-7.27
43.3	42.2	42.9		J	0.558	42.8	43.3	42.2	3	-6.74
43.2	41.7	42.2		K	0.764	42.4	43.1	41.6	3	-7.63
44.2	43.0	43.4		L	0.611	43.5	44.1	42.9	3	-5.09
46.7	45.1	45.8		UBA (A)	0.802	45.9	46.7	45.1	3	0.00
					xAv	44.4	45.4	43.5		
44.0					Median					



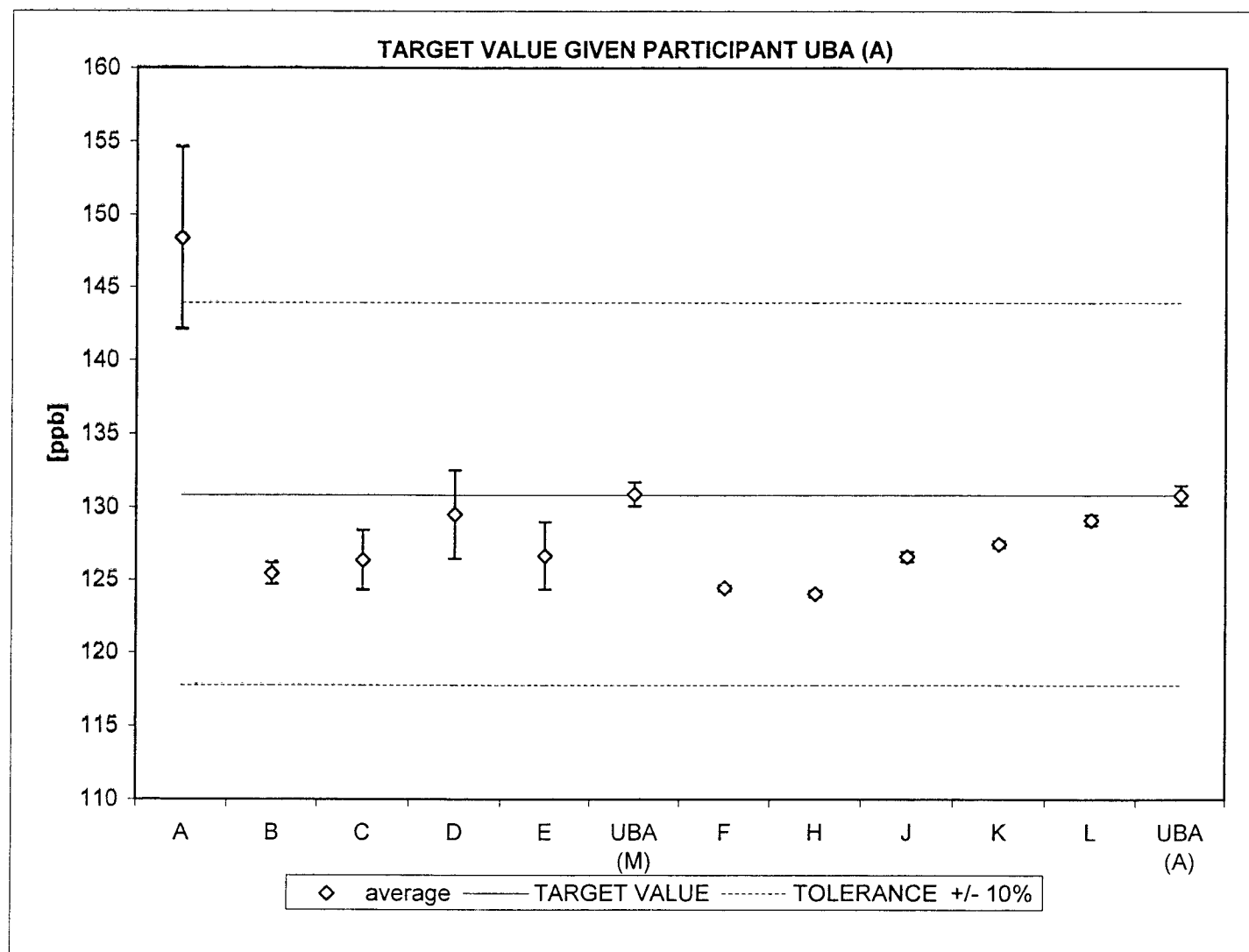
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

SO₂ Run No.: 15

TARGET VALUE GIVEN PARTICIPANT UBA (A)

130.8 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
142.7	155.1	147.3		A	6.270	148.4	154.6	142.1	3	13.40
125.0	126.3	125.0		B	0.751	125.4	126.2	124.7	3	-4.13
124.3	124.9	128.4	127.9	C	2.075	126.4	128.4	124.3	4	-3.42
129.1	126.7	132.7		D	3.020	129.5	132.5	126.5	3	-1.02
125.0	128.3			E	2.333	126.7	129.0	124.3	2	-3.20
130.8	131.8	130.1		UBA (M)	0.822	130.9	131.7	130.1	3	0.05
124.2	124.5	124.6		F	0.208	124.4	124.6	124.2	3	-4.89
123.8	124.1	124.2		H	0.208	124.0	124.2	123.8	3	-5.20
126.3	126.5	127.0		J	0.347	126.6	127.0	126.3	3	-3.23
127.2	127.7	127.5		K	0.252	127.5	127.7	127.2	3	-2.57
128.8	129.1	129.5		L	0.351	129.1	129.5	128.8	3	-1.30
130.1	131.4	131.0		UBA (A)	0.666	130.8	131.5	130.2	3	0.00
					xAv	129.1	130.6	127.7		
127.6					Median					

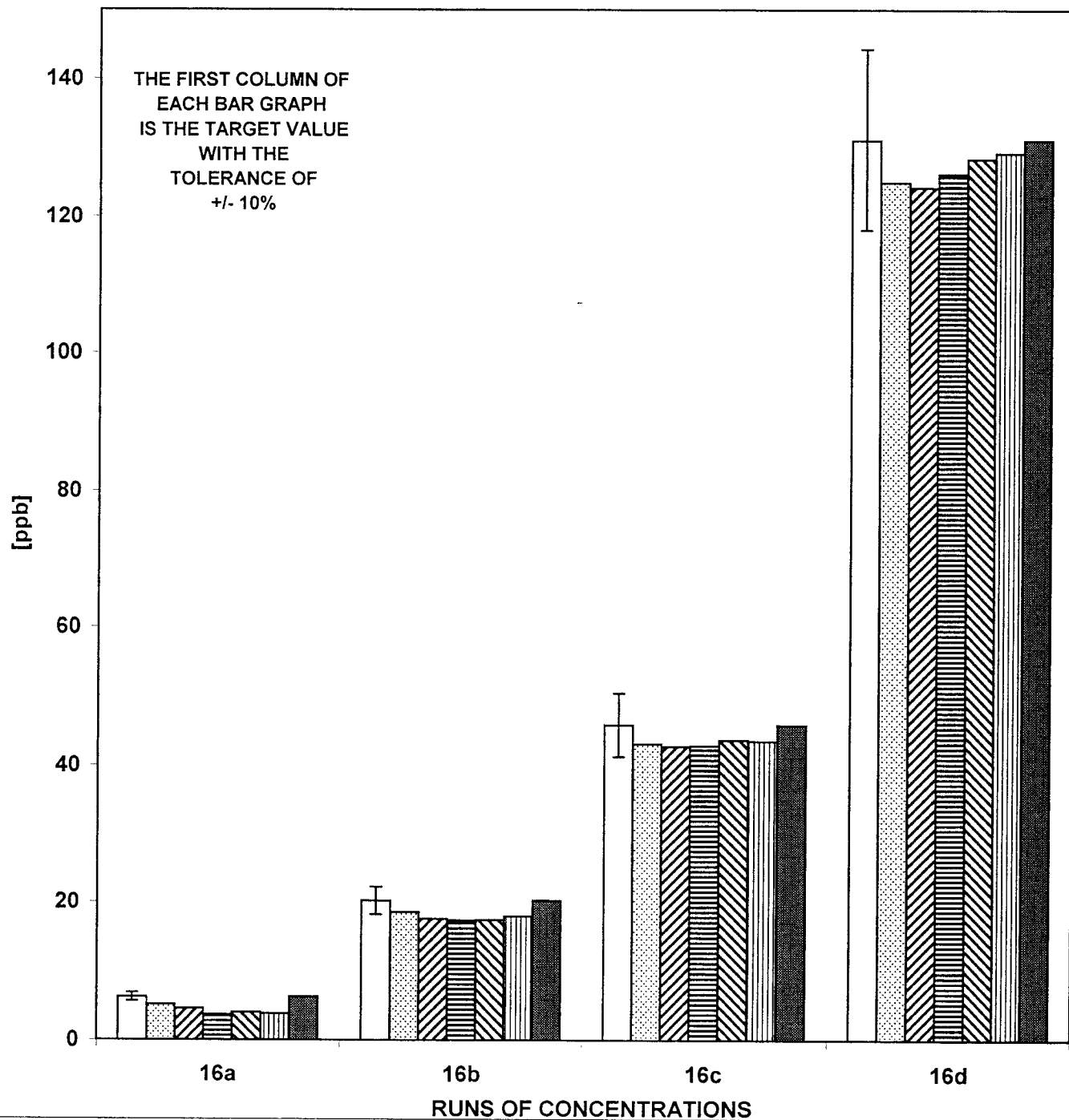


WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

SO₂ RUN No.: 16

Runs	TARGET VALUE	F	H	J	K	L	UBA (A)
16a	6.2	5.1	4.6	3.7	4.0	3.8	6.2
16b	20.2	18.5	17.6	17.3	17.4	17.9	20.2
16c	45.9	43.2	42.8	42.9	43.8	43.6	45.9
16d	131.2	125.1	124.3	126.3	128.5	129.4	131.2

OVERNIGHT RUN 15 - 16 May 2002



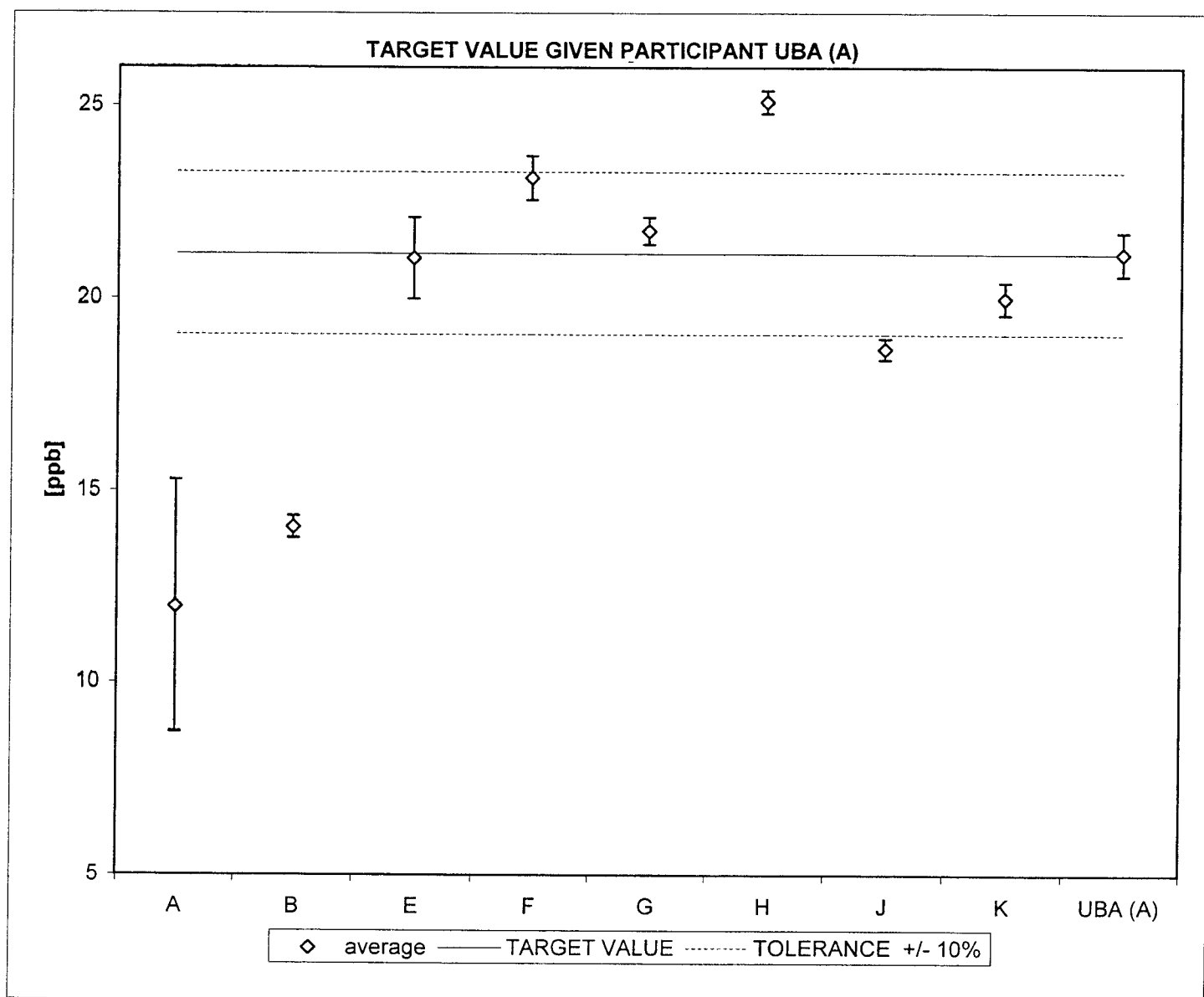
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

O₃ Run No.: 18

TARGET VALUE GIVEN PARTICIPANT UBA (A)

21.2 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
11.0	15.7	9.3		A	3.284	12.0	15.3	8.7	3	-43.39
13.7	14.2	14.2		B	0.286	14.1	14.3	13.8	3	-33.59
20.3	21.8			E	1.061	21.1	22.1	20.0	2	-0.57
22.5	23.3	23.6		F	0.569	23.1	23.7	22.6	3	9.27
21.4	21.8	22.1		G	0.351	21.8	22.1	21.4	3	2.82
24.8	25.1	25.4		H	0.300	25.1	25.4	24.8	3	18.56
18.4	18.7	18.9		J	0.281	18.7	19.0	18.4	3	-11.81
19.7	20.3			K	0.424	20.0	20.4	19.6	2	-5.53
20.7	21.8	21.0		UBA (A)	0.567	21.2	21.7	20.6	3	0.00
					xAv	19.7	20.5	18.9		
20.7					Median					



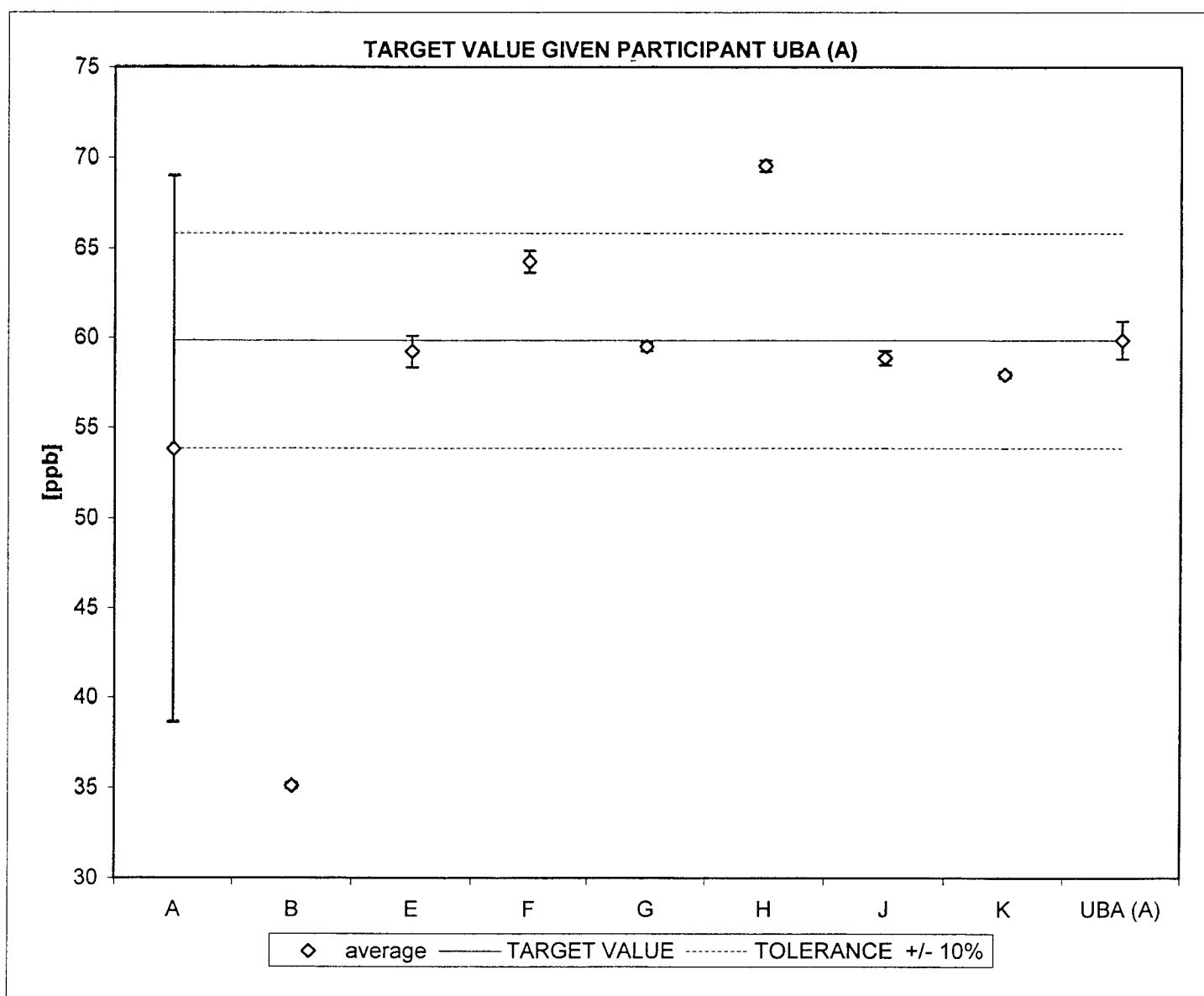
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

O₃ Run No.: 19

TARGET VALUE GIVEN PARTICIPANT UBA (A)

59.8 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
71.1	42.7	47.6		A	15.184	53.8	69.0	38.6	3	-10.09
35.3	35.1	35.0		B	0.151	35.1	35.3	35.0	3	-41.32
58.5	58.9	60.2		E	0.889	59.2	60.1	58.3	3	-1.06
63.7	64.1	64.9		F	0.611	64.2	64.8	63.6	3	7.35
59.2	59.5	59.7		G	0.252	59.5	59.7	59.2	3	-0.61
69.2	69.6	69.8		H	0.306	69.5	69.8	69.2	3	16.21
58.4	58.9	59.2		J	0.400	58.8	59.2	58.4	3	-1.68
57.7	58.0	58.0		K	0.173	57.9	58.1	57.7	3	-3.23
60.4	60.5	58.6		UBA (A)	1.069	59.8	60.9	58.8	3	0.00
					xAv	57.5	59.7	55.4		
59.2					Median					



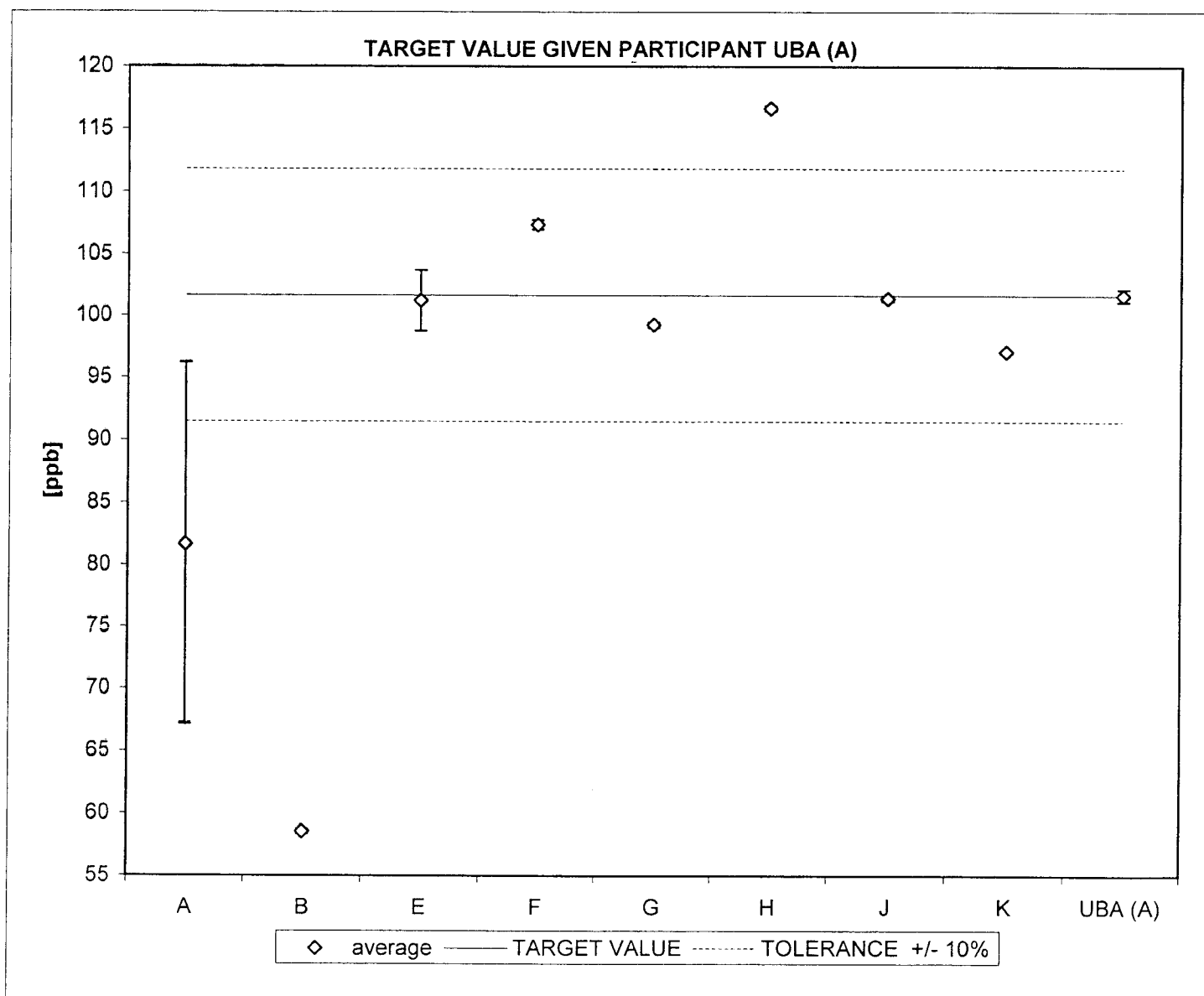
WHO - INTERCOMPARISON WORKSHOP 13 - 17 May 2002 / UBA

O₃ Run No.: 20

TARGET VALUE GIVEN PARTICIPANT UBA (A)

101.7 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
71.4	91.9			A	14.510	81.7	96.2	67.2	2	-19.68
58.3	58.7	58.7		B	0.199	58.6	58.8	58.4	3	-42.40
101.6	98.6	103.5		E	2.470	101.2	103.7	98.8	3	-0.43
107.1	107.2	107.8		F	0.379	107.4	107.7	107.0	3	5.61
99.0	99.4	99.4		G	0.231	99.3	99.5	99.0	3	-2.36
116.4	116.7	116.8		H	0.208	116.6	116.8	116.4	3	14.72
101.2	101.5	101.6		J	0.215	101.4	101.6	101.2	3	-0.25
97.0	97.2	97.0		K	0.115	97.1	97.2	97.0	3	-4.52
101.1	101.8	102.1		UBA (A)	0.513	101.7	102.2	101.2	3	0.00
					xAv	96.1	98.2	94.0		
101.1					Median					

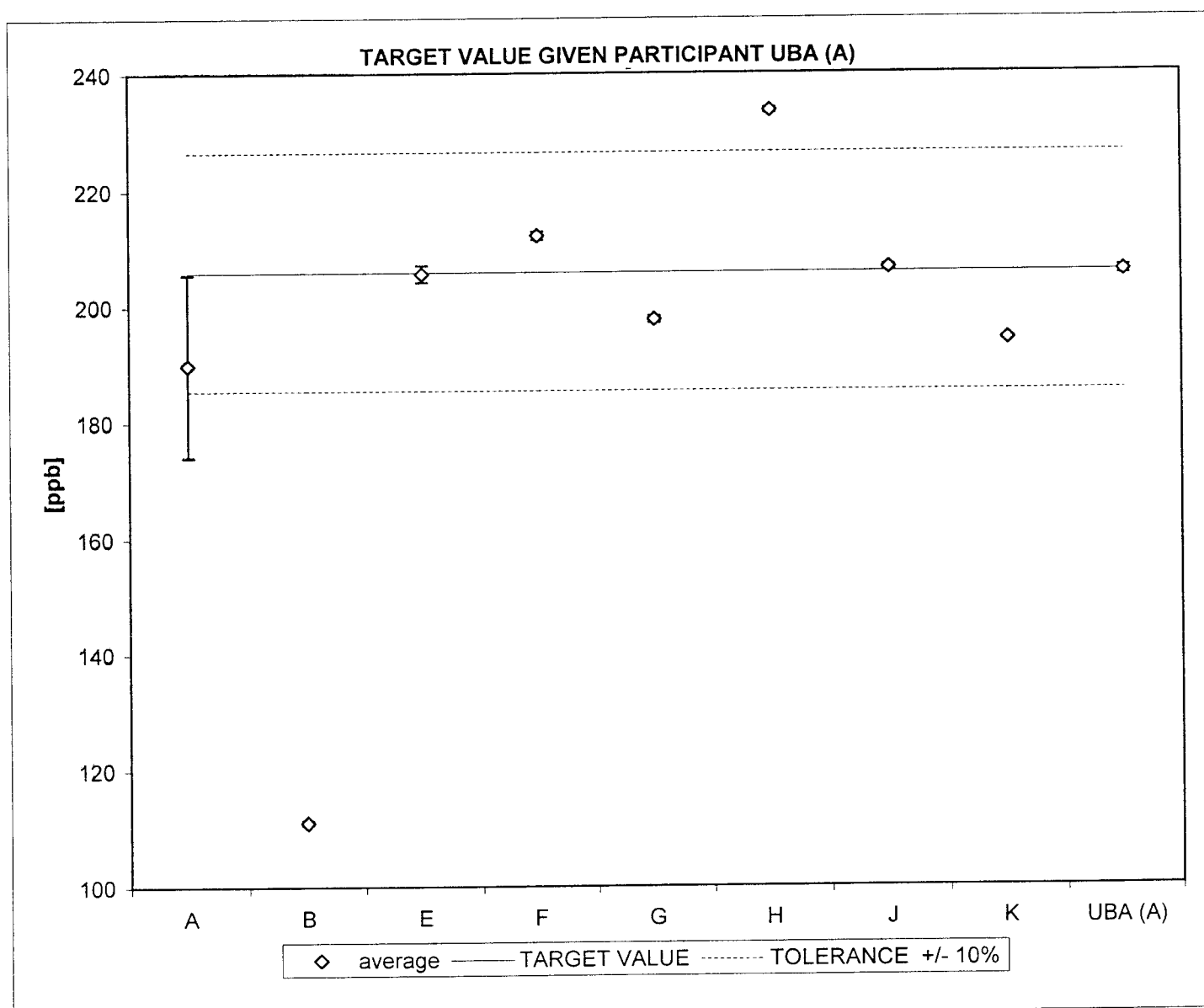


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O₃ Run No.: 21

TARGET VALUE GIVEN PARTICIPANT UBA (A)
205.9 ppb

1	2	3	4	CODE	st.dev	average	av.+st.	av. - st.	n	T%
200.9	178.6			A	15.768	189.8	205.5	174.0	2	-7.84
110.7	111.0	111.5		B	0.404	111.1	111.5	110.7	3	-46.06
204.6	206.7			E	1.485	205.7	207.1	204.2	2	-0.12
211.6	212.0	213.0		F	0.721	212.2	212.9	211.5	3	3.06
197.0	198.0	198.0		G	0.577	197.7	198.2	197.1	3	-4.00
233.0	233.6	233.9		H	0.458	233.5	234.0	233.0	3	13.40
206.1	206.6	207.0		J	0.463	206.6	207.0	206.1	3	0.33
194.0	194.0	194.5		K	0.289	194.2	194.5	193.9	3	-5.70
205.3	205.7	206.7		UBA (A)	0.721	205.9	206.6	205.2	3	0.00
					xAv	195.2	197.5	192.8		
205.3					Median					

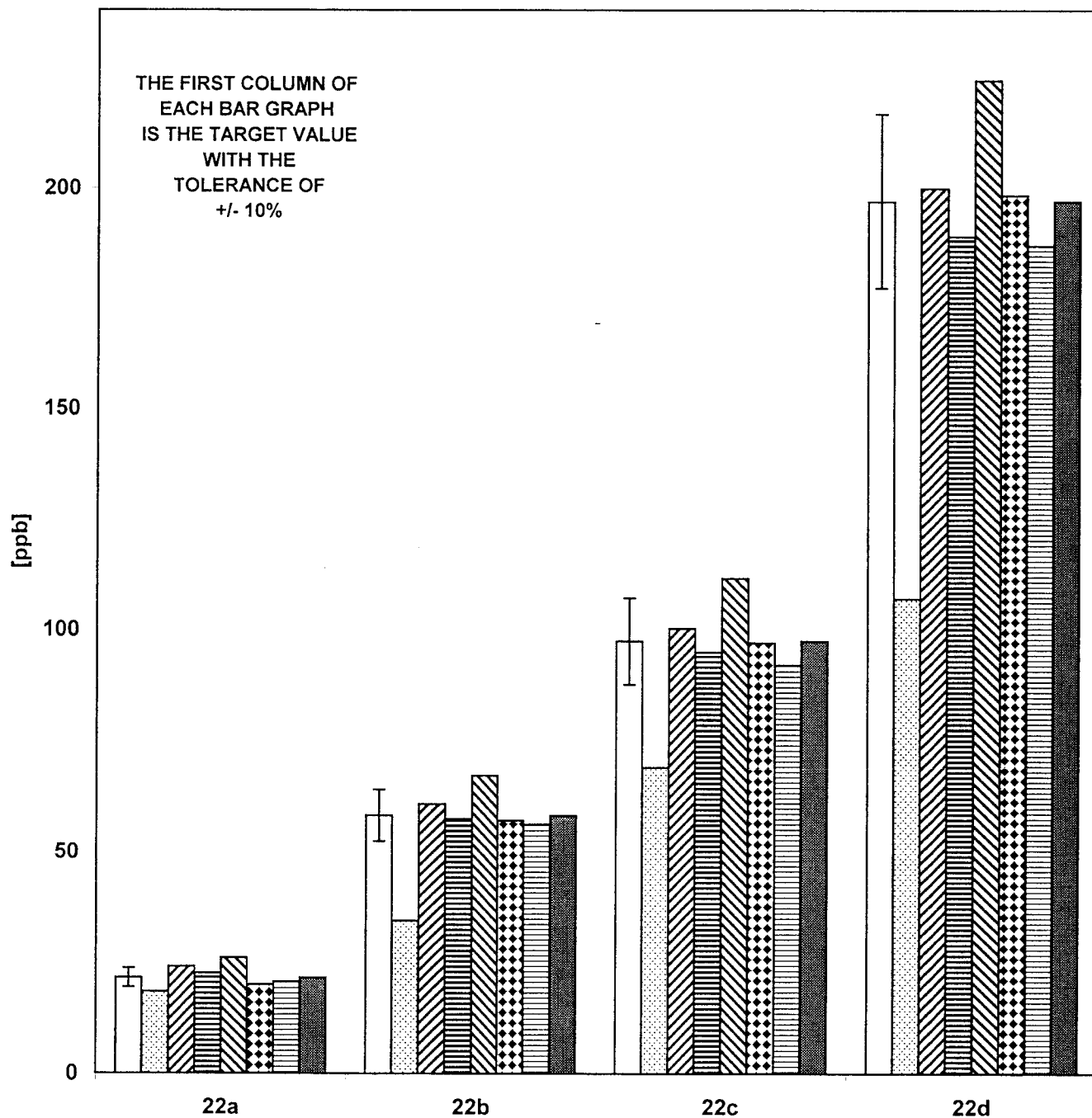


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O₃ RUN No.: 22

Runs	TARGET VALUE	B	F	G	H	J	K	UBA (A)
22a	21.5	18.4	24.0	22.5	26.0	19.9	20.6	21.5
22b	58.3	34.4	60.9	57.5	67.3	57.2	56.3	58.3
22c	97.5	69.1	100.3	95.0	111.8	97.2	92.1	97.5
22d	197	107.1	200.1	189.1	224.3	198.4	187.0	197.0

OVERNIGHT RUN 16 - 17 May 2002



□ TARGET VALUE

■ B

▨ F

▩ G

▤ H

▥ J

▧ K

■ UBA (A)