TÜV Immissionsschutz und Energiesysteme GmbH
TÜV Rheinland Group
D - 51105 Köln, Am Grauen Stein, Tel: 0221/806-2756, Fax: 0221/806-1349

TÜV IMMISSIONSSCHUTZ
UND ENERGIESYSTEME GMBH

Translation of the report on the suitability test of the ambient air measuring system Ozone Analyser Model 49i of the company Thermo Electron Corporation for the component Ozone

TÜV-Report-No.: 936/21203248/B1
Cologne, January 5, 2006

TÜV Immissionsschutz und Energiesysteme GmbH holds an accreditation under the terms of DIN EN ISO/IEC 17025 and DIN EN ISO 9002 in the following field of work:

- Determination of emissions and immissions of air pollutants and odorants;
- Verification of the correct installation and the function as well as the calibration of continuous operating emission measuring systems including systems for data evaluation and remote monitoring of emissions;
- Suitability testing of measuring systems for continuous monitoring of emissions and immissions as well as for electronic systems for data evaluation and remote monitoring of emissions

The accreditation is valid up to 04-12-2010.
DAR-Registration number: DAP-PL-3856.99.

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DAP-PL-3856.99

Translation of the report on the suitability test of the ambient air measuring system Ozone Analyser Model 49i of the company Thermo Electron Corporation for the component Ozone

Measuring system tested:	Ozone Analyser Model 49i
Manufacturer of the Instrument:	Thermo Electron Corporation 27 Forge Parkway Franklin, MA 02038 USA Frauenauracher Straße 96 91056 Erlangen Germany
Time period of testing:	June 2005 to December 2005
Date of report:	January 5, 2006
Number of report:	936/21203248/B1
Scope of report:	In total 462 pages Appendix from page 89 Manual from page 112 with 350 pages

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1 Summary and proposal for declaration of suitability

1.1 Abstract

The report 936/21203248/B1 at hand is a revised version of the suitability test report 936/21203248/B of 05.01.2006. The revision was necessary in order to document in the report the gain of knowledge since the implementation of the standard EN 14625.

By order of the Thermo Electron Corporation the TÜV Immissionsschutz und Energiesysteme GmbH has accomplished the suitability test of the measuring system Ozone Analyser Model 49i for the component Ozone.

The testing was performed in accordance to the following guidelines and requirements:

- VDI 4202 Part 1: Minimum requirements for suitability tests of automated ambient air quality measuring systems; Point-related measurement methods of gaseous and particulate pollutants, from June 2002
- VDI 4203 Part 3: Testing of automated measuring systems; Test procedures for point –related ambient air quality measuring systems of gaseous and particulate pollutants, from August 2004
- EN 14625 Ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry, from July 2005

The measuring system tested operates using the ultraviolet photometry principle.

The test work took place in the laboratory and during a field test with a duration of three months as an endurance test. The tested measuring ranges are:

Component		Measuring range		
Ozone	O_3	360	µg/m³	VDI 4202 Bl. 1
Ozone	O_3	500	µg/m³	EN 14625

Note: 0 – 250 ppb correlates to 0 – 250 nmol/mol CO or 0 – 500 mg/m³
(at 293 K and 1013 mbar)

The minimum requirements and the requirements according to EN 14625 have been fulfilled in the suitability test.

Therefore the TÜV Immissionsschutz und Energiesysteme GmbH proposes the publication as a suitability-tested measuring system for continuous monitoring of ozone in the ambient air.

1.2 Proposal for declaration of suitability

Due to the positive achieved results, the following recommendation for declaration of suitability as suitability-tested measuring system is given:

1.2.1	**Measurement task**	:	Measuring system for determination of the ozone concentration in the ambient air
1.2.2	**Name of device**	:	Ozone Analyser Model 49i
1.2.3	**Measured components**	:	Ozone
1.2.4	**Manufacturer**	:	Thermo Electron Corporation 27 Forge Parkway Franklin, MA 02038 USA Frauenauracher Straße 96 91056 Erlangen Germany
1.2.5	**Suitability**	:	For continuous ambient air measurement of O_3 in stationary operation
1.2.6	**Measuring ranges during the suitability test**	:	0 to 360 µg/m³ Ozone 0 to 500 µg/m³ Ozone
1.2.7	**Software version**	:	V 01.01.02.105
1.2.8	**Restrictions**	:	
1.2.9	**Remarks**	:	
1.2.10	**Test institute**	:	TÜV Immissionsschutz und Energiesysteme GmbH, Köln TÜV Rheinland Group Responsible auditor: Guido Baum
1.2.11	**Test report**	:	936/21203248/B1 of January 5, 2006

1.3 Summary of test results

Minimum requirement		Requirement	Test results	ful-filled?	Page
4	Requirements on the instrument design				
4.1	General requirements				
4.1.1	Measured value display	Must exist.	A measured value display exists.	yes	22
4.1.2	Easy maintenance	Maintenance of the measuring systems should be possible without larger effort, if possible from outside.	The Maintenance of the measuring systems is possible without higher complexity.	yes	23
4.1.3	Functional check	If the operation or the functional check of the measuring system require particular instruments, they shall be considered as part of the measuring system and shall be applied in the corresponding subtests and included in the assessment. Test gas units included in the measuring system shall indicate their operational readiness to the measuring system by a status signal and shall provide direct as well as remote control via the measuring system. The uncertainty of the test gas shall not exceed 1 % of reference value B_2 within three month.	not applicable	not applicable	24
4.1.4	Set-up times and warm-up times	The instruction manual must include information to this topic.	The set-up time amounts to 90 minutes. The warm-up time is specified with 90 minutes in the manual and in the tests performed a period of 90 minutes was found.	yes	25
4.1.5	Instrument design	The instruction manual must include information to this topic.	In the manual the instrument design and the basic conditions are described in details.	yes	26
4.1.6	Unintended adjustment	Must be secure against unintended adjustment	The measuring equipment is protected against unauthorized adjusting by means of passwords.	yes	28
4.1.7	Data output	Must be provided digitally and/or analogue.	Measurement signals and operating states are recognized by downstream evaluating-systems correctly. All measurement signals can be provided in digital form and in analogue mode.	yes	29

Minimum requirement	Requirement	Test results	ful-filled?	Page
4.2 Requirements for the mobile Application	Permanent operational standby mode must be secure. The requirements of the stationary application shall comply with the requirements for the mobile application.	An evaluation is dropped, because this possible application was not tested.	not applicable	30
5. Performance requirements				
5.1 General				
5.2 General requirements on measuring systems				
5.2.1 Measuring range	The upper limit of the range shall be higher than B_2.	The measuring ranges can be chosen optional according to the requirements.	yes	31
5.2.2 Negative output signals	Negative output signals or measured values may not be suppressed (life zero).	The position of the zero point measuring signal is so far of remote electrical zero, that the permissible zero point drift can surely be registered.	yes	32
5.2.3 Analytical function	The relationship between the output signal and the value of the air quality characteristic shall be repesented by the analytical function and determined by regression analysis	The measuring equipment allows the formation of one-hour mean values.	yes	33
5.2.4 Linearity	Deviations of the group averages of measured values about the calibration function are smaller than 5 % of B_1 in the range of zero to B_1, and smaller than 1 % of B_2 in the range of zero to B_2.	As given in table 9 and table 10, the two candidates meet the requirements of the guideline of VDI 4202	yes	35
5.2.5 Detection limit	Maximum B_0.	The detection limit is with 0.57 µg/m³ respectively 0.54 µg/m³ at zero and 1.02 µg/m³ respectively 0.93 µg/m³ at span point within the minimum requirements of VDI 4202.	yes	39
5.2.6 Response time	Maximum 5 % of the response time (180 seconds).	The maximal permissible response time of 180 seconds is fallen below clearly.	yes	41
5.2.7 Dependence of the zero point on ambient temperature	The measured value at zero shall not exceed the reference value B_0 if ambient temperature is changed by 15 K in the range of +5 °C to +20 °C or 20 K in the range of +20 °C und +40 °C.	The change of the zero point is at all ambient temperatures within the limit of the minimum requirement.	yes	43
5.2.8 Dependence of the measured value on ambient temperature	The temperature dependence of the measured value in the range of reference value B_1 shall not exceed 5 % of the measured value if ambient temperature is changed by 15 K in the range of +5 °C to +20 °C or 20 K in the range of +20 °C to +40 °C.	The change of the span point is at all ambient temperatures within the limit of the minimum requirement.	yes	46
5.2.9 Drift of zero point	In 24 hours and in the maintrance interval maximum B_0.	In Figure 8 and Figure 9 is to be seen, that the zero point drifts meets the minimum requirements .	yes	49

Minimum requirement	Requirement	Test results	fulfilled?	Page
5.2.10 Drift of the measured value	In 24 hours and in the maintenance interval maximum 5 % of B1.	In Figure 10 and Figure 11 is to be seen, that the span point drift meets the minimum requirements.	yes	52
5.2.11 Cross-sensitivities	At the zero point maximum B0 and at the B2 level maximum 3 % of B2.	The cross-sensitivities of the measuring systems fulfil the minimum requirements.	yes	55
5.2.12 Reproducibility RD	RD ≥ 10 based on B1.	The minimum value of 10 for the reproducibility RD required by the VDI 4202 part 1 is exceeded clearly. Thus the minimum standards are kept.	yes	58
5.2.13 Hourly averages	Creation must be possible.	The measuring equipment allows the formation of one-hour mean values.	yes	63
5.2.14 Mains voltage and frequency	Variation of the measured value at B_1 maximum B_0 in the voltage interval (230 +15/-20)V and variation of the measured value for mobile application maximum B_0 in the frequency interval of (50 ± 2) Hz.	The measuring system fulfils the minimum requirements regarding the variations of the mains voltage and the mains frequency. The minimum requirements are fallen below clearly.	yes	65
5.2.15 Failure in the mains voltage	In case of malfunction of the measuring system or failure in the mains voltage, uncontrolled emission of operating and calibrating gas shall be avoided. The instrument parameters shall be secured by buffering against loss caused by failure in the mains voltage. When mains voltage returns, the instrument shall automatically reach the operation mode and start the measurement according to the operating instructions.	The minimum requirements are kept during a power breakdown. The operability of the analyser is safeguarded and calibrating gas does not exhaust .	yes	69
5.2.16 Operating states	Measuring systems shall be able to telemetrically transmit important operating states by status signals.	The essential operating states are controllable via telemetric status signals.	yes	70
5.2.17 Switch-over	Switch-over between measurement and functional check and/or calibration shall be possible telemetrically control or manual intervention.	The switch-over between the modes of operation is manual and telemetric possible .	yes	71
5.2.18 Availability	Minimum 90 %.	The availability is higher than 90 %, so that the minimum requirement is fulfilled.	yes	72
5.2.19 Efficiency of the converter	Minimum 95 %.	not applicable.	not applicable	74
5.2.20 Maintenance interval	If possible 28 days, minimum 14 days.	According to the orders of the VDI 4202 part 1 can be awarded to the measuring equipment at a field testing-period of 3 months with the present results the maximum possible maintenance interval of 1 month.	yes	75
5.2.21 Overall uncertainty	Compliance with the requirements for the data quality.	The measuring system falls below the required expanded uncertainty of 15 % clearly by a result of maximum 7.77 %.	yes	77

2 Terms of reference

2.1 Kind of testing

On behalf of the company Thermo Electron Corporation, TÜV Immissionsschutz und Energiesysteme GmbH performed a complete suitability test for the measuring system Ozone Analyser Model 49i according to the guidelines for the minimum requirements according to VDI 4202 and EN 14625.

2.2 Objective

The ambition of the test was to show, that the measuring system fulfils the German minimum requirements for the VDI 4202 part 1 and the European minimum requirements for the EN 14625. Therefore the measuring system is tested in the following measuring ranges:

Table 1: Tested components and measuring ranges

Component		Measuring range		
Ozone	O_3	360	µg/m³	VDI 4202 part. 1
Ozone	O_3	500	µg/m³	EN 14625

3 Description of the tested system

3.1 Measuring principle

The analyser Model 49i measures the ozone concentration based on the UV-adsorption-method. This principle uses the characteristic that ozone molecules (O_3) absorb infrared radiation at a wavelength of 254 nm. The relationship between intensity of the absorbance of the UV-light and the ozone concentration follows the law of Lambert-Beer.

The relationship is given by the following equation:

$$\frac{I}{I_0} = \exp(-K \cdot l \cdot c)$$

with:

I/I_0	The transparency of the ozone sample, that is the relation of the intensity of the radiation, which is measured by the detector, if the absorption cell is filled by sample air and when the cell is filled by ozone free sample respectively.
K	Absorption coefficient of ozone at 253.7 nm in m²/µg
l	Absorption path or distance, which light passes during the absorption
c	Mass concentration of the ozone at standard conditions (1013 mbar, 273K)

3.2 Extent and set-up of the measuring system

The sample is drawn into the model 49i through the sample bulkhead with the labelling SAMPLE and is divided into two streams (see Figure 1). One stream passes an ozone scrubber and is used as reference gas (I_0). The reference gas flows to an magnetic valve. The sample gas (I) flows directly to the sampling-magnetic valve. The magnetic valves switch in an alternating mode in a 10 s rhythm between the Cell A and Cell B. When Cell A is filled with reference gas, is Cell B filled with sample gas and vice versa.

The UV-intensities of both cells are measured by detector A and B. When the magnetic valves conduct the reference- and sample-gas to the opposite cell, the light intensities are disregarded for some seconds to enable a purging process of the cells. For each cell is the ozone concentration calculated by the ozone analyser Model 49i. The mean concentration is shown at the display in front of the analyser and emitted by the analogue output. The data are also provided by an serial- and Ethernet-interface.

Figure 2 shows the arrangement of the components in the analyser.

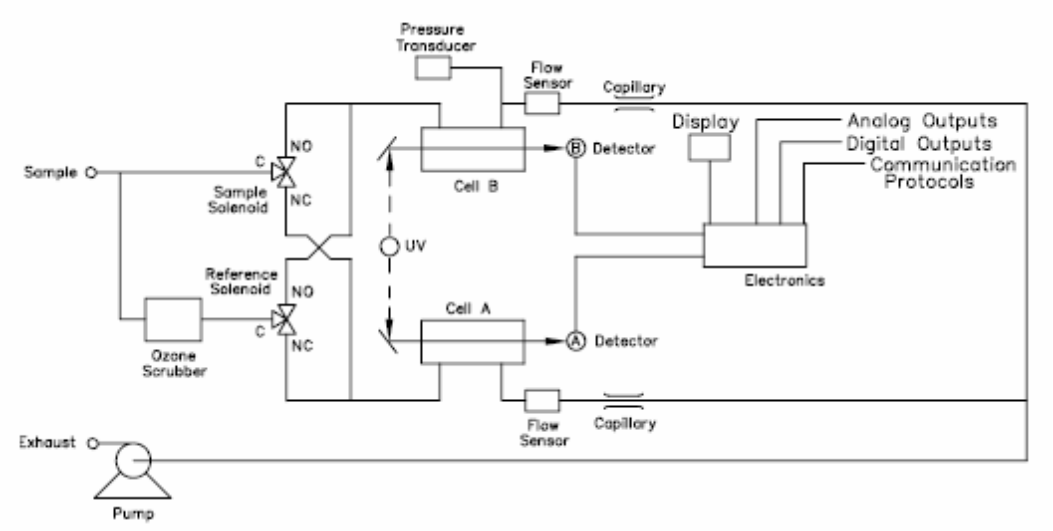


Figure 1: Model 49i – Scheme oft the measuring principle

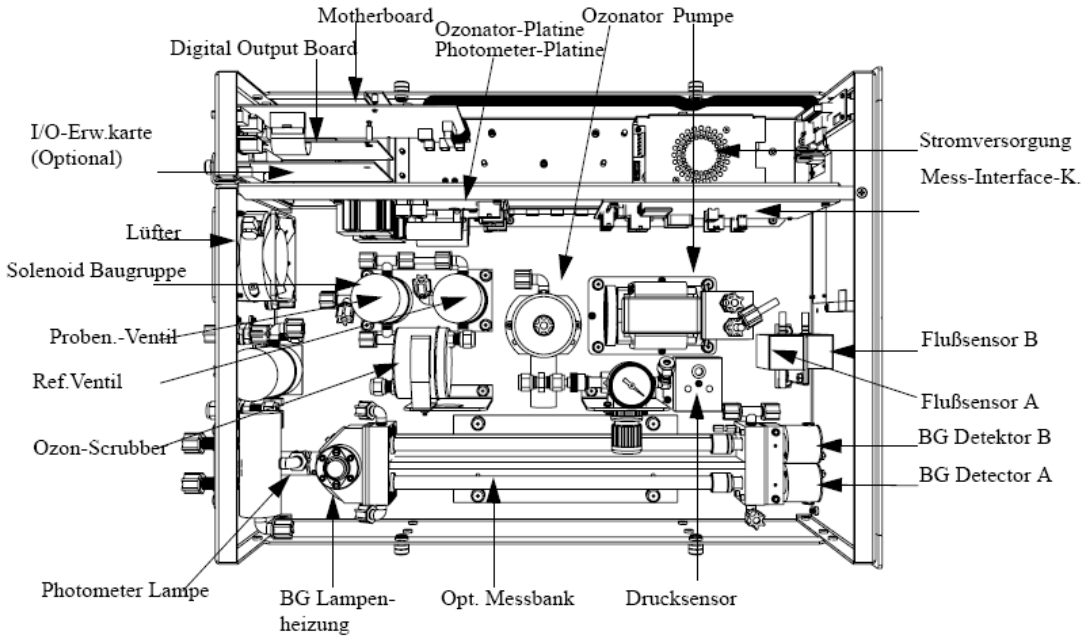


Figure 2: Hardware of the analyser model 49i

4 Test Program

4.1 Laboratory test

According to the guidelines the following test program has arose for the laboratory test:

- Inspection of the general analyser functions
- Determination of the device characteristic with test gases,
- Determination of the cross-sensitivity of the measuring system against accompanying substances in the ambient air,
- Check of the stability of the zero-point and reference-point in the permissible ambient temperature range,
- Determination of changes in mains voltage on the measured signal
- Response time
- Detection limit

The lab test has been done with two identical analysers of the type Ozone Analyser Model 49i with the following serial numbers:

Unit 1: S.–No. Pilot 1

Unit 2: S.–No. Pilot 2

4.2 Field test

The field test took place at a large parking lot in Cologne. The analysers have been installed during the field test in an air conditioned container. Figure 3 shows the installed measuring systems.

The endurance test took place from 19.09.2005 to 19.12.2005. The analysers had during this period the following configuration:

Component		Measuring range	
Ozone	O_3	0 - 500	µg/m³

The evaluation based on the in Table 1 mentioned certification interval.

Figure 3: Front shoot of the analysers in the measuring container

For the field test the following test program was established:

- Functional check of the general device functions,
- Functional check of the measuring systems at the beginning and at the end of the field test,
- Determination of the detection limit,
- Determination of reproducibility R_D,
- Determination of the drift behaviour at zero-point and reference point,
- Determination of maintenance interval,
- Determination of availability.

The following analysers have been tested:

Unit 1: S.–No. Pilot 1

Unit 2: S.–No. Pilot 2

5 Reference method

5.1 Component Ozone

A ozone generator of the manufacturer MCZ has been used for the creation of the test gas concentrations. The check of the produced concentrations has been done by the methods according to guidelines DIN ISO 13964 „Determination of ozone in the ambient air“ and VDI 2468 part 6 „Measuring of ozone concentrations, direct UV-photometric method (basis method)“.The employed ozone generator it selves has been validated in the run-up to the examinations by an to an national reference laboratory reducible primary UV calibration photometer.

Independent from this have been done measurements in comparison to the KJ-method according to the guideline VDI 2468 part 1 „Measurement of ozone- and peroxide-concentrations – manual photometric method Kaliumjodid-method“. Even if this method is only restricted applicable for ambient air measurement, it is suitable to validate the test gases in an independent way. Some examples of the results from the measurements and the uncertainties are shown in Table 2 und Table 3.

Table 2: Comparison of the ozone concentrations created by the ozone generator with the independent determination by the Kaliumjodid-method and the UV-reference photometer at a reference concentration of 360 µg/m³

No.	Value Ozone generator	Value Kaliumjodid [µg/m³]	Deviation [%]	Value UV-Reference [µg/m³]	Deviation [%]
1	360	365	1.39	362.9	0.81
2	360	367	1.94	362.8	0.78
3	360	366	1.67	362.9	0.81
4	360	369	2.50	362.8	0.78
5	360	358	-0.56	361.9	0.53
6	360	362	0.56	361.1	0.31
7	360	366	1.67	361.2	0.33
8	360	359	-0.28	362.1	0.58
9	360	365	1.39	362.4	0.67
10	360	369	2.50	362.8	0.78
Average		**364.6**	**1.28**	**362.3**	**0.64**

Table 3: Comparison of the ozone concentrations created by the ozone generator with the independent determination by the Kaliumjodid-method and the UV-reference photometer at a reference concentration of 100 µg/m³

No.	Value Ozone generator	Value Kaliumjodid [µg/m³]	Deviation [%]	Value UV-Reference [µg/m³]	Deviation [%]
1	100	98.0	-2.00	98.5	-1.50
2	100	101.2	1.20	98.5	-1.50
3	100	105.3	5.30	98.4	-1.60
4	100	102.5	2.50	98.9	-1.10
5	100	107.0	7.00	98.7	-1.30
6	100	99.0	-1.00	99.2	-0.80
7	100	103.9	3.90	99.4	-0.60
8	100	106.0	6.00	99.2	-0.80
9	100	96.6	-3.40	99.3	-0.70
10	100	102.0	2.00	99.0	-1.00
	Average	**102.15**	**2.15**	**98.9**	**-1.09**

5.2 Assembly in the lab and field

The set-up of the testing arrangement in the laboratory was matched to the requirements of the specific tests and was duplicated in a simplified manner in the field test site (see Figure 4).

Figure 4: Set up of the ozone generator and the computer for controlling

6 Test results

6.1 4.1.1 Measured value display

The measuring system shall be fitted with a measured value display.

6.2 Equipment

Camera

6.3 Testing

The equipment of the measuring system has been tested visually for the presence of the measured value display.

6.4 Evaluation

The measuring system has a measured value display, which indicates in addition to the measured value important system parameters.

6.5 Assessment

A measured value display exists.

Minimum requirement fulfilled? yes

6.6 Documentation

At the front view of the analyser the display of the measured value can bee seen.

Figure 5: Front-view of the analyser

6.1 4.1.2 Easy maintenance

Necessary maintenance of the measuring systems should be possible without larger effort, if possible from outside.

6.2 Equipment

Common tools.

6.3 Testing

The maintenance for the analyses has been done like in the manual described. For the realisation have only common tools been used.

6.4 Evaluation

The maintenance of the measuring systems is trouble-free possible by use of common tools.

6.5 Assessment

The Maintenance of the measuring systems is possible without higher complexity.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 4.1.3 Functional check

If the operation or the functional check of the measuring system require particular instruments, they shall be considered as part of the measuring system and shall be applied in the corresponding sub-tests and included in the assessment.
Test gas units included in the measuring system shall indicate their operational readiness to the measuring system by a status signal and shall provide direct as well as remote control via the measuring system.
The uncertainty of the test gas shall not exceed 1 % of reference value B_2 within three month.

6.2 Equipment

Not applicable.

6.3 Testing

The measuring system can be ordered with a functional check unit. This unit was not part of the suitability test. During the suitability test, the measuring system was checked by an external ozone generator and zero gas (synthetic air).

6.4 Evaluation

not applicable

6.5 Assessment

not applicable

Minimum requirement fulfilled? not applicable

6.6 Documentation

Here not essential.

6.1 4.1.4 Set-up times and warm-up times

The set-up times and warm-up times shall be specified in the instruction manual.

6.2 Equipment

Clock, zero- and test gases.

6.3 Testing

The set-up time has been verified during the assembly in the lab and in the field on the basis of the data in the manual. The warm-up time has been defined by giving up zero and test gases after turning the analysers on.

6.4 Evaluation

For the set-up time there is no declaration in the manual. It depends on the circumstances at the mounting place and consists of the time for connecting the power supply, the gas tubes and the data logging system. Experimentally, for the set up time a period of 90 minutes has been defined.

The warm-up time is specified in the manual with 90 minutes. In our tests the measuring system needed latest 90 minutes to measure stabile values. This period of time is based on a activation of the analysers after a longer duration of shutdown, so that it was secure, that the analysers were totally un-tempered before the restart. Other tests in which the analysers have been switched off for a shorter time resulted in a shorter warm up time of about 15 to 30 minutes.

6.5 Assessment

The set-up time amounts to 90 minutes. The warm-up time is specified with 90 minutes in the manual and in the tests performed a period of 90 minutes was found.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 4.1.5 Instrument design

The instruction manual shall include specifications of the manufacturer regarding the design of the measuring system. The main elements are:
Instrument shape (e.g. bench mounting, rack mounting, free mounting)
Mounting position (e.g. horizontal or vertical mounting)
Safety requirements
Dimensions
Weight
Power consumption.

6.2 Equipment

The power consumption has been detected by using the test instrument Metratester 5 from the company Gossen Metrawatt.

6.3 Testing

The content of the manual has been checked regarding to the instrument design. The declaration of the power consumption of the analysers has been checked in a regular measuring operation.

6.4 Evaluation

The documentation in the manual includes all information for the instrument design. The essential data are given in Table 4:

Table 4: Data of the analyser Thermo 49i

Instrument shape	built-in type
Mounting position	horizontal
Sample flow rate	1 – 3 liters/minute
Operating temperature	20 – 30 °C (electric secure use in the band 0-45 °C) in not condense surroundings
Dimensions (H x B x T)	425,5 mm x 218,9 mm x 584,2 mm
Weight	16 kg
Power requirements	100 VAC @ 50/60 Hz 115 VAC @ 50/60 Hz 220-240 VAC @ 50/60 Hz 275 watts
Analogue outputs	6 voltage outputs; 0-100 mV, 1, 5, 10 V (user selectable), possible 5% of full scale over/under range, 12 bit resolution, user selectable for measurement input
Digital inputs	16 digital inputs, user select programmable, TTL-Level (HIGH)
Serial pots	1 RS-232 or RS-485 with two connectors, baud rate 1200-115200, data bits, parity, and stop bits, protocols: C-Link, MODBUS and Streaming-Data (all user selectable)
Ethernet connection	RJ45 connector for 10 Mbs Ethernet-connection, static or dynamic TCP/IP addressing
Software version	V 01.01.02.105

The determination of the power consumption has been done in a period of 24 h in regular measuring operation during the field test. At a supply voltage of 230 V the results displayed in Table 5 have been found.

Table 5: Test of the power consumption during regular operation

	Current consumption [A]	**Power consumption [W]**
Unit 1	0.65	149
Unit 2	0.64	147

6.5 Assessment

In the manual the instrument design and the basic conditions are described in details. Regarding the power consumption, the detected values fall below the specifications listed in the manual.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 4.1.6 Unintended adjustment

It shall be possible to secure the adjustment of the measuring system against illicit or unintended adjustment during operation.

6.2 Equipment

Special checking facilities are not necessary.

6.3 Testing

The options to avoid an unintended or illicit adjustment of the settings of the measuring system were activated. Then it was tested whether an unauthorized or unintentional change is possible.

6.4 Evaluation

The menu areas in which a change of analyser parameters is possible can be safeguarded by means of a password.

6.5 Assessment

The measuring equipment is protected against unauthorized adjusting by means of passwords.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 4.1.7 Data output

The output signals shall be provided digitally (e. g. RS 232) and/or as analogue signals (e. g. 4 mA to 20 mA).

6.2 Equipment

Evaluating-system, Data logger and MultiMate .

6.3 Testing

The operating status and the measurement signals were recorded by connection of the measuring instruments tested to the evaluating-system.

6.4 Evaluation

The measuring equipment has a great number at analogous and digital options for the connection of data loggers. Furthermore the digital variants can be adapted in particular to the individual requirements of the ambient air quality measuring network operator.

The measuring equipment has analogue outputs that can be chosen in the ranges 0-100 mV, 1, 5, and 10V. The analogue output of 0 to 10 V was mainly employed for the suitability test.

The measuring equipment has analogous status outputs for all important device functions as failures, calibrating-cycles, measuring range changeover and diagnostic modes. The recording of the measuring data was made during the aptitude test by means of analogous voltage signals, however, the possibility to provide the measurement signals as a current signal through a spare-part (option) exists. Also a digital data transfer is possible.

6.5 Assessment

Measurement signals and operating states are recognized by downstream evaluating-systems correctly. All measurement signals can be provided in digital form and in analogue mode.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 4.2 Requirements for the mobile Application

Measuring systems for mobile application shall also comply with the requirements on measuring systems for stationary application in the case of mobile application. The measuring system shall be in a permanent operational stand-by mode during mobile application, e.g. measurements in running traffic, time-limited measurements at different locations or measurement on aircraft.

6.2 Equipment

Measuring vehicle.

6.3 Testing

The suitability of the measuring equipment for a mobile application (in running vehicles, airplanes etc.) was not tested. However, the measuring equipment can be used without problems for temporary measurements at different places.

6.4 Evaluation

The measuring equipment can be used without problems for temporary measurements at different places. The transportation of the measuring equipment was not tested explicitly. Therefore the usual protective measures are to be planned during the transportation against vibrations. Furthermore the set-up and warm-up times are to be considered.

6.5 Assessment

An evaluation is dropped, because this possible application was not tested.

Minimum requirement fulfilled? not applicable

6.6 Documentation

Here not essential.

6.1 5.2.1 Measuring range

The upper limit of measurement of the systems shall be greater or equal to reference value B_2.

EN 14625: Certifying-range 0 - 500 µg/m³ (corresponds to 250 ppb)

6.2 Equipment

The measuring system to be tested.

6.3 Testing

It was tested whether the measuring range of the measuring system can be tuned freely and at least the required values are reached.

6.4 Evaluation

The measuring ranges can be chosen between 0-0.05 ppm and 0-200 ppm freely. It is possible, to indicate the measurement result on the display in different units (for example [ppb], [µg/m³]).

6.5 Assessment

The measuring ranges can be chosen optional according to the requirements. Also the measuring range requirements are kept according to EN 14625.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.2 Negative output signals

Negative output signals or measured values may not be suppressed (life zero).

6.2 Equipment

Zero- and test-gas in suitable concentration, multimeter

6.3 Testing

Through the zero point calibration with a specific ozone concentration the zero point of the measuring system was displaced so far, that applying up zero gas negative measurement signals were indicated. At the reference point the display range was determined by application of ozone concentrations above the full range.

6.4 Evaluation

From the experiments the following output variations at a configured analogue output range of 0 to 10 volt resulted:

Table 6: Overview of the life zero

	Minimum display field	Maximum display field
Unit 1	-0.6 Volt	11.62 Volt
Unit 2	-0.61Volt	11.58 Volt

6.5 Assessment

The position of the zero point measuring signal is so far of remote electrical zero, that the permissible zero point drift can surely be registered.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.3 Analytical function

The relationship between the output signal and the value of the air quality characteristic shall be represented by the analytical function and determined by regression analysis.

6.2 Equipment

For the examination different ozone concentrations were generated by means of a ozone generator. The ozone generator was actuated with synthetic air from cylinders.

6.3 Testing

The examination was made by application of graded ozone concentrations to the measuring system to be tested by means of the ozone generator.

6.4 Evaluation

The slope and the intercept of an axis of the calibrating-function

$$Y = m * x + b$$

were determined through linear regression and subsequently are given in Table 7 and Table 8 for the five calibrating-cycles together with the coefficients of correlation:

Table 7: Individual results of the 5 series of experiments for the determination of the calibrating-function

Unit 1

Number	**1**	**2**	**3**	**4**	**5**
Slope m [(µg/m³)/(µg/m³)]	1.0025	1.0001	1.0033	1.0008	1.0022
Intercept of the axis b [µg/m³]	0.19	0.39	0.22	-0.20	0.56
Correlation coefficient	1	1	0.999	1	1

Unit 2

Number	**1**	**2**	**3**	**4**	**5**
Slope m [(µg/m³)/(µg/m³)]	0.9987	0.9987	1.0014	1.0020	1.0017
Intercept of the axis b [µg/m³]	0.86	0.88	0.33	0.40	0.40
Correlation coefficient	1	1	0.999	0.999	0.999

The analytical function was determined through conversion of the calibrating-function and reads as follows:

$$X = 1/m * y - b/m$$

In the following table the values for the slopes and the intercepts of an axis for the analytical functions are given.

Table 8: Individual results of the 5 series of experiments for the determination of the analytical function

Unit 1

Number	**1**	**2**	**3**	**4**	**5**
Slope 1/m [(µg/m³)/(µg/m³)]	0.9975	0.9999	0.9967	0.9992	0.9978
Intercept of the axis b/m [µg/m³]	0.1895	0.3900	0.2193	-0.1944	0.5588

Unit 2

Number	**1**	**2**	**3**	**4**	**5**
Slope 1/m [(µg/m³)/(µg/m³)]	1.0013	1.0013	0.9986	0.9980	0.9983
Intercept of the axis b/m [µg/m³]	0.8611	0.8811	0.3295	0.3992	0.3993

6.5 Assessment

The relations between output signal and measurement variable are sufficiently representable by means of the analytical function and were determined through regression analysis.

Minimum requirement fulfilled? yes

6.6 Documentation

The single values are given in Table 48 to Table 52 in the appendix. A graphical representation can be taken from the Figure 6 and from Figure 7.

6.1 5.2.4 Linearity

Reliable linearity is given, if deviations of the group averages of measured values about the calibration function are smaller than 5 % of B_1 in the range of zero to B_1, and smaller than 1 % of B_2 in the range of zero to B_2.

EN 14625: 8.4.6 „lack of fit" (deviation of the linear regression function) 5 nmol/mol (corresponds to 5 ppb or 10 µg/m³) at zero and ≤ 4 % at the span point.

6.2 Equipment

Different ozone concentrations were made using a ozone generator type CGM 2000 from the manufacturer MCZ. The ozone generator runs with synthetic air out of cylinders.

6.3 Testing

The examination was made by application of graded ozone concentrations to the measuring system to be tested by means of a ozone generator analogously to the examination of the analytical function. The results were evaluated according to the rules of the linearity check.

The guideline VDI 4203 part 3 as well as the EN 14625 demands for this examination for the application of test gases at 6 different, uniformly distributed point in the respective measuring ranges. In order to meet the criteria of both guidelines, the number of the measurement points was expanded, so that for the measuring range of 0 - 360 µg/m³ as well as for the range 0- 500 µg/m³ a sufficient number of measured values could be recorded.

6.4 Evaluation

For each individual concentration level the mean value was determined about the five series of measurements. The deviation of the group mean values to the target values from the analysis function was determined and compared with the minimum requirements.

Thus a maximum deviation for values between zero and B_1 of 0.82 µg/m³ respectively 0.28 µg/m³ and a maximum deviation for values between zero and B_2 of 1.42 µg/m³ respectively 1.18 µg/m³ were derived. The detailed results of the investigations can be found in Table 9 and Table 10.

Regarding the EN 14625 criteria's the following results have been determined:

For device 1 a deviation from the linear regression line of 0.60 µg/m³ (equivalent to 0.30 ppb) at zero and maximum 1.64 % of measured value at a concentrations higher than zero could be determined.

For device 2 a deviation from the linear regression line of 0.02 µg/m³ (equivalent to 0.01 ppb) at zero and maximum 1.16 % of measured value at a concentrations higher than zero could be determined.

Table 9: Linearity Thermo 49i from group mean values, device 1

Test gas value [µg/m³]	Measuring [µg/m³]	Deviation [µg/m³]	Allowed deviation VDI 4202 [µg/m³]	Allowed deviation EN 14625 [µg/m³]	Deviation [% of measured value]
0	0,60	0,6	4	10	-----
50	50,82	0,82	4	2	1,64
100	99,54	-0,46	3,6	4	-0,46
150	149,84	-0,16	3,6	6	-0,11
200	201,22	1,22	3,6	8	0,61
250	251,42	1,42	3,6	10	0,57
300	300,26	0,26	3,6	12	0,09
350	350,16	0,16	3,6	14	0,05
400	400,78	0,78	3,6	16	0,20
450	451,68	1,68	3,6	18	0,37
500	501,22	1,22	3,6	20	0,24

Table 10: Linearity Thermo 49i from group mean values, device 2

Test gas value [µg/m³]	Measuring [µg/m³]	Deviation [µg/m³]	Allowed deviation VDI 4202 [µg/m³]	Allowed deviation EN 14625 [µg/m³]	Deviation [% of measured value]
0	0,02	0,02	4	10	-----
50	50,28	0,28	4	2	0,56
100	101,16	1,16	3,6	4	1,16
150	150,40	0,4	3,6	6	0,27
200	201,16	1,16	3,6	8	0,58
250	251,70	1,7	3,6	10	0,68
300	301,18	1,18	3,6	12	0,39
350	350,44	0,44	3,6	14	0,13
400	398,92	-1,08	3,6	16	-0,27
450	451,56	1,56	3,6	18	0,35
500	500,88	0,88	3,6	20	0,18

6.5 Assessment

As given in table 9 and table 10, the two candidates meet the requirements of the guideline of VDI 4202 and the EN 14625 in full extent.

Minimum requirement fulfilled? yes

6.6 Documentation

In Table 11 and Table 12 as well as in Figure 6 and Figure 7 the results of the group mean value investigations are given comprehensively in graphic and in tabular form. The single values are given in the appendix in Table 48 to Table 52.

Table 11: Statistical characteristics on basis of the group mean values for device 1

Characteristics device 1				
Standard deviation	s	=	0.643	
Coefficient of correlation	r	=	1.0000	
Y = b* x + c Slope	b	=	1.002	
Intercept	c	=	0.234	µg/m³
Mean value	Measuring value	=	250.0	µg/m³
Mean value	Expected value	=	250.7	µg/m³

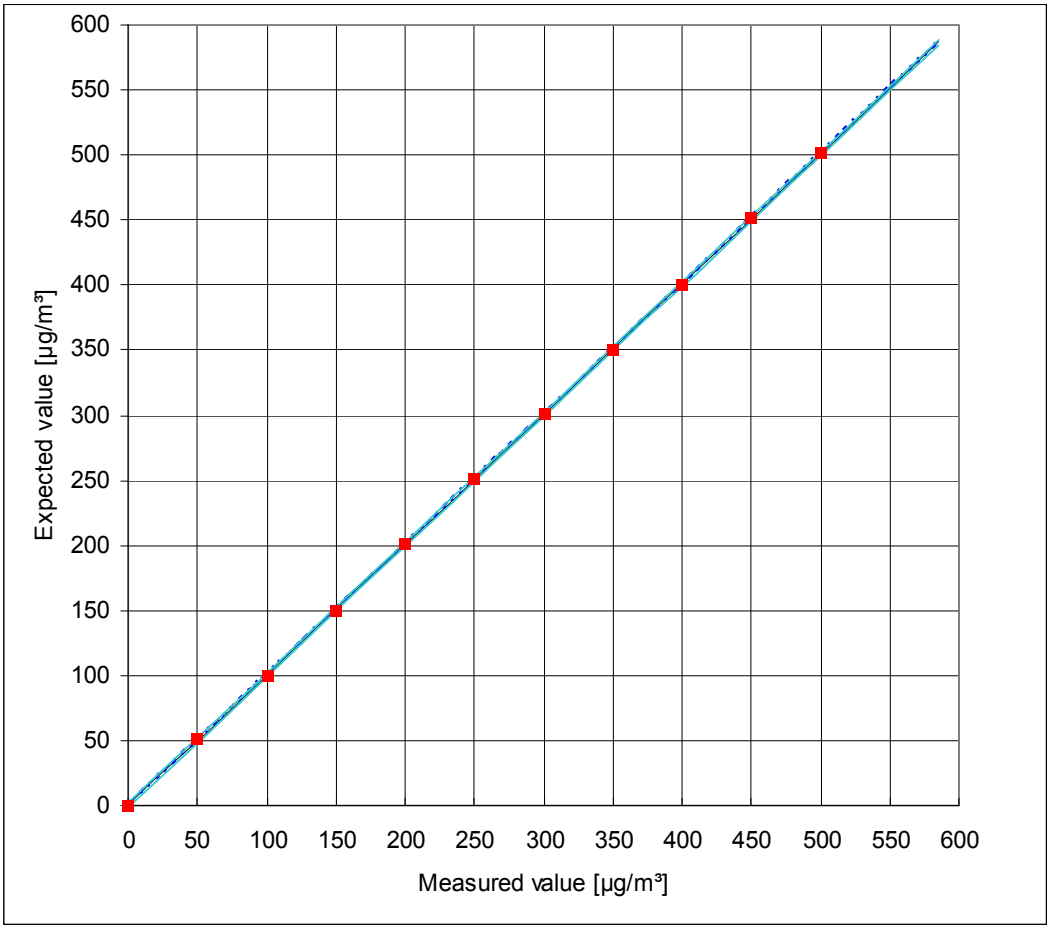


Figure 6: Analytical function from the group mean values for device 1

Table 12: Statistical characteristics on basis of the group mean values for device 2

Characteristics device 2				
Standard deviation	s	=	0.838	
Coefficient of correlation	r	=	1.0000	
Y = b* x + c Slope	b	=	1.001	
Intercept	c	=	0.573	µg/m³
Mean value	Measuring value	=	250.0	µg/m³
Mean value	Expected value	=	250.7	µg/m³

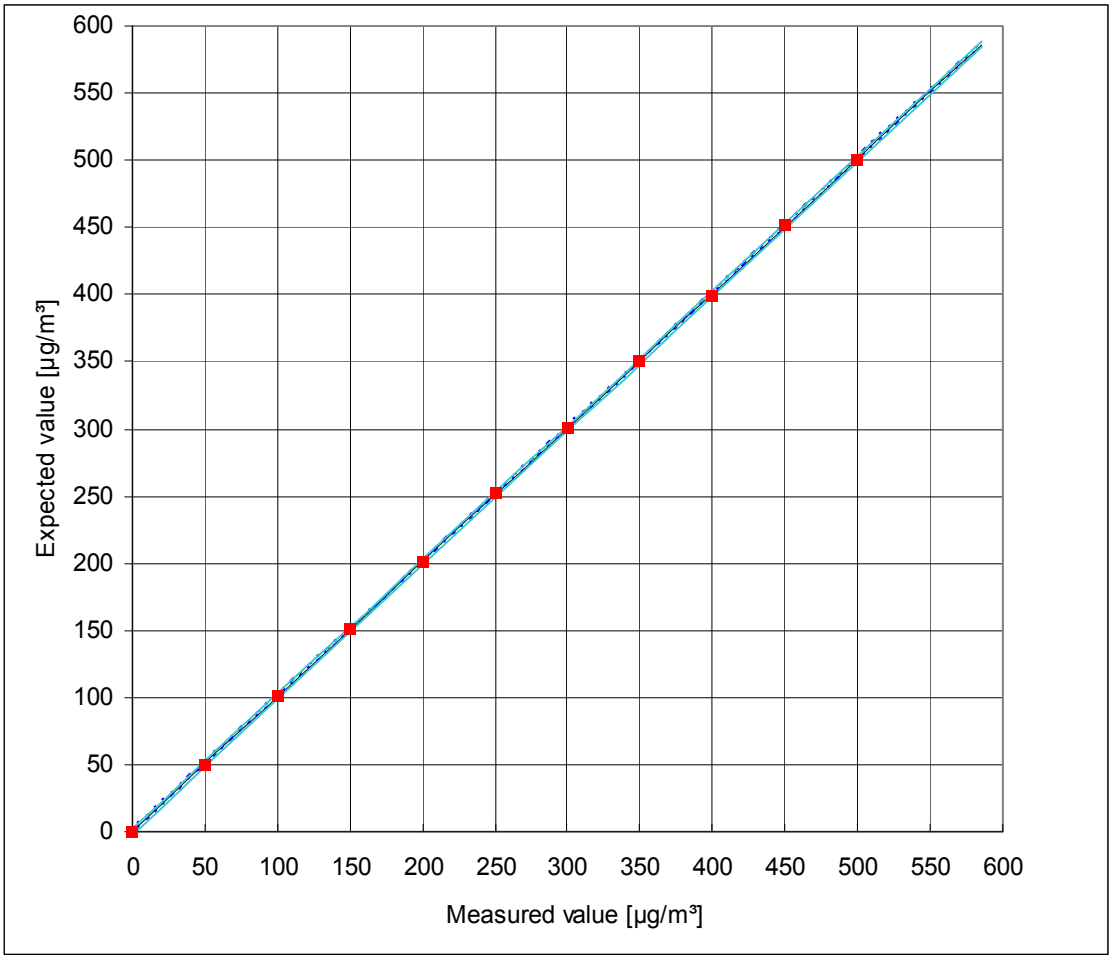


Figure 7: Analytical function from the group mean values for device 2

6.1 5.2.5 Detection limit

The detection limit of the measuring system shall be smaller or equal to reference value B_0. The detection limit shall be determined in the field.

EN 14625 8.4.5 repeating standard deviation *at zero ≤ 1.0 nmol/mol (corresponds to 1 ppb or 2 µg/m³); at the span point ≤ 3 nmol/mol (corresponds to 3 ppb or 6 µg/m³)*

6.2 Equipment

Zero gas and test gas in suitable concentrations.

6.3 Testing

The examination was done through alternating application of zero and reference gas. The detection limit is determined in the lab and at the end of the field test. The detection limit is determined according to the guideline VDI 4203 part 3 from 15 measured values each. According to the EN 14625 for the determination of the detection limit 20 measured values each are necessary. The EN 14625 demands only for one time of testing of the detection limit in the lab. In order to meet the requirements of both guidelines, the detection limit was determined in the lab with 20 single measured values in each case and in the field test with 15 single measured values in each case.

6.4 Evaluation

On basis of the measuring data recorded in lab and field the evaluation was carried out. The test criterion of the detection limit is regarded as fulfilled, if the detection limit in the lab and field is smaller than B0 = 4 µg/m³. The Table 13 and Table 14 show in conclusion the results of the investigations. According to the requirements of the VDI the detection limit is defined as 3* standard deviation (VDI 2449 part 1).

The repeating standard deviation of this measurement demanded for in EN 14625 is calculated as follows:

$$s_r = \sqrt{\frac{\sum \left(x_i - \bar{x}\right)^2}{n-1}}$$

In this case is

s_r the repeating standard deviation

x_i the i-th measurement

$\bar{x}$ the mean value of the 20 measurements

n the number of the measurements

Table 13: Survey of the detection limits Thermo 49i device 1

Measurement		Zero point		Span point	
		Lab	Field	Lab	Field
		µg/m³	µg/m³	µg/m³	µg/m³
Number	n	20	15	20	15
Mean value	x	1.91	-1.46	79.39	83.95
Repeating standard deviation	**s**	**0.17**	**0.19**	**0.30**	**0.34**
DL = 3 * standard deviation	**3s**	**0.51**	**0.57**	**0.90**	**1.02**
Requirements of VDI 4202	µg/m³	4	4	4	4
Met requirements?		**yes**	**yes**	**yes**	**yes**
Requirements of EN 14625	µg/m³	2	----	6	----
Met requirements?		**yes**	**----**	**yes**	**----**

Table 14: Survey of the detection limits Thermo 49i device 2

Measurement		Zero point		Span point	
		Lab	Field	Lab	Field
		µg/m³	µg/m³	µg/m³	µg/m³
Number	n	20	15	20	15
Mean value	x	1.14	-0.12	78.37	84.64
Repeating standard deviation	**s**	**0.19**	**0.18**	**0.33**	**0.31**
DL = 3 * standard deviation	**3s**	**0.57**	**0.54**	**0.99**	**0.93**
Requirements of VDI 4202	µg/m³	4	4	4	4
Met requirements?		**yes**	**yes**	**yes**	**yes**
Requirements of EN 14625	µg/m³	2	----	6	----
Met requirements?		**yes**	**----**	**yes**	**----**

6.5 Assessment

The detection limit is with 0.57 µg/m³ respectively 0.54 µg/m³ at zero and 1.02 µg/m³ respectively 0.93 µg/m³ at span point within the minimum requirements of VDI 4202.

Minimum requirement fulfilled? yes

The determined repeating standard deviation of EN 14625 is 0.17 µg/m³ (equal to 0.09 ppb) respectively 0.19 µg/m³ (equal to 0.10 ppb) at zero and 0.30 µg/m³ (equal to 0.15 ppb) respectively 0.33 µg/m³ (equal to 0.17 ppb) at span.

6.6 Documentation

The individual results are in the appendix performed in Table 53and Table 54.

6.1 5.2.6 Response time

The response time (90% time) of the measuring system shall be smaller or equal to 5 % of the averaging time 180 s).

EN 14625: 8.4.3 Response time (rise) and response time (fall) each ≤ 180 s. Difference between rise and fall time ≤ 10 % relative Difference or 10 s, depending on which value is higher.

6.2 Equipment

Zero and reference gas in suitable concentration as well as a data recording system were used for the determination of the response time.

6.3 Testing

The rise and fall times were registered by means of data recording system and examined for the 90 %-time.

6.4 Evaluation

The rise and fall times are stated in Table 15:

Table 15: Increasing and falling response times of the two measuring units

Start value [µg/m³]	Final value 90% [µg/m³]	Time unit 1 [s]	Time unit 2 [s]	Requirement according to VDI 4202 and EN 14625 [s]	Requirement fulfilled?
0	324	58	56	180	yes
360	36	62	63	180	yes
	Difference	**4**	**7**		
0	324	59	57	180	yes
360	36	63	65	180	yes
	Difference	**4**	**8**		
0	324	59	57	180	yes
360	36	66	63	180	yes
	Difference	**7**	**6**		
0	324	55	54	180	yes
360	36	64	62	180	yes
	Difference	**9**	**8**		

According to EN 14625 in addition the difference between rise and fall time may be at maximum 10 % or 10 s. Depending on whether which value is higher.

The relative difference of the response time is calculated according to following equation:

$$t_d = \left| \frac{t_r - t_f}{t_r} \right| \times 100\%$$

With: t_d the relative difference between rise - and fall time

t_r the response time (rise) (Mean value of 4 measurements) (s)

t_f the response time (fall) (Mean value of 4 measurements) (s)

For device 1 a maximum t_r of 59 s, a maximum t_f of 66 s and a t_d of 10.39 % has been calculated.
For device 2 a maximum t_r of 57 s, a maximum t_f of 65 s and a t_d of 12.95 % has been calculated.
A relative difference between rise and fall time of more than 10 % has been determined. The absolute difference is less than 10 seconds, so this requirement is fulfilled.

6.5 Assessment

The maximal permissible response time of 180 seconds is fallen below clearly. The difference between rise and fall time is smaller than 10 seconds like required in the EN 14625.

Minimum requirement fulfilled? yes

6.6 Documentation

The test results are stated in Table 15.

6.1 5.2.7 Dependence of the zero point on ambient temperature

The temperature dependence of the measured value at zero shall not exceed the reference value B_0 if ambient temperature is changed by 15 K in the range of +5 °C to +20 °C or 20 K in the range of +20 °C und +40 °C.

EN 14625 8.4.9 Sensitivity coefficient of the ambient temperature ≤ 1.0 nmol/mol/K (corresponds to 1 ppb/K or 2 (µg/m³)/K)

6.2 Equipment

Climate chamber.

6.3 Testing

According to VDI 4202 part 1 the temperature dependence of the zero point is to be tested between + 5°C and + 40°C. The following temperature levels are tested subsequently in this case: 20°C → 5°C → 20°C → 40°C → 20°C. The test gases are applied three times per temperature point and the temperature program is run through for three times.

Differing from that the EN 14625 demands for an examination in the temperature range of 0°C to + 30°C. The following temperature points are tested subsequently in this case: 20°C → 0°C → 20°C → 30°C →20°C.

6.4 Evaluation

At every temperature level the deviations were determined to the starting point at 20°C. For every temperature step the mean value was calculated and compared with the minimum requirements. The permissible deviation from the starting point must not exceed B0 that is 4 µg/m³ at any temperature point.

Table 16: Mean values and evaluation of the temperature dependence according to VDI 4202, device 1

T [°C]	Mean value unit 1 [µg/m³]	Deviation to the mean value [µg/m³]	Allowed deviation [µg/m³]	Requirement fulfilled? VDI 4202
20	0.38	----	----	----
5	0.98	0.60	4	ja
20	0.33	----	----	----
40	0.36	0.03	4	ja
20	0.36	----	----	----

Table 17: Mean values and evaluation of the temperature dependence according to VDI 4202, device 2

T [°C]	Mean value unit 2 [µg/m³]	Deviation to the mean value [µg/m³]	Allowed deviation [µg/m³]	Requirement fulfilled? VDI 4202
20	0.58	----	----	----
5	1.16	0.58	4	ja
20	0.09	----	----	----
40	0.04	-0.05	4	ja
20	0.80	----	----	----

The greatest deviation of both devices 0.60 µg/m³ for device 1 and 0.58 µg/m³ for device 2 have been taken for the calculation of total uncertainty of VDI 4202.

Following EN 14625 the sensitivity coefficient of the ambient temperature must not exceed 2 µg/m³ per K temperature change.

The sensitivity coefficient results from following equation:

$$b_{st} = \left| \frac{x_T - \frac{x_1 + x_2}{2}}{T - T_1} \right|$$

In this case is:

b_{st} the dependence of the measured value from the ambient temperature (mg/m³)

x_T the mean value of the measurements at T_{min} or T_{max} (µg/m³)

x_1 the first mean value of the measurements at T_1 (µg/m³)

x_2 the second mean value of the measurements at T_1 (µg/m³)

T_1 the ambient air temperature in the lab (K)

T the ambient air temperature T_{min} or T_{max} (K)

Table 18: Sensitivity coefficient of the ambient temperature at the zero point according to EN 14625, device 1

	T [°C]	Mean value unit 1 [µg/m³]	determinated b_{st} [µg/m³]/K	allowed b_{st} [µg/m³]/K	Fulfilled ? EN 14625
T_1	20	0.38			
T_{min}	0	1.31	0.05	2	yes
T_1	20	0.36			
T_1	20	0.36			
T_{max}	30	0.36	0.00	2	yes
T_1	20	0.33			

Table 19: Sensitivity coefficient of the ambient temperature at the zero point according to EN 14625, device 2

	T [°C]	Mean value unit 2 [µg/m³]	determinated b_{st} [µg/m³]/K	allowed b_{st} [µg/m³]K	Fulfilled ? EN 14625
T_1	20	0.58			
T_{min}	0	0.62	0.00	2	yes
T_1	20	0.80			
T_1	20	0.80			
T_{max}	30	0.04	0.04	2	yes
T_1	20	0.09			

The maximum coefficient of this respectively the coefficient of the investigations on the Span-point has been used for the calculation of the total uncertainty regarding EN 14625.

6.5 Assessment

The change of the zero point is at all ambient temperatures within the limit of the minimum requirement. The criteria of the EN 14625 is fulfilled as well.

Minimum requirement fulfilled? yes

6.6 Documentation

The single dates of the investigations are to be taken from the appendix in Table 55.

6.1 5.2.8 Dependence of the measured value on ambient temperature

The temperature dependence of the measured value in the range of reference value B_1 shall not exceed 5 % of the measured value if ambient temperature is changed by 15 K in the range of +5 °C to +20 °C or 20 K in the range of +20 °C to +40 °C.

EN 14625: 8.4.9 Sensitivity coefficient of the ambient temperature ≤ 1.0 nmol/mol/K (corresponds to 1 ppb/K or 2 (µg/m³)/K)

6.2 Equipment

Climate chamber.

6.3 Testing

According to VDI 4202 part 1 the temperature dependence of the zero point is to be tested between + 5°C and + 40°C. The following temperature levels are tested subsequently in this case: 20°C → 5°C → 20°C → 40°C → 20°C. The test gases are applied three times per temperature point and the temperature program is run through for three times.

The concentration of the test gas is about B_1 (B_1 = 80 µg/m³).

Differing from that the EN 14625 demands for an examination in the temperature range of 0°C to + 30°C. The following temperature points are tested subsequently in this case: 20°C → 0°C → 20°C → 30°C →20°C.

The test gas concentration is between 70 - 80 % of the certificated range (approx. 320 µg/m³).

6.4 Evaluation

At every temperature level the deviations were determined to the starting point at 20°C. For every temperature step the mean value was calculated and compared with the minimum requirements. The permissible deviation from the starting point must not exceed 5 % of B_1 (4 µg/m³) at any temperature point.

Table 20: Mean values and evaluation of the temperature dependence of the span point according to VDI 4202, device 1

T [°C]	Mean value unit 1 [µg/m³]	Deviation to the mean value [µg/m³]	Allowed deviation [µg/m³]	Requirement fulfilled? VDI 4202
20	80.97	----	----	----
5	79.33	-1.64	4	yes
20	80.69	----	----	----
40	81.37	0.68	4	yes
20	80.97	----	----	----

Table 21: Mean values and evaluation of the temperature dependence of the span point according to VDI 4202, device 2

T [°C]	Mean value unit 2 [µg/m³]	Deviation to the mean value [µg/m³]	Allowed deviation [µg/m³]	Requirement fulfilled? VDI 4202
20	80.82	----	----	----
5	79.12	-1.70	4	yes
20	80.59	----	----	----
40	81.43	0.84	4	yes
20	80.02	----	----	----

The greatest deviation of both devices -1.64 µg/m³ for device 1 and -1.70 µg/m³ for device 2 have been taken for the calculation of total uncertainty of VDI 4202.

According to EN 14625 the sensitivity coefficient of the ambient temperature must not exceed to 2 µg/m³ per K temperature change.

The sensitivity coefficient results from following equation:

$$b_{st} = \left| \frac{x_T - \frac{x_1 + x_2}{2}}{T - T_1} \right|$$

In this case is:

b_{st} the dependence of the measured value from the ambient temperature (µg/m³)

x_T the mean value of the measurements at T_{min} or T_{max} (µg/m³)

x_1 the first mean value of the measurements at T_1 (µg/m³)

x_2 the second mean value of the measurements at T_1 (µg/m³)

T_1 the ambient air temperature in the lab (K)

T the ambient air temperature T_{min} or T_{max} (K)

Table 22: Sensitivity coefficient of the ambient temperature at the span point according to EN 14625, device 1

	T [°C]	Mean value unit 1 [µg/m³]	determinated b_{st} [µg/m³]/K	allowed b_{st} [µg/m³]/K	Fulfilled ? EN 14625
T_1	20	323.89			
T_{min}	0	317.31	0.30	2	yes
T_1	20	322.76			
T_1	20	322.76			
T_{max}	30	325.47	0.22	2	yes
T_1	20	323.87			

Table 23: Sensitivity coefficient of the ambient temperature at the span point according to EN 14625, device 2

	T [°C]	Mean value unit 2 [µg/m³]	determinated b_{st} [µg/m³]/K	allowed b_{st} [µg/m³]/K	Fulfilled ? EN 14625
T_1	20	323.27			
T_{min}	0	316.47	0.32	2	yes
T_1	20	322.36			
T_1	20	322.36			
T_{max}	30	325.71	0.25	2	yes
T_1	20	324.07			

The maximum coefficient of this respectively the coefficient of the investigations on the Zero-point has been used for the calculation of the total uncertainty regarding EN 14625.

6.5 Assessment

The change of the span point is at all ambient temperatures within the limit of the minimum requirement. The criterion of the EN 14625 is fulfilled also.

Minimum requirement fulfilled? yes

6.6 Documentation

The single dates of the investigations are to be taken from the appendix in Table 56 and Table 57.

6.1 5.2.9 Drift of zero point

The temporal change in the measured value at zero concentration shall not exceed the reference value B_0 in 24 h and in the maintenance interval.

EN 14625: 8.4.4 Short term drift at zero ≤ 2.0 nmol/mol/12h (corresponds to 2 ppb/12h or 4 (µg/m³)/12h)
EN 14625: 8.5.4 Long term drift at zero ≤ 5.0 nmol/mol (corresponds to 10 µg/m³)

6.2 Equipment

For the determination of the zero point drift synthetic air has been used.

6.3 Testing

The offering of zero air was made over a time interval of 15 minutes daily. The last 5 minutes of this time interval were recorded, averaged and evaluated.

6.4 Evaluation

The following graphics show the process of the test gas offerings for both analysers during three months field test operation.

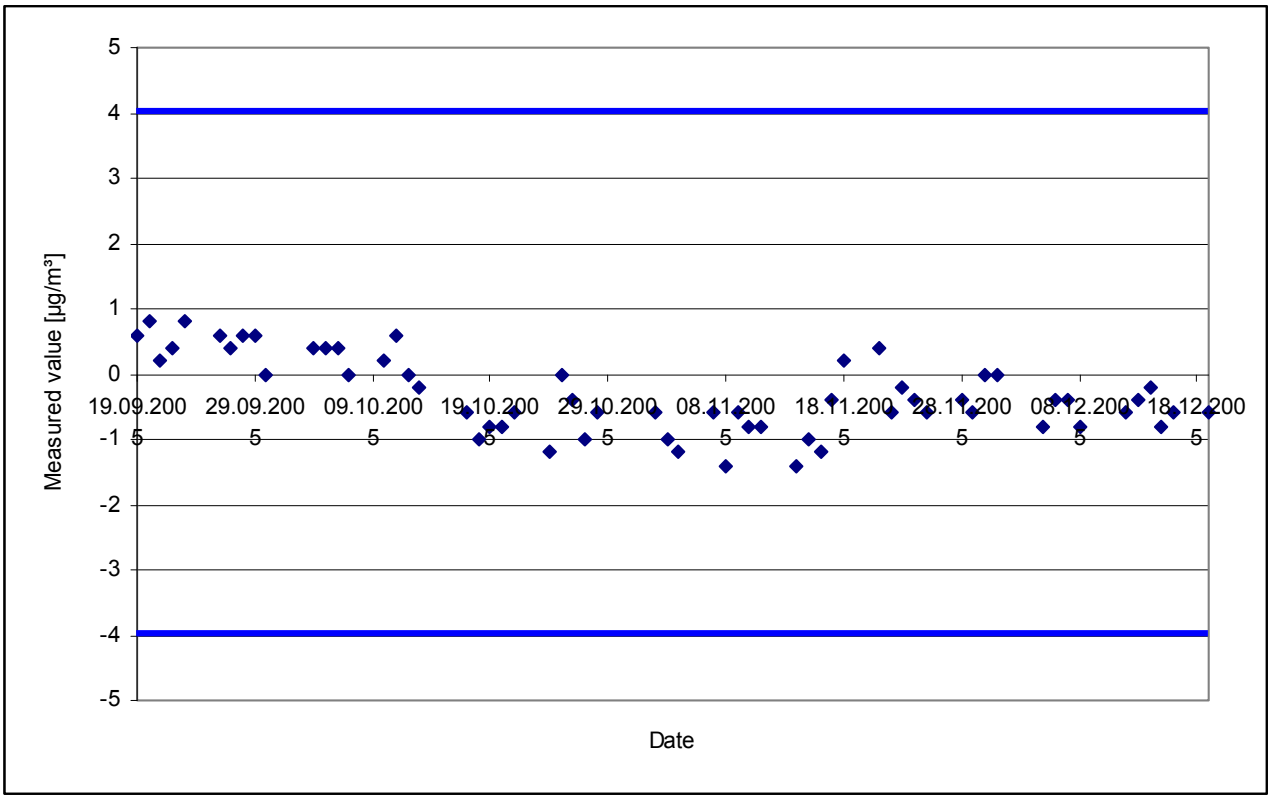


Figure 8: Temporal change of the zero points during the field test, unit 1

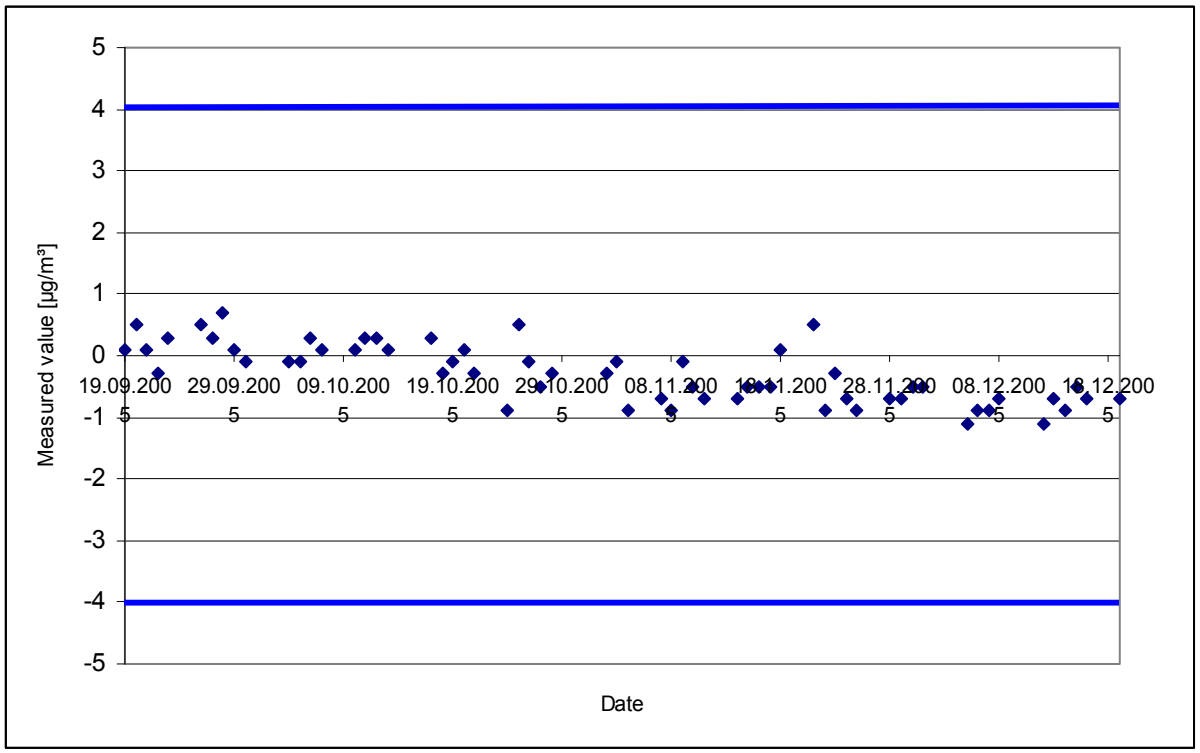


Figure 9: Temporal change of the zero points during the field test, unit 2

The minimum standard requires, that the temporal change of the measured value at the zero point in 24 h and in the maintenance interval must not exceed the basic value B_0 (corresponds 4 µg/m³ for O_3). No exceeding of the 24 hour drift results from the data derived. The calculation of the regression functions gives the following values for the zero point drift for analyser 1 and 2 in the 24 hour interval

The allowed long term drift at zero is according to EN 14625 10 µg/m³. This requirement is fulfilled during the whole field test.

The middle temporal change in 24 h conducted during the field test:

Unit 1: -0.0119 µg/(m³*d)

Unit 2: -0.0131 µg/(m³*d)

In the maintenance interval of a month the middle temporal change conducts:

Unit 1: -0.357 µg/(m³*month) equal to -0.179 ppb/month

Unit 2: -0.393 µg/(m³*month) equal to -0.197 ppb/month

Following the EN 14625 the short-term drift is to be determined in the lab with in each case 20 single measurements before and after a 12 h duration of time.

Short term drift at zero level:

$$D_{S,Z} = (C_{Z,2} - C_{Z,1})$$

In this case is:

$D_{S,Z}$ the 12-hour-drift at zero level (µg/m³)

$C_{Z,1}$ the mean of the zero gas measurement at the beginning of the drift period (µg/m³)

$C_{Z,2}$ the mean of the zero gas measurement at the end of the drift period (µg/m³)

The following short-term drifts are resulting at the zero level:

Unit 1: 0.12 (µg/m³)/12 h equal to 0.06 ppb/ 12 h

Unit 2: -0.16 (µg/m³)/12 h equal to -0.08 ppb/12 h

6.5 Assessment

In Figure 8 and Figure 9 is to be seen, that the zero point drifts meets the minimum requirements . Also the short-term drift of the EN 14625 fulfils the required criterion. The requirement of the long-term drift to EN 14625 is in the allowed limits.

Figure 8Minimum requirement fulfilled? yes

6.6 Documentation

See Figure 8 and Figure 9. The single values of the short term drift according to EN 14625 are shown in Table 58 and Table 59 in the appendix.

6.1 5.2.10 Drift of the measured value

The temporal change in the measured value in the range of reference of reference value B_1 shall not exceed 5 % of B_1 in 24 h and in the maintenance interval.

EN 14625: 8.4.4 Short term drift at span level ≤ 6.0 nmol/mol/12h (corresponds to 6 ppb/12h or 12 (µg/m³)/12h)
EN 14625: 8.5.4 Long term drift at span level ≤ 5 % of the measuring range (corresponds to 25 µg/m³ at a range of 0 to 500 µg/m³)

6.2 Equipment

Ozone generator

6.3 Testing

The offering of test gas was made over a period of 15 minutes daily. The last 5 minutes of this time interval were recorded, averaged and evaluated.

6.4 Evaluation

The following graphics show the process of the test gas offerings for both analysers during three months field test operation.

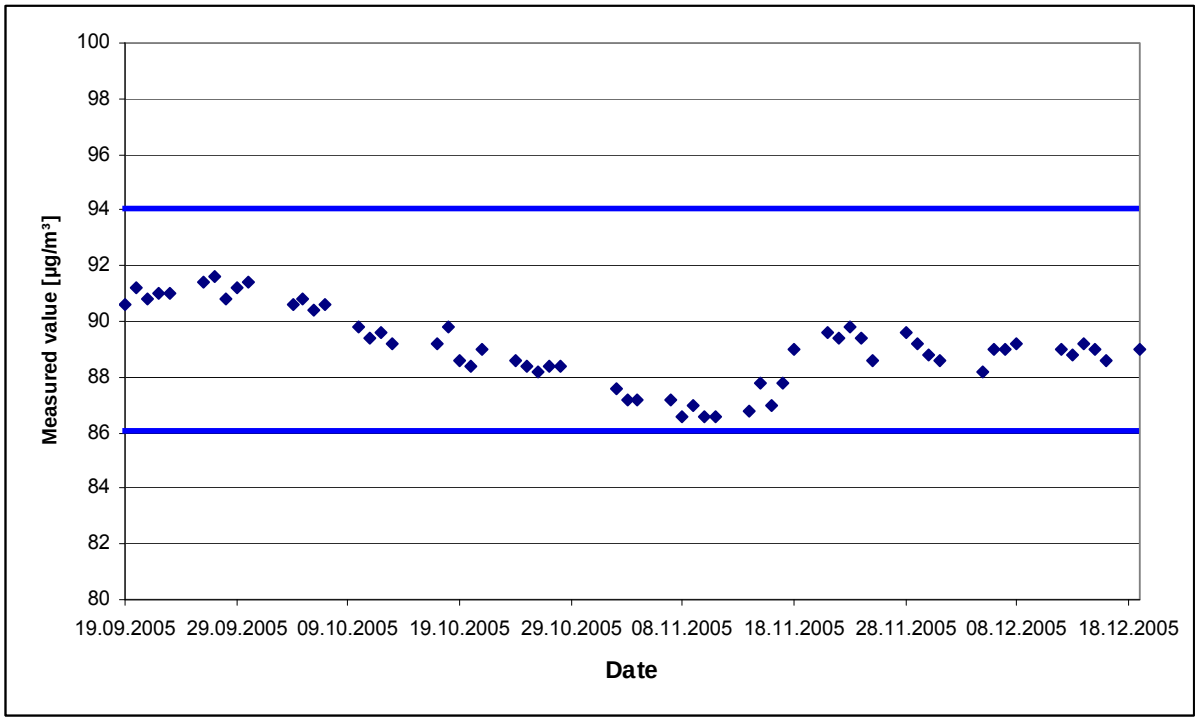


Figure 10: Temporal change of the span points during the field test, unit 1

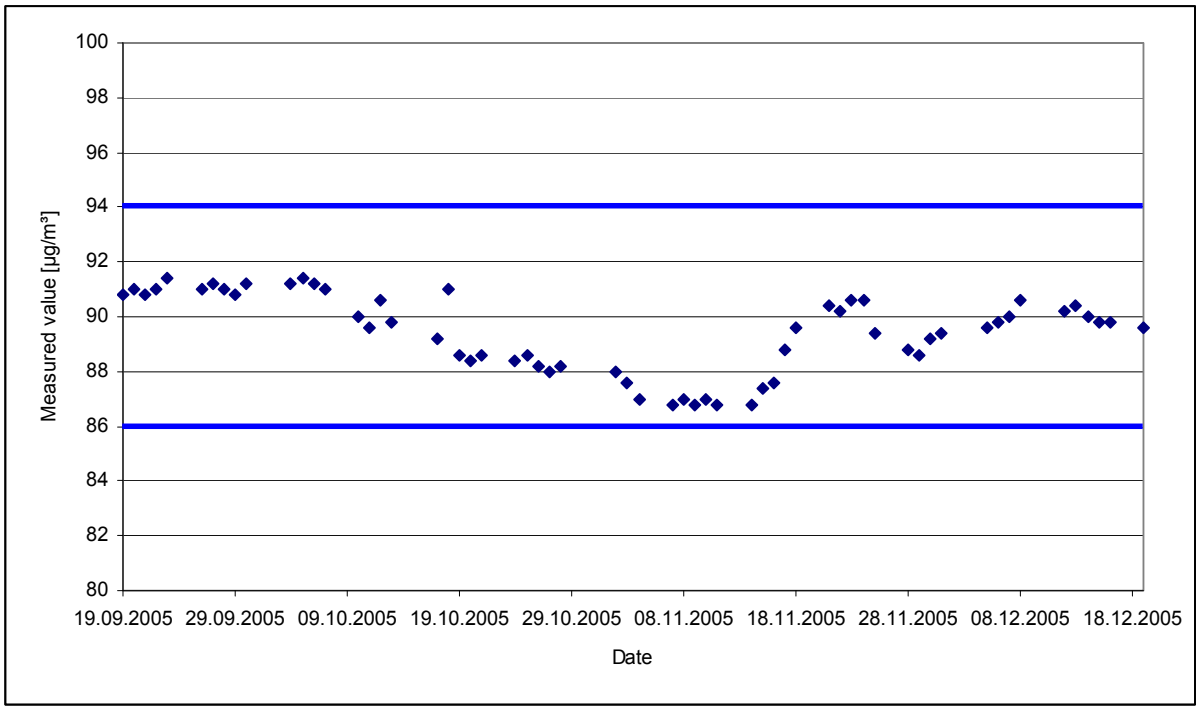


Figure 11: Temporal change of the span points during the field test, unit 2

The minimum standard requires, that the temporal change of the measured value in 24 h at the span point and in the maintenance interval must not exceed 5% of the basic value B_1 (corresponds 4 µg/m³ for ozone).

Out of the data results no exceeding of the 24 hour drift. The calculation of the regression function gives the following values for the span point drift for analyser 1 and 2 in the 24 hour interval.

The allowed long term drift at span level according to EN 14625 is 25 µg/m³ and is kept during the whole field test.

The middle temporal change in 24 h conducted during the field test:

Unit 1: -0.027 µg/(m³*d)

Unit 2: -0.019 µg/(m³*d)

In the maintenance interval of a month the middle temporal change conducts:

Unit 1: -0.81 µg/(m³*month) equal to -0.41 ppb/month equal to -0.16 % of range

Unit 2: -0.57 µg/(m³*month) equal to -0.29 ppb/month equal to -0.12 % of range

Following the EN 14625 the short-term drift in the lab is determinated with in each case 20 single measurements before and after a 12 h duration of time.

Short term drift at span level:

$$D_{S,S} = (C_{S,2} - C_{S,1}) - D_{S,Z}$$

In this case is:

$D_{S,S}$ the 12-hour-drift at span level (µg/m³)

$C_{S,1}$ the mean of the zero gas measurement at the beginning of the drift period (µg/m³)

$C_{S,2}$ the mean of the zero gas measurement at the end of the drift period (µg/m³)

The following short-term drifts are resulting at the span level:

Unit 1: -2.67 (µg/m³)/12 h equal to -1.34 ppb/12 h

Unit 2: 0.57 (µg/m³)/12 h equal to 0.29 ppb/12 h

6.5 Assessment

In Figure 10 and Figure 11 is to be seen, that the span point drift meets the minimum requirements. Also the short-term drift of the EN 14625 fulfils the required criterion. The requirement of the long-term drift to EN 14625 is in the allowed limits.

Minimum requirement fulfilled? yes

6.6 Documentation

See Figure 10 and Figure 11. The single values of the short term drift according to EN 14625 are shown in Table 58 and Table 59 in the appendix.

6.1 5.2.11 Cross-sensitivities

The absolute values of the sum of the positive and the sum of the negative deviations caused by cross-sensitivities of interfering components in the measured sample shall not exceed B_0 at the zero point and shall not exceed 3 % of B_2 in the range of B_2. The concentration of interfering components shall correspond to the B_2 value of the respective interfering component. If reference values have not been specified, the test institute shall specify and declare suitable reference values in agreement with other test institutes. Especially the components listed in table 1 shall be taken into account in the check of cross-sensitivities. If necessary, additional components shall be taken into account on the basis of the measurement method.

EN 14625 8.4.11 Interferences – allowed deviations for H_2O ≤ 10 nmol/mol (corresponds to 10 ppb or 20 µg/m³); for Toluene and Xylene each ≤ 5 nmol/mol (corresponds to 5 ppb or 10 µg/m³)

6.2 Equipment

Ozone generator, reference gases, mass-flow-controller

6.3 Testing

For the determination of the cross-sensitivities the components listed in Table 24 have been taken into account. On the basis of the measuring method additional components are considered.

Table 24: Interfering components and values

Interferent	Value
CO_2	700 mg/m³
CO	60 mg/m³
H_2O	30 % bis 90 % relative humidity
SO_2	700 µg/m³
NO	100 µg/m³ to 1000 µg/m³
NO_2	400 µg/m³
N_2O	500 µg/m³
H_2S	30 µg/m³
NH_3	30 µg/m³
Benzene	1 mg/m³
Toluene	1,9 mg/m³
Xylene	2,4 mg/m³

6.4 Evaluation

The differences detected are given in the following table with and without interfering component for the zero and span point of the two analysers. At the bottom of the table the sums of the positive and the negative deviations are summarized. The values are to be compared with the minimum requirement that demands for a deviation of the positive and negative sums at the zero point of 4 µg/m³ (B_0) and a deviation of 10.8 µg/m³ (3 % of B_2) at the span point.

Table 25: Cross-sensitivities Thermo 49i according to VDI 4202 part 1

Interferent			Analyser 1		Analyser 2	
			Deviation [µg/m³]		Deviation [µg/m³]	
			ZP	SP	ZP	SP
CO_2	700	mg/m³	0.03	1.33	0,07	1,53
CO	60	mg/m³	0.27	-0.47	0,30	-0,20
H_2O	80	rel.-%	-1.97	-3.27	-1,60	-3,13
SO_2	700	µg/m³	2.63	2.87	2,50	3,47
NO	1000	µg/m³	-0.20	0.73	-0,20	0,60
NO_2	400	µg/m³	0.03	-3.33	0,20	-3,20
N_2O	500	µg/m³	0.03	-0.20	0,07	0,07
H_2S	30	µg/m³	0.13	0.40	0,10	0,47
NH_3	30	µg/m³	0.10	-1.07	0,17	-1,07
Benzene	1	mg/m³	-0.13	0.80	0,20	1,67
Toluene	1,9	mg/m³	0.20	1.93	0,13	1,07
Xylene	2,4	mg/m³	0.20	1.87	0,07	1,00
Sum of negative deviations			**-2.30**	**-8.34**	**-1.80**	**-7.60**
Sum of positive deviations			**3.62**	**9.93**	**3.81**	**9.88**
Allowed deviation [µg//m³]			4	10.8	4	10.8
Requirement fulfilled?			yes	yes	yes	yes

The cross sensitivity fulfills the requirements. For the calculation of total uncertainty regarding VDI 4202 the greatest total cross sensitivity for each device has been used. This is 9.93 µ/m³ for device 1 und 9.88 µg/m³ for device 2.

Table 26: Interfering components according to EN 14625

Cross-sensitivity according to EN 14625			Unit 1		Unit 2	
			Deviation [µg/m³]		Deviation [µg/m³]	
			ZP	SP	ZP	SP
H_2O	80	rel-%	-1.97	-3.27	-1.60	-3.13
Maximum deviation			20	20	20	20
Fulfilled ?			**yes**	**yes**	**yes**	**yes**
Toluene	1,9	mg/m³	0.20	1.93	0.13	1.07
Maximum deviation			10	10	10	10
Fulfilled ?			**yes**	**yes**	**yes**	**yes**
Xylene	2,4	mg/m³	0.20	1.87	0,07	1,00
Maximum deviation			10	10	10	10
Fulfilled ?			**yes**	**yes**	**yes**	**yes**

Regarding EN 14625 the following deviations in ppb have been determined:

Cross-sensitivity according to EN 14625			**Unit 1**		**Unit 2**	
			Deviation [ppb]		**Deviation [ppb]**	
			ZP	SP	ZP	SP
H_2O	80	rel-%	-0,98	-1,64	-0,80	-1,57
Maximum deviation			10	10	10	10
Fulfilled ?			**yes**	**yes**	**yes**	**yes**
Toluene	1,9	mg/m³	0,10	0,97	0,07	0,54
Maximum deviation			5	5	5	5
Fulfilled ?			**yes**	**yes**	**yes**	**yes**
Xylene	2,4	mg/m³	0,10	0,94	0,04	0,50
Maximum deviation			5	5	5	5
Fulfilled ?			**yes**	**yes**	**yes**	**yes**

For the calculation of total uncertainty regarding EN 14625 the deviations in ppb have been used.

6.5 Assessment

The cross-sensitivities of the measuring systems fulfil the minimum requirements. As to see in Table 26, the requirements of the EN 14625 are kept for H_2O, Toluene and Xylene as well.

Minimum requirement fulfilled? yes

6.6 Documentation

The single values are given in Table 60 to Table 63.

6.1 5.2.12 Reproducibility R_D

The reproducibility R_D of the measuring system shall be determined by parallel measurements with two identical measuring systems and shall be at least equal to 10. B_1 shall be used as the reference value.

EN 14625: 8.5.5 Standard deviation under field conditions ≤ 5 % of the average over 3 month.

6.2 Equipment

In addition to the measuring system a ozone test gas has been used for the enrichment of the sampled air .

6.3 Testing

In the lab test zero gas and test gas was offered the device by 10 turns in repetition. The concentration levels were applied in each case for 15 minutes. The last 5 minutes were recorded as a mean value and used for the further calculations.

For the calculation of the reproducibility in the field the data were selected from a level of 80 µg/m³ ± 20 %. Additionally the reproducibility was calculated about all measured values in the field test.

6.4 Evaluation

The Table 30 shows the single values of the results achieved in the lab test. In Table 27 the statistical parameters of the evaluation are given.

Table 27: Evaluation of the reproducibility R_D in the lab test

Repeatability in the lab test				
No. of values	n	=	10	
Reference value		=	80	µg/m³
t-value for the selected safety	t95	=	2.229	
Standard deviation out of parallel measurements	sd	=	0.699	
Reproducibility R_D	**R(d)**	**=**	**51**	
Mean value	Unit 1	=	81.3	µg/m³
Mean value	Unit 2	=	82.2	µg/m³

The following picture shows the evaluation of the repeatability in the field for the value pairs in the range of B_1 ± 20 % (64 – 96 µg/m³):

Table 28: Evaluation of the reproducibility R_D near B_1 in the field test

Repeatability in the field test				
No. of values	n	=	29	
Reference value		=	80	µg/m³
t-value for the selected safety	t95	=	2.045	
Standard deviation out of parallel measurements	sd	=	0.647	
Reproducibility R_D	**R(d)**	**=**	**60**	
Standard deviation	s	=	0.393	
Coefficient of correlation	r	=	0.9989	
Y = b* x + c Slope	b	=	1.004	
Intercept	c	=	0.48	µg/m³
Mean value	Unit 1	=	78.8	µg/m³
Mean value	Unit 2	=	79.6	µg/m³

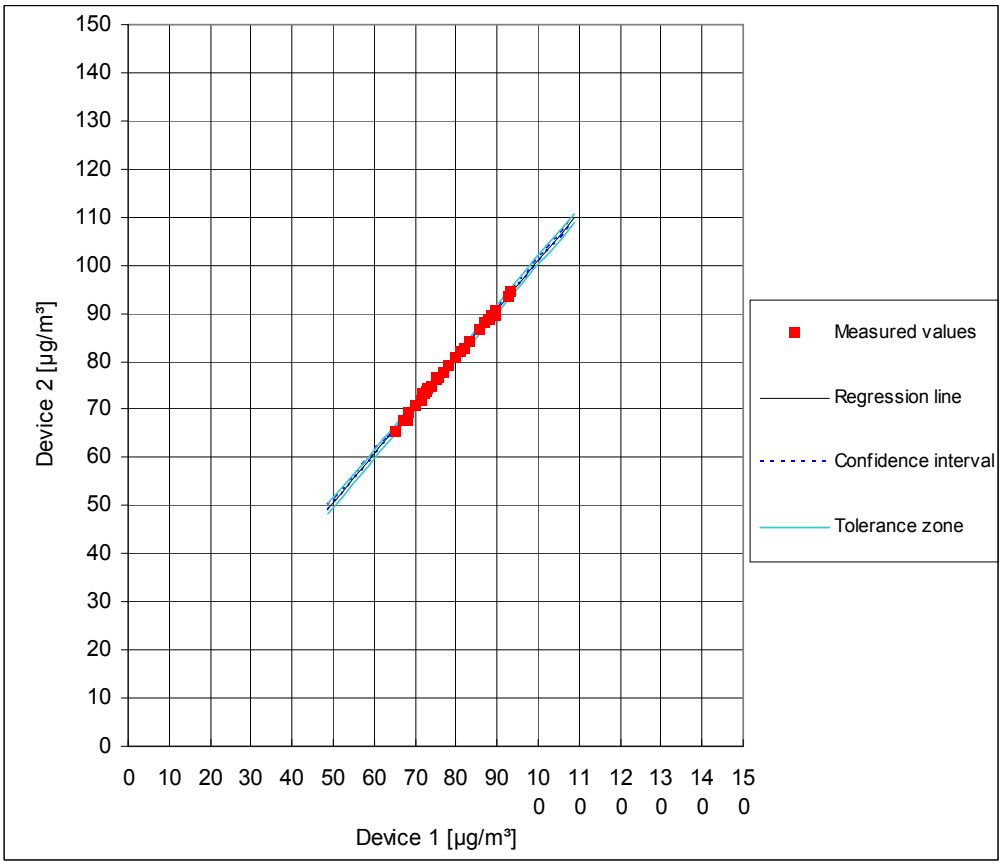


Figure 12: Graphics of the reproducibility R_D from the data near B_1 out of the field test

In addition the reproducibility R_D of all measured values in the field test has been calculated.

Table 29: Evaluation of the reproducibility R_D of all data in the field test

Repeatability in the field test				
No. of values	n	=	2193	
Reference value		=	80	µg/m³
t-value for the selected safety	t95	=	1.961	
Standard deviation out of parallel measurements	sd	=	1.103	
Reproducibility R_D	**R(d)**	**=**	**37**	
Standard deviation	s	=	0.632	
Coefficient of correlation	r	=	0.9998	
Y = b* x + c Slope	b	=	0.983	
Intercept	c	=	1.57	µg/m³
Mean value	Unit 1	=	14.3	µg/m³
Mean value	Unit 2	=	15.6	µg/m³

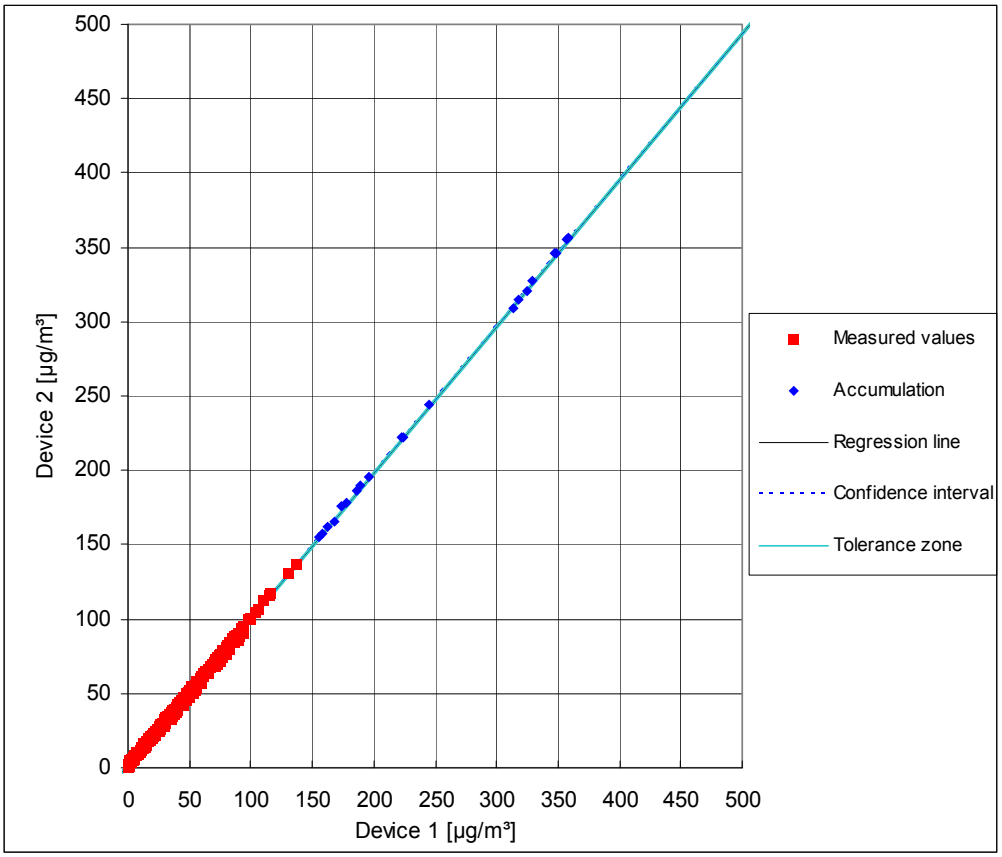


Figure 13: Graphics of the reproducibility from all data out of the field

The minimum value of 10 stated in VDI 4202 part 1 is exceeded in both cases. For the calculation of total uncertainty regarding VDI 4202 the repeatability at B_1 = 60 has been used.

The standard deviation under field conditions required in the EN 14625 is calculated as follows:

$$s_{r,f} = \frac{\left(\sqrt{\frac{\sum_{i=1}^{n} d_{f,i}^2}{2n}}\right)}{av} \times 100$$

where:

$s_{r,f}$ is the reproducibility standard deviation under field conditions (%)

n is the number of parallel measurements

av is the average value during the field test

$d_{f,i}$ is the i-th difference of one parallel measurement

Because of the very low O_3-content in ambient air during the field test, the determination of the standard deviation according to EN 14625 during the field test with reference to the mean value of all measured values is not reasonable. Therefore the information threshold for O_3 of 180 µg/m³ was drawn on for the determination of the standard deviation. Hence there is a standard deviation of 0.6%. For that the field test data were corrected by the allowed drift. This value must be smaller or equal than the required criterion of 5 % of in this case the information threshold for O_3 of 180 µg/m³. Thus the standard deviation is kept under field conditions.

6.5 Assessment

The minimum value of 10 for the reproducibility R_D required by the VDI 4202 part 1 is exceeded clearly. Thus the minimum standards are kept. Also the standard deviation required for in the EN 14625 is kept.

Minimum requirement fulfilled? yes

6.6 Documentation

Table 30: Single values of the laboratory test for the reproducibility R_D

No.	Unit 1	Unit 2
1	81.1	81.95
2	81.15	81.75
3	81.2	82.05
4	81.2	81.15
5	81.25	82.15
6	81.4	82.5
7	81.45	82.8
8	81.45	82.2
9	81.45	82.95
10	81.5	82.65

6.1 5.2.13 Hourly averages

The measurement method shall allow for formation of hourly averages.

EN 14625: 8.4.12 The averaging effect must be ≤ 7 % of the measured value.

6.2 Equipment

A data logging system of the manufacturer Yokogawa with integration function, which can be programmed to an integration interval of one hour.

6.3 Testing

In the lab the formation of hour values was tested by connection of the data recording system with an integration time of an hour. During the field test the one-hour mean value formation was tested from the recorded minute integrals.

In addition the averaging effect according to EN 14625 has been tested.

6.4 Evaluation

The measuring equipment supplies measuring data continuously by an analogue or digital output. It was tested whether the data can be recorded with a suitable acquisition system and compacted to one-hour mean values. This was possible without problems.

The averaging effect has been calculated according to EN 14625:

$$X_{av} = \frac{C_{const}^{av} - 2C_{\mathrm{var}}^{av}}{C_{const}^{av}} * 100$$

with:

X_{av} is the averaging effect (%)

C_{const}^{av} is the average of at least four independent measurements during the constant concentration period

C_{var}^{av} is the average of at least four independent measurements during the variable concentration period

During the tests the following averages have been calculated:

Constant average [µg/m³]		Variable average [µg/m³]	
Unit 1	429.9	Unit 1	206.2
Unit 2	433.5	Unit 2	216.8

The calculated averaging effect from the values in Table 64 and Table 65 is:

Unit 1: 4.07 %

Unit 2: -0.02 %.

6.5 Assessment

The measuring equipment allows the formation of one-hour mean values. During the examination of the averaging effect according to EN 14625 no influence higher than 7% could be found.

Minimum requirement fulfilled? yes

6.6 Documentation

See Table 64 and Table 65 in the appendix.

6.1 5.2.14 Mains voltage and frequency

The change in the measured values at reference value B_1 caused by normal changes in the mains voltage in the interval (230 +15/-20) V shall not exceed B_0. In addition, for mobile applications the change in the measured value caused by changes in frequency of the mains voltage in the interval (50 ± 2) Hz shall not exceed B_0.

EN 14625: 8.4.10 Sensitivity coefficient to electrical voltage ≤ 0.30 nmol/mol/V (corresponds to 0.3 ppb/V or 0.6 (µg/m³)/V

6.2 Equipment

Mains voltage: Transformer with a control range of 210 to 245 V

Mains frequency: Frequency modulator with a control range of 48 Hz to 52 Hz.

6.3 Testing

Mains voltage:

For the test of the influence of the mains voltage, a transformer was switched into the power supply of the measuring equipment. At the zero and reference point the change of the measured value was checked for a variation of the mains voltage between 210 V and 245 V and compared with the measuring signal at 230 V.

According to the test orders of the EN 14625 the sensitivity coefficient of the mains voltage should be done with test gas concentrations around zero and at 70 - 80 % of the measuring range.

Mains frequency:

By switching a frequency-modulator into the current supply of the analysers the influence of the frequency change between 48 Hz and 52 Hz was compared with the measured value at 50 Hz.

6.4 Evaluation

At the variation of the mains voltage analyser 1 shows the following results :

Table 31: Variation of mains voltage analyser 1

Unit No. 1 ZP

			Deviation		Deviation
Measurement	**230 V**	**245 V**	**245 V to 230 V**	**245 V**	**245 V to 230 V**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	-4.0	-4.2	**-0.2**	-4.4	**-0.4**
2	-3.8	-4.0	**-0.2**	-4.0	**-0.2**
3	-4.2	-3.8	**0.4**	-4.0	**0.2**
Average	-4.0	-4.0	**0.0**	-4.1	**-0.1**

Unit No. 1 SP

			Deviation		Deviation
Measurement	**230 V**	**245 V**	**245 V to 230 V**	**245 V**	**245 V to 230 V**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	323.6	325.0	**1.4**	324.8	**1.2**
2	325.2	324.8	**-0.4**	326.4	**1.2**
3	325.2	324.8	**-0.4**	326.4	**1.2**
Average	324.7	324.9	**0.2**	325.9	**1.2**

At the variation of the mains voltage analyser 2 shows the following results:

Table 32: Variation of mains voltage analyser 2

Unit No. 2 ZP

			Deviation		Deviation
Measurement	**230 V**	**245 V**	**245 V to 230 V**	**245 V**	**245 V to 230 V**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	-3.60	-4.20	**-0.60**	-3.60	**0.00**
2	-3.80	-3.60	**0.20**	-3.80	**0.00**
3	-4.20	-4.00	**0.20**	-4.20	**0.00**
Average	-3.87	-3.93	**-0.06**	-3.87	**0.00**

Unit No. 2 SP

			Deviation		Deviation
Measurement	**230 V**	**210 V**	**210 V to 230 V**	**245 V**	**245 V to 230 V**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	324.0	323.8	**-0.2**	325.6	**1.6**
2	324.6	324.6	**0.0**	326.0	**1.4**
3	324.4	324.2	**-0.2**	325.8	**1.4**
Average	324.3	324.2	**-0.1**	325.8	**1.5**

In comparison to the B_0 value of carbon monoxide which is 4 µg/m³ is, all deviations at the zero and span point during the variation of the mains voltage are in the required limits.

The greatest deviation of both devices 1.4 µg/m³ for device 1 and 1.6 µg/m³ for device 2 have been taken for the calculation of total uncertainty of VDI 4202.

The mean values and the deviations in the frequency interval from 48 Hz to 52 Hz at the zero and reference point are to be taken from Table 33 und Table 34:

Table 33: Variation of mains frequency analyser 1

Unit Nr. 1 ZP

			Deviation		Deviation
Measurement	**50 Hz**	**48 Hz**	**48 Hz to 50 Hz**	**52 Hz**	**52 Hz to 50 Hz**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	-4,8	-4,6	**0,2**	-4,6	**0,2**
2	-4,4	-4,2	**0,2**	-4,0	**0,4**
3	-4,2	-4,2	**0,0**	-4,0	**0,2**
Average	-4,5	-4,3	**0,2**	-4,2	**0,3**

Unit Nr. 1 SP

			Deviation		Deviation
Measurement	**50 Hz**	**48 Hz**	**48 Hz to 50 Hz**	**52 Hz**	**52 Hz to 50 Hz**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	318,2	320,8	**2,6**	321,8	**3,6**
2	322,2	323,4	**1,2**	323,2	**1,0**
3	321,6	322,6	**1,0**	321,2	**-0,4**
Average	320,7	322,3	**1,6**	322,1	**1,4**

Table 34: Variation of mains frequency analyser 2

Unit Nr. 2 ZP

			Deviation		Deviation
Measurement	**50 Hz**	**48 Hz**	**48 Hz to 50 Hz**	**52 Hz**	**52 Hz to 50 Hz**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	-4,40	-4,20	**0,20**	-4,60	**-0,20**
2	-4,60	-4,40	**0,20**	-4,40	**0,20**
3	-4,20	-4,80	**-0,60**	-4,80	**-0,60**
Average	-4,40	-4,47	**-0,07**	-4,60	**-0,20**

Unit Nr. 2 SP

			Deviation		Deviation
Measurement	**50 Hz**	**48 Hz**	**48 Hz to 50 Hz**	**52 Hz**	**52 Hz to 50 Hz**
	[µg/m³]	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**	**[µg/m³]**
1	319,8	321,2	**1,4**	321,0	**1,2**
2	320,4	320,4	**0,0**	322,2	**1,8**
3	321,0	321,8	**0,8**	321,6	**0,6**
Average	320,4	321,1	**0,7**	321,6	**1,2**

The deviations in the tested frequency interval should be smaller than B_0 (4 µg/m³). This requirement is fulfilled.

The sensitivity coefficient of the voltage influence according to EN 14625 is calculated described in the following:

$$b_v = \left(\frac{C_{V2} - C_{V1}}{V_2 - V_1} \right)$$

where:

b_v is the voltage influence

C_{V1} is the average concentration of the measurements at voltage V_1

C_{V2} is the average concentration of the measurements at voltage V_2

V_1 is the minimum voltage V_{min}

V_2 is the maximum voltage V_{max}

The sensitivity coefficient to electrical voltage is:

Unit 1: 0.03 (µg/m³)/V corresponds to 0.02 (nmol/mol/V)

Unit 2: 0.05 (µg/m³)/V corresponds to 0.03 (nmol/mol/V)

6.5 Assessment

The measuring system fulfils the minimum requirements regarding the variations of the mains voltage and the mains frequency. The minimum requirements are fallen below clearly. The sensitivity coefficient of the voltage according to EN 14625 is also kept.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.15 Failure in the mains voltage

In case of malfunction of the measuring system or failure in the mains voltage, uncontrolled emission of operating and calibrating gas shall be avoided. The instrument parameters shall be secured by buffering against loss caused by failure in the mains voltage. When mains voltage returns, the instrument shall automatically reach the operation mode and start the measurement according to the operating instructions.

6.2 Equipment

No additional devices.

6.3 Testing

A power failure was simulated by separation of the power plug during the measuring operation. Longer interruptions of the voltage supply (72 h) were carried out additionally at several site alternations. After each restart the measuring system was checked for the correct operation mode.

6.4 Evaluation

When mains voltage returns, the analyser works after the warm up time in a correct way. The programmed parameters, especially the calibrating data are still secured after a power failure and the analyser is ready for measurement.

If gases are connected uncontrolled emissions of operating and calibrating gas after a malfunction of the power supply were not detected.

Is the analyser for the functional check fitted with an internal zero gas conditioning and an internal ozone generator, it is not possible, that test gas escapes, because the test gas flow is generated by an internal pump so that an connection of an pressure vessel is not necessary.

6.5 Assessment

The minimum requirements are kept during a power breakdown. The operability of the analyser is safeguarded and calibrating gas does not exhaust .

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.16 Operating states

Measuring systems shall be able to telemetrically transmit important operating states by status signals.

6.2 Equipment

In addition to the measuring systems a computer has been used to control the instruments.

6.3 Testing

The analysers have been connected by a data logging system and a network to an external computer in order to control the analyser. Afterwards different operating states were simulated (readiness for operation, maintenance, and malfunction) and recorded by means of data transmission.

6.4 Evaluation

The model 49i can be integrated and remotely operated by a modem and/or the available interfaces in a network.

Both RS 232/RS 485 communication as well as an Ethernet-communication between a computer or between several analysers are possible.

Status signals about the operating state of the measuring system as well as measured data can be sent telemetrically over the available interfaces. In addition to the analogous communication the above described digital data buses are available.

During the tests the status signals were recorded by the downstream data logging system correctly.

To further communication options and technical details the manual is referred to at this place.

6.5 Assessment

The essential operating states are controllable via telemetric status signals.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.17 Switch-over

Switch-over between measurement and functional check and/or calibration shall be possible telemetrically by computer control or manual intervention.

6.2 Equipment

In addition to the measuring systems a computer has been used to control the instruments .

6.3 Testing

The analysers have been connected by a data logging system and a network to an external computer in order to control the analyser. With this external computer a functional check of the analyser has been performed. Afterwards a calibration was activated by the network.

6.4 Evaluation

The switch-over between measure- and calibrating-mode occurred automatically both during the excitation of the analyser front as also computer-assisted. In addition to the status signals send the mode of operation is readable at the device display.

6.5 Assessment

The switch-over between the modes of operation is manual and telemetric possible .

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.18 Availability

The availability of the measuring system shall be at least 90 %.

EN 14625: 8.5.7 Availability of the measuring system > 90 %.

6.2 Equipment

No additional devices.

6.3 Testing

The total operating time is calculated from the start- and final-time. The other periods of time are taken from the documentation of the test.

6.4 Evaluation

The percentile availability is calculated as follows:

Formula 1: Calculation of the availability

$$V = \frac{t_E - (t_K + t_A + t_W)}{t_E} * 100\%$$

with:

- t_E Operating time
- t_K Calibration time
- t_A Outage time
- t_W Maintenance time
- V Availability

The periods of time for the determination of the availability for both analysers are to be seen in Table 35:

Table 35: Availability Thermo 49i

		Unit 1	Unit 2
Operating time t_E	h	2193	2193
Calibration time t_K	h	46	46
Outage time t_A	h	0	0
Maintenance time t_W	h	2	2
Availability V	%	98 %	98 %

The calibrating-times result from the daily test gas tasks for the determination of the drift behaviour and the maintenance interval. There were no device-caused outage times with both analysers during the whole field test. The maintenance time results from the times which were needed for the replacement of the Teflon filters contained in the sample gas manifold.

According to EN 14625 the availability of the analyser is calculated as:

$$A_a = \frac{t_u}{t_t} * 100$$

where:

A_a is the availability of the analyser (%)

t_u is the total time period with validated measuring data

t_t is the time period of the field test (three months) minus the time for regular calibration, conditioning and maintenance of the instrumentation

With the values of Table 35 the availability is calculated to 98 %.

6.5 Assessment

The availability is higher than 90 %, so that the minimum requirement is fulfilled. The performance criteria according to EN 14625 are fulfilled by an availability of 98 %.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.19 Efficiency of the converter

In case of measuring systems with a converter, the efficiency of the converter shall be at least 95 %.

6.2 Equipment

Not applicable

6.3 Testing

Not applicable

6.4 Evaluation

Not applicable

6.5 Assessment

not applicable.

Minimum requirement fulfilled? not applicable

6.6 Documentation

Here not essential.

6.1 5.2.20 Maintenance interval

The maintenance interval of the measuring system shall be determined and specified. The maintenance interval should be 28 days, if possible, but at least 14 days.

EN 14625: 8.5.6 maintenance interval minimum 14 days

6.2 Equipment

Test standards for determination of the drift behaviour.

6.3 Testing

Within the framework of the examination is to be investigated which maintenance operations in which intervals are necessary for the perfect effectiveness of the measuring system. As far as no extensive maintenance operations are necessary physically in shorter intervals, the maintenance interval basically results from the drift behaviour of the measuring equipment.

6.4 Evaluation

A theoretical maintenance interval results from the average temporal change of the zero point for the two measuring systems.

Table 36: Maintenance interval at zero level from the drift tests

	Daily Drift [µg/(m³*d)]	Interval [Days] VDI 4202	Interval [Days] EN 14625
Unit 1	-0.0119	336	840
Unit 2	-0.0131	305	763

For the drift of the measured value and the resulted calibration work the following temporal periods have been found. The Intervals are calculated by a regression of the drift behaviour:

Table 37: Maintenance interval at span level from the drift tests

	Daily Drift [µg/(m³*d)]	Interval [Days] VDI 4202	Interval [Days] EN 14625
Unit 1	-0.027	148	926
Unit 2	-0.019	210	1316

The number of the days results from the permissible drift in the maintenance interval of 4 µg/m³ (VDI 4202) respectively 10 µg/m³ (EN 14625, zero) and 25 µg/m³ (EN 14625, span), divided by the drift determined daily.

Besides the drift additional maintenance operations influence the duration of the maintenance interval, which at the Thermo 49i devices are limited to the replacement of sample inlet Teflon filter at the analyser entry in the incoming. The filters were replaced during the field test monthly.

Only from the results of the drift investigations the measuring system has reached a maintenance interval of at least 148 days. As a precaution the dust filter contained in the sample inlet should be exchanged every 4 weeks. The necessary interval is to be determined finally site-specific.

6.5 Assessment

According to the orders of the VDI 4202 part 1 can be awarded to the measuring equipment at a field testing-period of 3 months with the present results the maximum possible maintenance interval of 1 month. On the basis of the orders of the EN 14625 the determined maintenance interval is at least 763 days.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not essential.

6.1 5.2.21 Overall uncertainty

The expanded uncertainty of the measuring system shall be determined. The value determined shall not exceed the corresponding data quality objectives in the EU Daughter Directives on air quality.

6.2 Equipment

No further equipment necessary.

6.3 Testing

Calculation of the expanded uncertainty out of the data from the tests.

6.4 Evaluation

The determination of the expanded uncertainty u_M of the measured values from the measuring system done according to appendix C of the VDI 4203 part 1 from the uncertainty contributions u_k of the relevant procedure characteristics.

Table 38: Expanded uncertainty for single values, device 1, reference value 180 µg/m³

Performance characteristic Device 1	**Requirement**	**Result**		**Uncertainty u**	**Squared uncertainty u²**
				µg/m³	(µg/m³)²
Reproducibility	10	60		0.67	0.44
Linearity	4 µg/m³	1.42	µg/m³	0.82	0.67
Temperature dependence at zero	4 µg/m³	0.60	µg/m³	0.35	0.12
Temperature dependence at span	5 % von B_1	-1.64	µg/m³	-0.95	0.90
Drift at zero	4 µg/m³	-0.36	µg/m³	-0.21	0.04
Drift at span	5 % von B_1	-0.81	µg/m³	-0.47	0.22
Mains voltage	4 µg/m³	1.40	µg/m³	0.81	0.65
Cross-sensitivities	10.8 µg/m³	9.93	µg/m³	5.73	32.87
Uncertainty of test gas	3.6 µg/m³	3.60	µg/m³	3.60	12.96
				Σu^2	48.88
				U(c) = 2u(c)	13.98
				U(c) / Reference	**7.77**

Table 39: Expanded uncertainty for single values, device 2, reference value 180 µg/m³

Performance characteristic Device 2	**Requirement**	**Result**		**Uncertainty u**	**Squared uncertainty u²**
				µg/m³	(µg/m³)²
Reproducibility	10	60		0.67	0.44
Linearity	4 µg/m³	1.18	µg/m³	0.68	0.46
Temperature dependence at zero	4 µg/m³	0.58	µg/m³	0.33	0.11
Temperature dependence at span	5 % von B_1	-1.70	µg/m³	-0.98	0.96
Drift at zero	4 µg/m³	-0.39	µg/m³	-0.23	0.05
Drift at span	5 % von B_1	-0.57	µg/m³	-0.33	0.11
Mains voltage	4 µg/m³	1.60	µg/m³	0.92	0.85
Cross-sensitivities	10.8 µg/m³	9.88	µg/m³	5.70	32.54
Uncertainty of test gas	3.6 µg/m³	3.60	µg/m³	3.60	12.96
				Σu^2	48.50
				U(c) = 2u(c)	13.93
				U(c) / Reference	**7.74**

Table 40: Expanded uncertainty for average values, device 1, reference value 180 µg/m³

Performance characteristic Device 1	**Uncertainty (Single value)**	**Time basis**	**Number nk**	**Squared uncertainty (average)**
				(µg/m³)²
Reproducibility	0.67	1 hour	7884	0.000
Linearity	0.82	1 year	1	0.672
Temperature dependence at zero	0.35	1 year	1	0.120
Temperature dependence at span	-0.95	1 year	1	0.897
Drift at zero	-0.21	4 weeks	12	0.004
Drift at span	-0.47	4 weeks	12	0.018
Mains voltahe	0.81	1 year	1	0.653
Cross-sensitivities	5.73	3 months	4	8.217
Uncertainty of test gas	3.60	1 year	1	12.960
			$\Sigma u_m^2(c_k)$	23.541
			$U(\bar{c}) = 2u(\bar{c})$	9.70
			$\frac{U(\bar{c})}{Bezug}$	5.39

Table 41: Expanded uncertainty for average values, device 2, reference value 180 µg/m³

Performance characteristic Device 2	**Uncertainty (Single value)**	**Time basis**	**Number nk**	**Squared uncertainty (average)**
				(µg/m³)²
Reproducibility	0.67	1 hour	7884	0.000
Linearity	0.68	1 year	1	0.464
Temperature dependence at zero	0.33	1 year	1	0.112
Temperature dependence at span	-0.98	1 year	1	0.963
Drift at zero	-0.23	4 weeks	12	0.004
Drift at span	-0.33	4 weeks	12	0.009
Mains voltahe	0.92	1 year	1	0.853
Cross-sensitivities	5.70	3 months	4	8.135
Uncertainty of test gas	3.60	1 year	1	12.960
			$\Sigma u_m^2(c_k)$	23.501
			$U(\bar{c}) = 2u(\bar{c})$	9.70
			$\frac{U(\bar{c})}{Bezug}$	5.39

For the calculation of the expanded measurement uncertainties, the single results of the respective test points have been evaluated in summary. As far as there are several independent results from single investigations available, the respective adverse value was used.

The expanded uncertainties are 7.77 % respectively 7.74 % for U(c) and 5.39 % respectively 5.39 % for $U(\bar{c})$.

6.5 Assessment

The measuring system falls below the required expanded uncertainty of 15 % clearly by a result of maximum 7.77 %.

Minimum requirement fulfilled? yes

6.6 Documentation

Here not necessary.

6.1 5.4 Requirements on multiple-component measuring systems

Multiple-component measuring systems shall comply with the requirements set for each component, also in case of simultaneous operation of all measuring channels.

6.2 Equipment

not applicable

6.3 Testing

not applicable

6.4 Evaluation

not applicable

6.5 Assessment

not applicable.

Minimum requirement fulfilled? not applicable

6.6 Documentation

Here not essential.

7 Further test points according to EN 14625

7.1 8.4.7 Sensitivity coefficient to sample gas pressure

The sensitivity coefficient to sample gas pressure must be smaller than
≤ 2.0 nmol/mol/kPa (corresponds to 2 ppb/kPa or 4 (µg/m³)/kPa).

7.2 Equipment

Zero gas, span gas, ozone generator, mass-flow-controller and unit to measure the sample gas pressure.

7.3 Testing

The measurements have been done at a concentration of about 70 % to 80 % of the maximum of the ozone certification range at pressures of 80 kPa ± 0.2 kPa and 110 kPa ± 2 kPa. At every pressure three single measurements are to be carried out after a space of time which corresponds to an independent measurement. The mean values of these measurements at all pressures are calculated.

The volume flow of the test gas system was chosen higher for the generation of the overpressure than the volume flow sucked by the analysers. The bypass in the incoming line to the analysers was closed to reach the necessary overpressure. The low air pressure was made by the analyser pump itself when the bypass was closed and the test gas flow was reduced synchronously.

7.4 Evaluation

The sensitivity coefficient to sample gas pressure is calculated as follows:

$$b_{gp} = \left| \frac{\left(C_{P1} - C_{P2}\right)}{\left(P_2 - P_1\right)} \right|$$

where:

b_{gp} is the sample gas pressure influence

C_{P1} is the average of the measurements at sample gas pressure P_1

C_{P2} is the average of the measurements at sample gas pressure P_2

P_1 is the sample gas pressure P_1

P_2 is the sample gas pressure P_2

The sensitivity coefficient to sample gas pressure is:

Unit 1: 0.20 (µg/m³)/kPa corresponds to 0.10 (nmol/mol/kPa)
Unit 2: 0.17 (µg/m³)/kPa corresponds to 0.09 (nmol/mol/kPa)

The calculated values for both analysers are deeper than 2 ppb/kPa, so that the requirements according to EN 14625 are kept.

7.5 Assessment

The sensitivity coefficient to sample gas pressure keeps the requirements of the EN 14625.

Minimum requirement fulfilled? yes

7.6 Umfassende Darstellung

Table 42: Test results of the variation of the sample gas pressure for the component ozone

Unit 1				
Sample gas pressure	1. Rep.	2. Rep.	3. Rep.	Average
[kPa]	[µg/m³]	[µg/m³]	[µg/m³]	[µg/m³]
ca. 110.0	406	406	405	406
99.8	403	404	403	403
ca. 80.0	399	400	400	400
	Difference 80.0 kPa and 110.0 kPa:			6

Unit 2				
Sample gas pressure	1. Rep.	2. Rep.	3. Rep.	Average
[kPa]	[µg/m³]	[µg/m³]	[µg/m³]	[µg/m³]
ca. 110.0	405	403	404	404
99.8	401	400	400	400
ca. 80.0	399	398	399	399
	Difference 80.0 kPa and 110.0 kPa:			5

7.1 8.4.8 Sensitivity coefficient to sample gas temperature

The sensitivity coefficient to sample gas temperature should be smaller than ≤ *1.0 nmol/mol/K (corresponds to 1 ppb/K or 2 (µg/m³)/K).*

7.2 Equipment

Climate chamber, zero- and span-gas.

7.3 Testing

The examination was made parallel to the checkpoint 8.4.9 sensitivity coefficient of the ambient temperature. By the choice of the tubing length in the climate chamber it was secured that the temperature of the test gas reached the required temperatures between 0°C and 30°C when entering the inlet of the analyser.

7.4 Evaluation

The sensitivity coefficient to sample gas temperature is calculated as follows:

$$b_{gt} = \frac{(C_{T2} - C_{T1})}{(T_2 - T_1)}$$

where:

b_{gt} is the sample gas temperature influence

C_{T1} is the average concentration of the measurements at sample gas temperature T_1

C_{T2} the average concentration of the measurements at sample gas temperature T_2

T_1 is the sample gas temperature T_1

T_2 is the sample gas temperature T_2

The sensitivity coefficient to sample gas temperature is at the span point:

Unit 1: 0.27 (µg/m³)/K corresponds to 0.14 (nmol/mol/K)

Unit 2: 0.31 (µg/m³)/K corresponds to 0.16 (nmol/mol/K)

The minimum requirement of the EN 14625 of b_{gt} ≤ *1 nmol/mol/K* is in the allowed limits.

7.5 Assessment

The minimum requirements are kept.

Minimum requirement fulfilled? yes

7.6 Documentation

See tables in the appendix of the climate chamber tests.

7.1 Appendix G (normative) Type approval according to EN 14625

The type approval of the analyser consists of the following steps:

1) The value of each individual performance characteristic tested in the laboratory shall fulfil the criterion stated in table 1 (see 8.2 in EN 14625).

2) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in the Directive 2002/3/EC. This criterion is the maximum uncertainty of hourly values of continuous measurements at the hourly alert threshold value. The relevant specific performance characteristics and the calculation procedure are given in annex G of the EN 14625.

3) The value of each of the individual performance characteristics tested in the field shall fulfil the criterion stated in table 1(see 8.2 of the EN 14625

4) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in the Directive 2002/3/EC. This criterion is the maximum uncertainty of hourly values of continuous measurements at the hourly alert threshold value. The relevant specific performance characteristics and the calculation procedure are given in annex G of the EN 14625

7.2 Equipment

Here not necessary.

7.3 Testing

At the end of the testing all elementary uncertainties have been calculated from of the test data.

7.4 Evaluation

to 1) The value of each single tested performance characteristic in the lab fulfils the criterion of the EN 14625

to 2) The expanded uncertainty, calculated of the specific performance characteristics obtained in the laboratory tests, fulfils the performance criterion.

to 3) The value of each single tested performance characteristic in the field fulfils the criterion of the EN 14625

to 4) The expanded uncertainty, calculated of the specific performance characteristics obtained in the laboratory and the field tests, fulfils the performance criterion.

7.5 Assessment

The minimum requirements are kept.

Minimum requirement fulfilled? yes

7.6 Documentation

The results to the topics 1 and 3 are summarized Table 43.

The results of topic 2 can be found in Table 44 and in Table 45.

The results of topic 4 can be found in Table 46 and in Table 47.

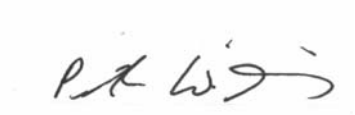
8 Recommendations for the use in practice

8.1 Work in the maintenance interval

In addition to the usual calibrating work it is important to frequently check the state of the inlet contained Teflon filter in front of the analyser, that can cause a reduction of the sample flow in case of too strong seizure with dust. The duration of the replacement interval of the filters which are to prevent the pollution of the devices through the sucked ambient air depends on the dust load at the location of installation. The alternating interval is committed to one month.

By the way, the statements of the manufacturer are to be considered.

Department of Environmental protection



Dipl.-Ing. Guido Baum

Dr. Peter Wilbring

Cologne, January 5, 2006
936/21203248/B1

9 Literature

- VDI 4202 Part 1: Minimum requirements for suitability tests of automated ambient air quality measuring systems; Point-related measurement methods of gaseous and particulate pollutants, from June 2002
- VDI 4203 Part 3: Testing of automated measuring systems; Test procedures for point –related ambient air quality measuring systems of gaseous and particulate pollutants, from August 2004
- EN 14625 Ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry, from March 2005
- DIN ISO 13964: Bestimmung von Ozon in der Außenluft – UV-photometrisches Verfahren, vom Dezember 1999
- VDI 2468 Blatt 1: Messen der Ozon- und Peroxid-Konzentration – Manuelles photometrisches Verfahren Kaliumjodid-Methode, vom Mai 1978
- Richtlinie 96/62/EG des Rates vom 27. September 1996 über die Beurteilung und die Kontrolle der Luftqualität ABl. L 296, S. 55

10 Appendix

Appendix 1: Requirements according to EN 14625

Appendix 2: Measured and calculated values

Appendix 3: Manual

Appendix 1 : Requirements according to EN 14625

Table 43: Summary of the performance standards according to EN 14625

Performance characteristic	Criterion	Test result	ful-filled?	Page
8.4.5 Repeatability standard deviation at zero	≤ 1,0 nmol/mol	Device 1: 0.09 nmol/mol Device 2: 0.10 nmol/mol	yes	39
8.4.5 Repeatability standard deviation at concentration c_t	≤ 3,0 nmol/mol	Device 1: 0.15 nmol/mol Device 2: 0.17 nmol/mol	yes	39
8.4.6 Lack of fit (residual from the linear regression function)	Highest deviation from the linear regression function for concentrations higher than zero ≤ 4 % of the measured value Deviation at zero ≤ 5,0 nmol/mol	At zero point: Device 1: 0.30 nmol/mol Device 2: 0.01 nmol/mol At span point: Device 1: 0.41 nmol/mol corresponds to 1.64% of nominal Device 2: 0.58 nmol/mol corresponds to 1.16% of nominal	yes	35
8.4.7 Sensitivity coefficient of the sample gas pressure	≤ 2,0 nmol/mol/kPa	Device 1: 0.10 nmol/mol/kPa Device 2: 0.09 nmol/mol/kPa	yes	81
8.4.8 Sensitivity coefficient of the sample gas temperature	≤ 1,0 nmol/mol/K	Device 1: 0.14 nmol/mol/K Device 2: 0.16 nmol/mol/K	yes	83
8.4.9 Sensitivity coefficient of surrounding temperature	≤ 1,0 nmol/mol/K	At zero point: Device 1: 0.03 nmol/mol/K Device 2: 0.02 nmol/mol/K At span point: Device 1: 0.15 nmol/mol/K Device 2: 0.16 nmol/mol/K	yes	43 46
8.4.10 Sensitivity coefficient of electrical voltage	≤ 1,0 nmol/mol/V	Device 1: 0.02 nmol/mol/V Device 2: 0.03 nmol/mol/V	yes	65
8.4.11 Interferents at zero and at concentration ct (at a level of the 8-hour mean limit value)	H_2O ≤ 10 nmol/mol Toluene ≤ 5,0 nmol/mol Xylene ≤ 5,0 nmol/mol	Device 1: H_20 -0.98 nmol/mol at zero point -1.64 nmol/mol at span point Toluene 0.1 nmol/mol at zero point 0.97 nmol/mol at span point Xylene 0.10 nmol/mol at zero point 0.94 nmol/mol at span point	yes	55

		Device 2: H_20 -0.80 nmol/mol at zero point -1.57 nmol/mol at span point Toluene 0.07 nmol/mol at zero point 0.54 nmol/mol at span point Xylene 0.04 nmol/mol at zero point 0.50 nmol/mol at span point		
8.4.12 Averaging effect	≤ 7,0 % of the measured value	Device 1: 4.07 % Device 2: -0.02 %	yes	63
8.4.3 Response time (rise)	≤ 180 s	Device 1: 59s Device 2: 57s	yes	41
8.4.3 Response time (fall)	≤ 180 s	Device 1: 66s Device 2: 65s	yes	41
8.4.3 Difference between rise time and fall time	≤ 10 % relative difference or 10 s, depending on which value is higher	Device 1: 10.39 %. absolute 9s Device 2: 12.95 %. absolute 8s	yes	41
8.5.6 Period of unattended operation	3 month or less if the manufacturer specifies a shorter period, but not less than 2 weeks	3 months	yes	75
8.5.7 Availability of the analyser	> 90 %	98 %	yes	72
8.5.5 Reproducibility standard deviation under field conditions	≤ 5,0 % of the average over a period of 3 month	0.6 %	yes	58
8.5.4 Long-term drift at zero	≤ 5,0 nmol/mol	Device 1: -0.179 nmol/mol Device 2: -0.197 nmol/mol	yes	49
8.5.4 Long-term drift at span level	≤ 5,0 % of the maximum of the tested range	Device 1: -0.41 nmol/mol = -0.16 % Device 2: -0.29 nmol/mol = -0.12 %	yes	52
8.4.4 Short-term drift at zero	≤ 2,0 nmol/mol over 12 h	Device 1: 0.06 nmol/mol Device 2: -0.08 nmol/mol	yes	49
8.4.4 Short-term drift at span level	≤ 6,0 nmol/mol over 12 h	Device 1: -1.34 nmol/mol Device 2: 0.29 nmol/mol	yes	52

Table 44 Expanded uncertainty out of the results from the lab test EN 14625, device 1

Instrument:	Thermo Model 49i				serial no.	Device 1	
component	O3				1h-limit value:	120	nmol/mol
No.	**Performance characteristic**	**Performance criteria**	**result**	**partial uncertainty**		**Square of uncertainty**	
1	Repeatability at zero	1,0 nmol/mol	0,090	$u_{r,Z}$	0,01	0,0001	
2	Repeatability at concentration ct	3,0 nmol/mol	0,150	$u_{r,lv}$	0,06	0,0035	
3	"lack of fit"	4,0%	1,640	$u_{l,lv}$	1,14	1,2910	
4	Sensitivity coefficient of sample gas pressure	2,0 nmol/mol/kPa	0,100	u_{gp}	1,04	1,0800	
5	Sensitivity coefficient of sample gas temperature	1,0 nmol/mol/K	0,140	u_{gt}	1,82	3,3075	
6	Sensitivity coefficient of surrounding temperature	1,0 nmol/mol/K	0,150	u_{st}	1,30	1,6875	
7	Sensitivity coefficient of electrical voltage	0,30 nmol/mol/V	0,020	u_V	0,30	0,0919	
8a	H20 with concentration 21 mmol/mol	10 nmol/mol	-1,598	u_{H2O}	1,08	1,1632	
8b	Toluol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,680	$u_{int,pos}$	0,77	0,5985	
8c	Xylol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,660	or $u_{int,neg}$			
9	Averaging effect	7,0%	4,070	u_{av}	2,82	7,9512	
18	Difference sample/calibration port	1,0%	0,000	u_{Dsc}	0,00	0,0000	
23	Uncertainty calibration gas	3,0%	2,000	ucg	1,20	1,4400	
				combined standard uncertainty	u_c	4,3144	nmol/mol
				expanded uncertainty	U_c	8,6289	nmol/mol
				expanded uncertainty actual	$U_{c,rel}$	7,19	%
				expanded uncertainty required	$U_{req,rel.}$	15	%

Table 45 Expanded uncertainty out of the results from the lab test EN 14625, device 2

Instrument:	Thermo Model 49i				serial no.	Device 2	
component	O3				1h-limit value:	120	nmol/mol
No.	**Performance characteristic**	**Performance criteria**	**result**	**partial uncertainty**		**Square of uncertainty**	
1	Repeatability at zero	1,0 nmol/mol	0,100	$u_{r,Z}$	0,01	0,0002	
2	Repeatability at concentration ct	3,0 nmol/mol	0,170	$u_{r,lv}$	0,07	0,0044	
3	"lack of fit"	4,0%	1,160	$u_{l,lv}$	0,80	0,6459	
4	Sensitivity coefficient of sample gas pressure	2,0 nmol/mol/kPa	0,090	u_{gp}	0,94	0,8748	
5	Sensitivity coefficient of sample gas temperature	1,0 nmol/mol/K	0,160	u_{gt}	2,08	4,3200	
6	Sensitivity coefficient of surrounding temperature	1,0 nmol/mol/K	0,160	u_{st}	1,39	1,9200	
7	Sensitivity coefficient of electrical voltage	0,30 nmol/mol/V	0,030	u_V	0,45	0,2067	
8a	H20 with concentration 21 mmol/mol	10 nmol/mol	-1,478	u_{H2O}	1,00	0,9950	
8b	Toluol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,383	$u_{int,pos}$	0,42	0,1760	
8c	Xylol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,343	or $u_{int,neg}$			
9	Averaging effect	7,0%	-0,020	u_{av}	-0,01	0,0002	
18	Difference sample/calibration port	1,0%	0,000	u_{Dsc}	0,00	0,0000	
23	Uncertainty calibration gas	3,0%	2,000	0	1,20	1,4400	
				combined standard uncertainty	u_c	3,2532	nmol/mol
				expanded uncertainty	U_c	6,5064	nmol/mol
				expanded uncertainty actual	$U_{c,rel}$	5,42	%
				expanded uncertainty required	$U_{req,rel.}$	15	%

Table 46 Expanded uncertainty out of the results from the lab and field test EN 14625, device 1

Instrument:	Thermo Model 49i				serial no.	Device 1	
component	O3				1h-limit value:	120	nmol/mol
No.	**Performance characteristic**	**Performance criteria**	**result**	**partial uncertainty**		**Square of uncertainty**	
1	Repeatability at zero	1,0 nmol/mol	0,090	$u_{r,Z}$	0,01	0,0001	
2	Repeatability at concentration ct	3,0 nmol/mol	0,150	$u_{r,lv}$	not considered, as ur,lv = 0,05 < ur,f	-	
3	"lack of fit"	4,0%	1,640	$u_{l,lv}$	1,14	1,2910	
4	Sensitivity coefficient of sample gas pressure	2,0 nmol/mol/kPa	0,100	u_{gp}	1,04	1,0800	
5	Sensitivity coefficient of sample gas temperature	1,0 nmol/mol/K	0,140	u_{gt}	1,82	3,3075	
6	Sensitivity coefficient of surrounding temperature	1,0 nmol/mol/K	0,150	u_{st}	1,30	1,6875	
7	Sensitivity coefficient of electrical voltage	0,30 nmol/mol/V	0,020	u_V	0,30	0,0919	
8a	H20 with concentration 21 mmol/mol	10 nmol/mol	-1,598	u_{H2O}	1,08	1,1632	
8b	Toluol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,680	$u_{int,pos}$	0,77	0,5985	
8c	Xylol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,660	or $u_{int,neg}$			
9	Averaging effect	7,0%	4,070	u_{av}	2,82	7,9512	
10	Reproducibility under field conditions	5,0% of the average of 3 Mon.	0,600	$u_{r,f}$	0,72	0,5184	
11	Long term drift at zero level	5,0 nmol/mol	-0,179	$u_{d,l,z}$	-0,10	0,0107	
12	Long term drift at span level	5,0% of max. of certification range	-0,160	$u_{d,l,lv}$	-0,11	0,0123	
18	Difference sample/calibration port	1,0%	0,000	u_{Dsc}	0,00	0,0000	
23	Uncertainty calibration gas	3,0%	2,000	ucg	1,20	1,4400	
				combined standard uncertainty	u_c	4,3763	nmol/mol
				expanded uncertainty	U_c	8,7527	nmol/mol
				expanded uncertainty actual	$U_{c,rel}$	7,29	%
				expanded uncertainty required	$U_{req,rel.}$	15	%

Table 47 Expanded uncertainty out of the results from the lab and field test EN 14625, device 2

Instrument:	Thermo Model 49i				serial no.	Device 2	
component	O3				1h-limit value:	120	nmol/mol
No.	**Performance characteristic**	**Performance criteria**	**result**	**partial uncertainty**		**Square of uncertainty**	
1	Repeatability at zero	1,0 nmol/mol	0,100	$u_{r,Z}$	0,01	0,0002	
2	Repeatability at concentration ct	3,0 nmol/mol	0,170	$u_{r,lv}$	not considered, as ur,lv = 0,06 < ur,f	-	
3	"lack of fit"	4,0%	1,160	$u_{l,lv}$	0,80	0,6459	
4	Sensitivity coefficient of sample gas pressure	2,0 nmol/mol/kPa	0,090	u_{gp}	0,94	0,8748	
5	Sensitivity coefficient of sample gas temperature	1,0 nmol/mol/K	0,160	u_{gt}	2,08	4,3200	
6	Sensitivity coefficient of surrounding temperature	1,0 nmol/mol/K	0,160	u_{st}	1,39	1,9200	
7	Sensitivity coefficient of electrical voltage	0,30 nmol/mol/V	0,030	u_V	0,45	0,2067	
8a	H20 with concentration 21 mmol/mol	10 nmol/mol	-1,478	u_{H2O}	1,00	0,9950	
8b	Toluol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,383	$u_{int,pos}$	0,42	0,1760	
8c	Xylol with concentration 0,5 µmol/mol	5,0 nmol/mol	0,343	or $u_{int,neg}$			
9	Averaging effect	7,0%	-0,020	u_{av}	-0,01	0,0002	
10	Reproducibility under field conditions	5,0% of the average of 3 Mon.	0,600	$u_{r,f}$	0,72	0,5184	
11	Long term drift at zero level	5,0 nmol/mol	-0,197	$u_{d,l,z}$	-0,11	0,0129	
12	Long term drift at span level	5,0% of max. of certification range	-0,120	$u_{d,l,lv}$	-0,08	0,0069	
18	Difference sample/calibration port	1,0%	0,000	u_{Dsc}	0,00	0,0000	
23	Uncertainty calibration gas	3,0%	2,000	0	1,20	1,4400	
				combined standard uncertainty	u_c	3,3342	nmol/mol
				expanded uncertainty	U_c	6,6684	nmol/mol
				expanded uncertainty actual	$U_{c,rel}$	5,56	%
				expanded uncertainty required	$U_{req,rel.}$	15	%

Appendix 2 : Measured and calculated values

Table 48: Linearity Thermo 49i 1/5

Manufacturer	**Thermo**	Zero gas	**Synth Air**	Span gas	**Ozone generator**
Type	**Model 49i**	Manufacturer	**Praxair**	Manufacturer	**MCZ**
Measuring range	**0 to 500 µg/m³**			Test	1 of 5
Component	**O3**				

No.	**Date**	**Values Expectancy [µg/m³]**	**Measured [µg/m³]**	**Regression**	
Unit 1		0	0.6		
		50	50.4		
		100	100.3		
		150	149.3		
		200	201.2		
		250	251.3		
		300	302.1		
		350	349.1		
		400	401.6	Slope	1.0025
		450	451.9	Intercept	0.19
		500	501.3	Correlation coefficient	1
Unit 2		0	0.2		
		50	50.8		
		100	101		
		150	150.8		
		200	200.9		
		250	252.2		
		300	300.6		
		350	349.2		
		400	398.2	Slope	0.9987
		450	450.7	Intercept	0.86
		500	501.2	Correlation coefficient	1

Table 49: Linearity Thermo 49i 2/5

Manufacturer	**Thermo**	Zero gas	**Synth Air**	Span gas	**Ozone generator**
Type	**Model 49i**	Manufacturer	**Praxair**	Manufacturer	**MCZ**
Measuring range	**0 to 500 µg/m³**			Test	2 of 5
Component	**O3**				

No.	**Date**	**Values**		**Regression**	
		Expectancy [µg/m³]	**Measured [µg/m³]**		
Unit 1		0.0	0.7		
		50.0	51.1		
		100.0	99.4		
		150.0	149.3		
		200.0	201.5		
		250.0	251.2		
		300.0	298.8		
		350.0	350.9		
		400.0	400.5	Slope	1.0001
		450.0	451.6	Intercept	0.39
		500.0	499.7	Correlation coefficient	1
Unit 2		0.0	0.1		
		50.0	50.4		
		100.0	101.8		
		150.0	149.5		
		200.0	201.4		
		250.0	251.4		
		300.0	301.2		
		350.0	350.8		
		400.0	399.2	Slope	0.9987
		450.0	451.1	Intercept	0.88
		500.0	499.2	Correlation coefficient	1

Table 50: Linearity Thermo 49i 3/5

Manufacturer	**Thermo**	Zero gas	**Synth Air**	Span gas	**Ozone generator**
Type	**Model 49i**	Manufacturer	**Praxair**	Manufacturer	**MCZ**
Measuring range	**0 to 500 µg/m³**			Test	3 of 5
Component	**O3**				

No.	**Datum**	**Wertepaare Erwartungswert [µg/m³]**	**Messwert [µg/m³]**	**Regression**	
Unit 1		0.0	0.5		
		50.0	52.1		
		100.0	98.2		
		150.0	150.2		
		200.0	202.0		
		250.0	252.2		
		300.0	298.6		
		350.0	352.0		
		400.0	401.6	Slope	1.0033
		450.0	452.1	Intercept	0.22
		500.0	502.1	Correlation coefficient	0.999
Unit 2		0.0	-0.3		
		50.0	49.5		
		100.0	102.2		
		150.0	150.6		
		200.0	199.4		
		250.0	252.2		
		300.0	300.7		
		350.0	352.3		
		400.0	398.2	Slope	1.0014
		450.0	452	Intercept	0.33
		500.0	500.7	Correlation coefficient	0.999

Table 51: Linearity Thermo 49i 4/5

Manufacturer	**Thermo**	Zero gas	**Synth Air**	Span gas	**Ozone generator**
Type	**Model 49i**	Manufacturer	**Praxair**	Manufacturer	**MCZ**
Measuring range	**0 to 500 µg/m³**			Test	4 of 5
Component	**O3**				

No.	**Datum**	**Wertepaare Erwartungswert [µg/m³]**	**Messwert [µg/m³]**	**Regression**	
Unit 1		0.0	0.4		
		50.0	49.7		
		100.0	100.7		
		150.0	149.1		
		200.0	199.3		
		250.0	251.1		
		300.0	300.2		
		350.0	348.0		
		400.0	399.1	Slope	1.008
		450.0	450.8	Intercept	-0.196
		500.0	501.6	Correlation coefficient	1
Unit 2		0.0	0.1		
		50.0	50.3		
		100.0	101.4		
		150.0	148.8		
		200.0	202		
		250.0	252.1		
		300.0	302.4		
		350.0	348.7		
		400.0	401	Slope	1.002
		450.0	452.1	Intercept	0.4
		500.0	501.1	Correlation coefficient	0.999

Table 52: Linearität Thermo 49i 5/5

Manufacturer	**Thermo**	Zero gas Manufacturer	**Synth Air Praxair**	Span gas Manufacturer	**Ozone generator MCZ**
Type	**Model 49i**				
Measuring range	**0 to 500 µg/m³**			Test	5 of 5
Component	**O3**				

No.	**Date**	**Values Expectancy [µg/m³]**	**Measured [µg/m³]**	**Regression**	
Unit 1		0.0	0.8		
		50.0	50.8		
		100.0	99.1		
		150.0	151.3		
		200.0	202.1		
		250.0	251.3		
		300.0	301.6		
		350.0	350.8		
		400.0	401.1	Slope	1.0022
		450.0	452	Intercept	0.56
		500.0	501.4	Correlation coefficient	1
Unit 2		0.0	0		
		50.0	50.4		
		100.0	99.4		
		150.0	152.3		
		200.0	202.1		
		250.0	250.6		
		300.0	301		
		350.0	351.2		
		400.0	398	Slope	1.0017
		450.0	451.9	Intercept	0.4
		500.0	502.2	Correlation coefficient	0.999

Table 53: Single values of the repeatability in the lab

Measurement No.	Unit 1		Unit 2	
	ZP	SP	ZP	SP
	[µg/m³]	[µg/m³]	[µg/m³]	[µg/m³]
1	2.4	1.5	79.5	78.5
2	2.1	1.4	79.6	78.6
3	1.9	1.2	79.8	78.4
4	2	1.1	79.6	78.7
5	2	1.4	79.3	78.8
6	1.9	1.1	79.7	78.3
7	1.9	1.1	79.2	78.1
8	1.9	1.2	79	77.8
9	1.8	1.2	79.6	78.5
10	2.1	1.4	78.8	77.9
11	1.7	0.9	79	77.9
12	2	1.1	78.9	77.8
13	1.9	1.2	79.5	78.4
14	1.6	0.7	79.6	78.5
15	1.8	1.1	79.2	78.2
16	1.9	1.1	79.2	78.4
17	1.8	1.1	79.7	78.6
18	1.9	1	79.7	79
19	1.7	0.9	79.5	78.6
20	1.8	1	79.4	78.4

Table 54: Single values of the repeatability in the field

Measurement No.	Unit 1		Unit 2	
	ZP	SP	ZP	SP
	[µg/m³]	[µg/m³]	[µg/m³]	[µg/m³]
1	-1.0	0.1	83.6	84.4
2	-1.8	-0.1	83.9	84.1
3	-1.6	0.2	84.0	84.3
4	-1.2	0.2	84.0	84.6
5	-1.3	-0.1	84.6	84.2
6	-1.6	0.0	83.6	84.4
7	-1.4	-0.2	84.6	84.9
8	-1.6	-0.2	84.2	84.6
9	-1.5	-0.3	83.8	84.2
10	-1.6	0.2	83.6	84.4
11	-1.4	-0.2	83.2	84.6
12	-1.4	-0.1	84.0	84.8
13	-1.7	-0.1	84.0	85.0
14	-1.5	-0.2	84.2	85.0
15	-1.6	-0.4	84.0	85.2
16	-1.4	-0.2	83.8	84.8
17	-1.2	-0.3	84.2	85.0
18	-1.5	0.0	84.0	84.8
19	-1.6	-0.2	83.6	84.8
20	-1.3	-0.4	84.0	84.6

Table 55: Single values and evaluation of the dependence of the zero value from ambient temperature according to VDI 4202 part 1

Temperature [°C]	Unit 1 Rep. 1	Rep. 2	Rep. 3	Unit 2 Rep. 1	Rep. 2	Rep. 3
20	-0.20	0.60	0.80	0.40	0.80	0.40
	0.20	0.20	0.80	0.20	0.80	0.60
	0.60	0.00	0.40	0.60	0.60	0.80
Average	0.20	0.27	0.67	0.40	0.73	0.60
5	1.20	1.20	1.00	1.20	1.40	0.80
	1.00	1.00	0.60	1.20	0.80	1.00
	1.20	0.80	0.80	1.40	1.40	1.20
Average	1.13	1.00	0.80	1.27	1.20	1.00
Deviation to 20°C	0.93	0.73	0.13	0.87	0.47	0.40
20	0.00	0.60	0.60	0.20	0.40	0.40
	0.40	0.20	0.40	-0.40	0.20	0.00
	0.20	0.00	0.60	0.40	-0.20	-0.20
Average	0.20	0.27	0.53	0.07	0.13	0.07
40	0.40	0.40	0.20	0.40	0.20	-0.40
	0.60	0.40	0.40	0.20	0.40	0.20
	0.40	0.00	0.40	-0.40	-0.20	0.00
Average	0.47	0.27	0.33	0.07	0.13	-0.07
Deviation to 20 °C	0.27	0.00	-0.20	0.00	0.00	-0.13
20	0.80	0.80	0.60	1.00	0.80	0.60
	0.40	0.40	0.20	0.80	0.60	0.60
	0.20	0.00	-0.20	0.80	1.20	0.80
Average	0.47	0.40	0.20	0.87	0.87	0.67
0						
	1.00	1.20	1.00	1.40	1.60	1.60
	1.40	1.60	1.40	1.00	1.40	1.60
	1.20	1.40	1.60	1.60	1.20	1.40
Average	1.20	1.40	1.33	1.33	1.40	1.53
Deviation to 20 °C	0.73	1.00	1.13	0.47	0.53	0.87

Table 56: Single values and evaluation of the dependence of the measured value from ambient temperature according to VDI 4202 part 1

Temperature [°C]	**Unit 1**			**Unit 2**		
	Rep. 1	**Rep. 2**	**Rep. 3**	**Rep. 1**	**Rep. 2**	**Rep. 3**
20	81.10	81.20	81.20	80.90	81.10	81.20
	81.60	80.60	81.10	80.80	80.90	81.00
	81.60	81.80	80.50	81.10	80.50	80.70
Average	**81.43**	**81.20**	**80.93**	**80.93**	**80.83**	**80.97**
5	79.10	78.90	78.80	79.10	78.90	79.30
	79.60	78.70	79.30	78.90	79.20	78.90
	79.40	79.20	79.10	78.60	79.30	79.50
Average	**79.37**	**78.93**	**79.07**	**78.87**	**79.13**	**79.23**
Deviation to 20°C	**-2.07**	**-2.27**	**-1.87**	**-2.07**	**-1.70**	**-1.73**
20	80.80	81.00	80.80	81.10	80.70	81.10
	80.40	80.90	81.40	80.70	80.60	80.60
	80.60	80.60	80.10	80.90	81.00	80.70
Average	**80.60**	**80.83**	**80.77**	**80.90**	**80.77**	**80.80**
40	81.70	81.90	82.00	81.60	81.60	81.80
	81.50	81.40	81.80	81.80	81.90	81.50
	81.20	81.70	81.60	81.70	81.50	81.60
Average	**81.47**	**81.67**	**81.80**	**81.70**	**81.67**	**81.63**
Deviation to 20 °C	**0.87**	**0.83**	**1.03**	**0.80**	**0.90**	**0.83**
20	81.60	81.20	81.30	80.80	81.20	80.60
	81.50	80.70	81.30	81.00	80.60	81.20
	81.20	81.40	81.10	80.80	80.70	81.40
Average	**81.43**	**81.10**	**81.23**	**80.87**	**80.83**	**81.07**

Table 57: Single values and evaluation of the dependence of the measured value from ambient temperature according to EN 14625

Temperature [°C]	**Unit 1 Rep. 1**	**Rep. 2**	**Rep. 3**	**Unit 2 Rep. 1**	**Rep. 2**	**Rep. 3**
20	323.40	323.80	324.60	323.00	323.20	324.00
	322.60	323.60	324.00	323.60	323.00	323.80
	323.80	323.00	326.20	322.80	322.40	323.60
Average	**323.27**	**323.47**	**324.93**	**323.13**	**322.87**	**323.80**
0	317.00	315.80	317.60	315.60	316.00	317.60
	318.00	316.40	317.80	314.80	316.80	318.00
	318.20	316.00	319.00	316.00	316.20	317.20
Average	**317.73**	**316.07**	**318.13**	**315.47**	**316.33**	**317.60**
Deviation to 20°C	**-5.53**	**-7.40**	**-6.80**	**-7.67**	**-6.53**	**-6.20**
20	321.20	323.00	322.00	321.20	322.80	321.80
	322.60	323.40	323.60	322.20	321.80	322.40
	323.00	322.80	323.20	322.80	323.00	323.20
Average	**322.27**	**323.07**	**322.93**	**322.07**	**322.53**	**322.47**
30	326.40	324.80	324.40	326.60	325.20	324.80
	325.80	326.00	324.80	326.20	326.20	326.00
	326.20	325.40	325.40	325.80	324.80	325.80
Average	**326.13**	**325.40**	**324.87**	**326.20**	**325.40**	**325.53**
Deviation to 20 °C	**3.87**	**2.33**	**1.93**	**4.13**	**2.87**	**3.07**
	0.00	0.00	0.00	0.00	0.00	0.00
20	323.80	324.80	324.60	323.80	325.40	324.60
	322.80	323.80	324.20	324.00	323.40	323.80
	323.60	324.20	323.00	323.60	324.20	323.80
Average	**323.40**	**324.27**	**323.93**	**323.80**	**324.33**	**324.07**

Table 58: Evaluation of the short term drift according to EN 14625. Unit 1

Start values			Values after 12 h	
ZP [µg/m³]	SP [µg/m³]		ZP [µg/m³]	SP [µg/m³]
0.4	365.0		0.8	362.2
0.8	370.5		1.0	368.5
0.2	368.1		0.8	365.3
-0.4	363.4		0.4	362.2
0.2	365.8		0.6	363.0
0.0	365.3		0.8	362.5
0.3	364.2		0.4	360.9
0.8	361.8		0.3	358.3
0.8	361.1		0.5	356.7
0.0	360.3		0.7	355.1
0.4	362.6		0.6	359.0
0.4	361.1		0.5	356.7
0.2	361.8		0.4	360.2
0.6	363.0		0.1	359.4
0.4	361.4		0.0	360.6
0.2	362.6		0.6	362.2
0.6	361.8		0.4	361.7
0.3	361.8		0.2	363.3
0.4	363.8		0.2	359.4
0.5	365.0		0.4	362.5
0.35	**363.53**		**0.47**	**360.98**

Table 59: Evaluation of the short term drift according to EN 14625. Unit 2

Start values			Values after 12 h	
ZP [µg/m³]	SP [µg/m³]		ZP [µg/m³]	SP [µg/m³]
-0.4	364.5		-0.4	363.3
-0.2	363.7		-0.6	362.5
-0.4	363.7		-0.4	364.9
-0.4	367.6		-0.6	361.7
-0.4	365.2		-0.4	365.7
-0.4	364.5		-0.2	363.3
-0.3	365.2		-0.4	362.5
-0.4	364.5		-0.6	366.5
0.2	363.7		-0.6	366.5
0.2	362.9		-0.2	365.7
-0.2	363.7		-0.6	364.9
-0.4	363.7		-0.2	364.1
-0.3	364.9		-0.3	366.5
-0.4	365.2		-0.4	365.7
0.1	362.9		-0.2	364.5
-0.4	363.7		-0.4	364.1
-0.3	363.3		-0.3	364.5
-0.2	363.7		-0.3	364.9
0.0	364.1		-0.4	365.7
0.2	365.2		-0.2	366.5
-0.22	**364.28**		**-0.38**	**364.69**

Table 60: Cross-sensitivities at the zero point unit 1

Interferents		1. Rev.	2. Rev.	3. Rev.	Average	Deviation
	mg/m³	ZP	ZP	ZP	ZP	ZP
CO2	SL	-1.8	-1.8	-1.8	-1.80	
	700	-1.7	-1.7	-1.9	-1.77	0.03
CO	SL	-1.6	-1.8	-1.4	-1.60	
	60	-1.5	-1.5	-1	-1.33	0.27
H2O	SL	-1.5	-1.2	0.6	-0.70	
	ca. 80 % rel.	-4.5	-1.8	-1.7	-2.67	-1.97
SO2	SL	-0.4	-0.5	-0.7	-0.53	
	0.7	2.4	2.2	1.7	2.10	2.63
NO	SL	-1.9	-1.8	-1.7	-1.80	
	1	-1.9	-2.1	-2	-2.00	-0.20
NO2	SL	-1.9	-1.8	-1.8	-1.83	
	0.36	-1.6	-1.9	-1.9	-1.80	0.03
N2O	SL	-2	-1.8	-1.9	-1.90	
	0.5	-1.9	-1.9	-1.8	-1.87	0.03
H2S	SL	-1.7	-1.8	-1.7	-1.73	
	0.03	-1.8	-1.6	-1.4	-1.60	0.13
NH3	SL	-2.4	-1.9	-2	-2.10	
	0.03	-2.1	-2	-1.9	-2.00	0.10
Benzene	SL	-0.9	-0.7	-0.9	-0.83	
	1	-1.3	-0.5	-1.1	-0.97	-0.13
Toluene	SL	-1.5	-1	-1.1	-1.20	
	0.5	-1.2	-0.9	-0.9	-1.00	0.20
Xylene	SL	-1	-1.1	-1.2	-1.10	
	0.5	-0.8	-0.8	-1.1	-0.90	0.20
		Sum of negative deviations [µg/m³]				-2.30
		Sum of positive deviations [µg/m³]				3.63

Table 61: Cross-sensitivities at the zero point unit 2

Interferents		1. Rev.	2. Rev.	3. Rev.	Average	Deviation
	mg/m³	ZP	ZP	ZP	ZP	ZP
CO2	SL	-1.1	-1.2	-1.2	-1.17	
	700	-1.2	-1.1	-1	-1.10	0.07
CO	SL	-0.6	-0.9	-0.8	-0.77	
	60	-0.5	-0.6	-0.3	-0.47	0.30
H2O	SL	-1.9	-1.3	-1.6	-1.60	
	ca. 80 % rel.	-4.7	-2.2	-2.7	-3.20	-1.60
SO2	SL	-1.3	-1	-1.1	-1.13	
	0.7	1.5	1.3	1.3	1.37	2.50
NO	SL	-0.9	-1.2	-0.9	-1.00	
	1	-1.1	-1.4	-1.1	-1.20	-0.20
NO2	SL	-1.2	-1.1	-1.1	-1.13	
	0.36	-0.7	-1.1	-1	-0.93	0.20
N2O	SL	-1.2	-1.2	-1.2	-1.20	
	0.5	-1	-1.1	-1.3	-1.13	0.07
H2S	SL	-0.9	-0.9	-0.8	-0.87	
	0.03	-1	-0.6	-0.7	-0.77	0.10
NH3	SL	-1.5	-1.2	-1.4	-1.37	
	0.03	-1.4	-1.1	-1.1	-1.20	0.17
Benzene	SL	-1.3	-1.4	-1.3	-1.33	
	1	-1.5	-0.8	-1.1	-1.13	0.20
Toluene		-1.3	-1.1	-1.2	-1.20	
	0.5	-1.1	-1	-1.1	-1.07	0.13
Xylene		-1.4	-1.2	-1.4	-1.33	
	0.5	-1.3	-1.2	-1.3	-1.27	0.07
		Sum of negative deviations [µg/m³]				-1.80
		Sum of positive deviations [µg/m³]				3.80

Table 62: Cross-sensitivities at the span point unit 1

Interferents		1. Rev.	2. Rev.	3. Rev.	Average	Deviation
	mg/m³	SP	SP	SP	SP	SP
CO2	SL	358.4	359.4	359.0	358.9	
	700	360.0	360.6	360.2	360.3	1.3
CO	SL	357.4	360.0	361.2	359.5	
	60	358.4	359.2	359.6	359.1	-0.5
H2O	SL	357.6	357.6	357.2	357.5	
	ca. 80 % rel.	354.0	354.2	354.4	354.2	-3.3
SO2	SL	356.6	361.6	359.2	359.1	
	0.7	361.0	362.4	362.6	362.0	2.9
NO	SL	350.6	350.2	352.2	351.0	
	1	351.0	351.4	352.8	351.7	0.7
NO2	SL	348.6	352.2	353.6	351.5	
	0.36	343.8	349.0	351.6	348.1	-3.3
N2O	SL	358.4	358.0	359.2	358.5	
	0.5	357.6	359.0	358.4	358.3	-0.2
H2S	SL	356.2	357.6	361.0	358.3	
	0.03	356.6	358.4	361.0	358.7	0.4
NH3	SL	353.0	356.2	355.8	355.0	
	0.03	352.2	354.8	354.8	353.9	-1.1
Benzene	SL	343.2	348.4	349.8	347.1	
	1	345.6	349.2	349.0	347.9	0.8
Toluene	SL	357.6	358.2	357.6	357.8	
	0.5	359.6	360.2	359.4	359.7	1.9
Xylene	SL	357.2	357.8	357.2	357.4	
	0.5	359.0	359.4	359.4	359.3	1.9
		Sum of negative deviations [µg/m³]				-8.33
		Sum of positive deviations [µg/m³]				9.93

Table 63: Cross-sensitivities at the span point unit 2

Interferents		1. Rev.	2. Rev.	3. Rev.	Average	Deviation
	mg/m³	SP	SP	SP	SP	SP
CO2	SL	356.8	357.2	357.2	357.1	
	700	358.2	358.8	358.8	358.6	1.5
CO	SL	354.6	357.6	358.8	357.0	
	60	356.2	356.8	357.4	356.8	-0.2
H2O	SL	355.0	355.6	355.2	355.3	
	ca. 80 % rel.	351.8	352.4	352.2	352.1	-3.1
SO2	SL	354.6	358.8	357.4	356.9	
	0.7	359.0	360.6	361.6	360.4	3.5
NO	SL	349.0	348.0	350.8	349.3	
	1	348.6	349.8	351.2	349.9	0.6
NO2	SL	346.4	351.0	351.4	349.6	
	0.36	341.6	347.4	350.2	346.4	-3.2
N2O	SL	356.0	355.8	357.0	356.3	
	0.5	355.8	356.8	356.4	356.3	0.1
H2S	SL	354.6	355.4	359.4	356.5	
	0.03	355.0	355.8	360.0	356.9	0.5
NH3	SL	351.8	355.2	354.0	353.7	
	0.03	352.0	352.8	353.0	352.6	-1.1
Benzene	SL	344.8	349.6	351.6	348.7	
	1	347.0	351.6	352.4	350.3	1.7
Toluene	SL	355.4	357.0	354.8	355.7	
	0.5	356.8	357.2	356.4	356.8	1.1
Xylene	SL	355.0	355.2	355.0	355.1	
	0.5	356.4	356.0	355.8	356.1	1.0
		Sum of negative deviations [µg/m³]				-7.60
		Sum of positive deviations [µg/m³]				9.87

Table 64: Single values of the averaging-test according to EN 14625 Unit 1

Constant concentration		Variable concentration	
Time [min]	Measured value [µg/m³]	Time [min]	Measured value [µg/m³]
00:45	429.7	00:45	281.0
01:30	429.8	01:30	173.5
02:15	429.7	02:15	251.8
03:00	430.0	03:00	136.2
03:45	430.0	03:45	258.1
04:30	429.8	04:30	153.6
05:15	429.8	05:15	261.5
06:00	429.9	06:00	153.6
06:45	429.8	06:45	261.5
07:30	429.8	07:30	152.2
08:15	430.0	08:15	250.7
09:00	429.8	09:00	151.9
09:45	430.0	09:45	259.6
10:30	429.9	10:30	151.2
11:15	430.0	11:15	249.9
12:00	430.0	12:00	149.3
12:45	430.0	12:45	254.4
13:30	430.0	13:30	151.8
14:15	430.0	14:15	263.3
15:00	429.9	15:00	157.7
Average	**429.9**	**Average**	**206.2**

Table 65: Single values of the averaging-test according to EN 14625 Unit 2

Constant concentration		Variable concentration	
Time [min]	Measured value [µg/m³]	Time [min]	Measured value [µg/m³]
00:45	433.3	00:45	295.5
01:30	433.1	01:30	182.5
02:15	433.5	02:15	264.8
03:00	433.5	03:00	143.2
03:45	433.5	03:45	271.4
04:30	433.5	04:30	161.5
05:15	433.5	05:15	275.0
06:00	433.5	06:00	161.5
06:45	433.6	06:45	275.0
07:30	433.5	07:30	160.1
08:15	433.4	08:15	263.6
09:00	433.4	09:00	159.8
09:45	433.5	09:45	273.0
10:30	433.5	10:30	159.0
11:15	433.5	11:15	262.8
12:00	433.6	12:00	157.0
12:45	433.6	12:45	267.6
13:30	433.5	13:30	159.7
14:15	433.5	14:15	276.9
15:00	433.5	15:00	165.9
Average	**433.5**	**Average**	**216.8**

Figure 14: Reading of the software version at the analyser display

Appendix 3 : Manual

TÜV RHEINLAND
ENERGIE UND UMWELT GMBH

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-11120-02-00

Addendum

Addendum to the performance test report for the measuring system Model 49i for ozone, manufactured by Thermo Fisher Scientific, TÜV report 936/21203248/B1 dated 5th January 2006 and statement dated 17th January 2011

Report no.: 936/21221382/A
Köln, 21.03.2013

luft@de.tuv.com

The department of Environmental Protection of TÜV Rheinland Energie und Umwelt GmbH
is accredited for the following work areas:

- Determination of air quality and emissions of air pollution and odour substances;
- Inspection of correct installation, function and calibration of continuously operating emission measuring instruments, including data evaluation and remote emission monitoring systems;
- Combustion chamber measurements;
- Performance testing of measuring systems for continuous monitoring of emissions and ambient air, and of electronic data evaluation and remote emission monitoring systems;
- Determination of stack height and air quality projections for hazardous and odour substances;
- Determination of noise and vibration emissions and pollution, determination of sound power levels and execution of sound measurements at wind energy plants

according to EN ISO/IEC 17025.

The accreditation is valid up to 22-01-2018. DAkkS-register number: D-PL-11120-02-00.

TÜV Rheinland Energie und Umwelt GmbH
D-51105 Köln, Am Grauen Stein, Tel: 0221 806-5200, Fax: 0221 806-1349

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Overview

The following addendum contains information regarding the Model 49i measuring system manufactured by Thermo Fisher Scientific for ozone as well as an assessment of the measuring system with consideration of compliance to the requirements of the 2012 version of Standard EN 14625.
The Model 49i measuring system manufactured by Thermo Fisher Scientific was performance tested and announced as follows:

- Model 49i for O_3 with notification of the German Federal Environment Agency (UBA) dated 21st February 2006 (BAnz., p. 2653, Chapter IV Number 3.2)

The original test of the Model 49i was performed in such a way that the tests have been evaluated and documented both with regard to the minimum requirements of Standard VDI 4202 sheet 1 as well as to the respective European Standard EN 14625 (Version 2005).

The European Standard EN 14625 has since been revised and newly published in the new version in December 2012. The revision also included a reworking of the minimum requirements of performance tests. It is therefore necessary to test for compliance with the requirements of the current Standard EN 14625 (December 2012) based on the available test results.

In addition to the assessment of the type 1 change “New coating of measuring cell”, thorough supplementary tests were carried out on the Model 49i in accordance with Standard EN 14625. The test results obtained were therefore also used in assessing the system’s conformity with the requirements of the 2012 version of EN 14625. The corresponding notice of change was made as follows:

- Model 49i for O_3 with notification of the German Federal Environment Agency (UBA) dated 23rd February 2012 (BAnz., p. 920, Chapter V Notice 1), statement dated 17th November 2011

Because the basic test of the measuring systems and the data from this field test were assessed and documented in the test report according to VDI sheet 1 and EN 14625 (Version 2005), a number of issues had to be addressed in the process of transferring the AMS into the EN 15267 certification system.

The following addendum to the performance test report provides explanations of these issues as well as the assessment and documentation of compliance with the requirements of the current Standard EN 14625 (December 2012) for the Thermo Fisher Scientific Model 49i AMS for ozone

Upon publication this addendum becomes a permanent part of the TÜV Rheinland test report no. 936/21203248/B1 and of the statement dated 17th January 2011 and can be viewed on the internet at www.qal1.de.

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1. Overview of test results for the AMS Model 49i in accordance with Standard EN 14625 (December 2012)

The following table provides an overview of the performance characteristics, performance criteria and the test results achieved (basis: test report 936/21203248/B1 dated 5th January 2006 and statement dated 17th November 2011) in accordance with Standard EN 14625. Furthermore, express reference is made to the changes between the requirements of the 2005 version and the current version from 2012. A corresponding statement on these issues can be found in the following chapters. The uncertainty calculation was also updated in compliance with the current Standard version from 2012.

Performance characteristic	Performance criterion	Test result	Compliant	Compliance documented in
8.4.5 Repeatability standard deviation at zero	≤ 1.0 nmol/mol	S_{rz} System 0529812870: 0,1 ppb S_{rz} System Pilot 1: 0,1 ppb	yes	Statement dated 17th November 2011
8.4.5 Repeatability standard deviation at concentration c_t	≤ 3.0 nmol/mol	$S_{r,ct}$ System 0529812870: 0,1 ppb $S_{r,ct}$ System Pilot 1: 0,1 ppb	yes	Statement dated 17th November 2011 + See Item 2
8.4.6 Lack of fit (residual from the linear regression function)	Largest residual from the linear regression function ≤ 4 % of measured value Residual at zero ≤ 5.0 nmol/mol	r_z System 0529812870: ZP -0,14 ppb r_{max} System 0529812870: SP -2,5 % r_z System Pilot 1: ZP -0,20 ppb r_{max} System Pilot 1: SP -2,7 %	yes	Statement dated 17th November 2011
8.4.7 Sensitivity coefficient of sample gas pressure	≤ 2.0 nmol/mol/kPa	b_{gp} System 1: 0,10 ppb/kPa b_{gp} System 2: 0,09 ppb/kPa	yes	936/21203248/B1 dated 5th January 2006
8.4.8 Sensitivity coefficient of sample gas temperature	≤ 1.0 nmol/mol/K	b_{gt} System 0529812870: 0,054 ppb/K b_{gt} System Pilot 1: 0,003 ppb/K	yes	Statement dated 17th November 2011
8.4.9 Sensitivity coefficient of surrounding temperature	≤ 1.0 nmol/mol/K	b_{st} System 0529812870: -0,23 ppb/K b_{st} System Pilot 1: -0,29 ppb/K	yes	Statement dated 17th November 2011
8.4.10 Sensitivity coefficient of electrical voltage	≤ 0.30 nmol/mol/V	b_v System 1: 0,02 ppb/V b_v System 2: 0,03 ppb/V	yes	936/21203248/B1 dated 5th January 2006 + See item 3
8.4.11 Interferents at zero and at concentration c_t	H_2O ≤ 10 nmol/mol Toluol ≤ 5.0 nmol/mol Xylol ≤ 5.0 nmol/mol	H_2O System 1: ZP -0,98 ppb / SP -1,64 ppb System 2: ZP -0,80 ppb / SP -1,57 ppb Toluol System 1: ZP 0,10 ppb / SP 0,97 ppb System 2: ZP 0,07 ppb / SP 0,54 ppb	yes	936/21203248/B1 dated 5th January 2006 + See item 4

Performance characteristic	Performance criterion	Test result	Com-pliant	Compliance documented in
		Xylol: System 1: ZP 0,10 ppb / SP 0,94 ppb System 2: ZP 0,04 ppb / SP 0,50 ppb		
8.4.12 Averaging effect	≤ 7,0 % des Messwerts	E_{av} System 0529812870: 3,15 % E_{av} System Pilot 1: 3,76 %	yes	Statement dated 17th November 2011
8.4.13 Difference between sample/calibration port	≤ 1,0 %	ΔX_{SC} System 1: ---- ΔX_{SC} System 2: ----	nicht an-wend-bar	936/21203248/B1 dated 5th Janua-ry 2006
8.4.3 Response time (ri-se)	≤ 180 s	t_r System 0529812870: max. 65 s t_r System Pilot 1: max. 63 s	yes	Statement dated 17th November 2011
8.4.3 Response time (fall)	≤ 180 s	t_f System 0529812870: max. 61 s t_f System Pilot 1: max. 61 s	yes	Statement dated 17th November 2011
8.4.3 Difference between rise time and fall time	≤ 10 s	t_d System 1: 5 s t_d System 2: 5 s	yes	yes, see Item 5
8.5.6 Period of unatten-ded operation	3,0 months or less if manufacturer indicates a shorter period, but not less than 2 weeks	System 1: 4 Wochen System 2: 4 Wochen	yes	936/21203248/B1 dated 5th Janua-ry 2006
8.5.7 Availability of the analyser	> 90 %	A_a System 1: 98 % A_a System 2: 98 %	yes	936/21203248/B1 dated 5th Janua-ry 2006
8.5.5 Reproducibility standard deviation under field condi-tions	≤ 5,0 % of the average of a three month period	$S_{r,f}$ System 0529812870: 0,826% $S_{r,f}$ System Pilot 1: 0,826 %	yes	Statement dated 17th November 2011
8.5.4 Long-term drift at zero	≤ 5,0 nmol/mol	$D_{l,z}$ System 0529812870: 1,00 ppb $D_{l,z}$ System Pilot 1: 1,04 ppb	yes	Statement dated 17th November 2011
8.5.4 Long-term drift at span level	≤ 5,0 % of maximum of certification range	$D_{l,s}$ System 0529812870: max. 1,45 % $D_{l,s}$ System Pilot 1: max. -1,48 %	yes	Statement dated 17th November 2011 + See Item 6
8.4.4 Short-term drift at zero	≤ 2,0 nmol/mol over 12 h	$D_{s,z}$ System 1: 0,06 ppb $D_{s,z}$ System 2: -0,08 ppb	yes	936/21203248/B1 dated 5th Janua-ry 2006
8.4.4 Short-term drift at span level	≤ 6,0 nmol/mol over 12 h	$D_{s,s}$ System 1: -1,34 ppb $D_{s,s}$ System 2: 0,29 ppb	yes	936/21203248/B1 dated 5th Janua-ry 2006
8.4.14 Residence time in the analyser	≤ 3 s	ca 2,9 s	yes	Statement dated 17th November 2011

2. Statement on test item "Repeatability standard deviation at concentration c_t"

[No. 8.4.5 of EN 14625, statement dated 17th November 2011, page 10 onwards]

The Spanish institute "Instituto de Salud Carlos III" determined this test item to be non-compliant with the requirements of test standards in its summary of the evaluation of the existing test reports ("EVALUATION OF TYPE APPROVAL REPORT 2010") for the Model 49i AMS.

During the necessary supplementary tests of the AMS due to the newly coated measuring cell, the test was repeated in 2011 in accordance with the standards. The test results were documented and presented in the statement dated 17th November 2011. The results obtained are considered accordingly in the calculation of total uncertainty.

This complies with the minimum requirements.

3. Statement on test item "Sensitivity coefficient of electrical voltage"

[No. 8.4.10 of EN 14625, test report 936/21203248/B1 page 66 onwards]

During the test of the Model 49i AMS a minor span level non-compliance with the requirements of Standard EN 14625 was determined. Instead of the specified test concentration between 70 % - 80 % of the certification range (corresponds to 175 ppb – 200 ppb), the test was carried out with only approx. 163 ppb (approx. 65 % of the certification range), meaning that the span level was officially too low.

A representative assessment of the sensitivity coefficients of voltage is however, from a purely technical perspective, possible at this test gas level. The obtained value of max. 0.03 ppb/V is also far below the minimum requirement of 0.30 ppb/V. The insufficient test gas level is also considered in the calculation of the measurement uncertainty. The result obtained can therefore be deemed representative.

4. Statement on test item "Interferents at zero and at concentration c_t"

[No. 8.4.11 of EN 14625, test report 936/21203248/B1 page 56 onwards]

The Spanish institute "Instituto de Salud Carlos III" determined this test item to be non-compliant with the requirements of test standards in its summary of the evaluation of the existing test reports ("EVALUATION OF TYPE APPROVAL REPORT 2010") for the Model 49i AMS.

A non-compliance in the span level was identified as a discrepancy to the requirements of Standard EN 14625. Instead of the required 120 ppb (1h alarm threshold), the test was carried out at approx. 175 ppb O_3 (= 70 % ZB), a span level which is officially too high.

A representative assessment of the influence of interferents should however, from a purely technical perspective, still be possible at this test gas level. Furthermore, in calculating the measurement uncertainty the excessive test gas level is taken into account for every interferent. The result obtained can therefore be deemed representative.

5. Statement on test item “Difference between rise time and fall time”

[No. 8.4.3 of EN 14625, statement dated 17th November 2011 page 6 onwards]

As part of the revision of Standard EN 14625, the minimum requirement for test item “Difference between rise time and fall time” was changed from requiring ≤10 % relative difference or 10 s, depending which is greater (2005 version), to solely requiring ≤10 s (version 2012).
The differences between rise time and fall time calculated during the performance test for O_3 are 5 s (system 0529812870) and 5 s (system Pilot 1).
This therefore complies with the requirements of the 2012 version of Standard EN 14625.

6. Statement on test item “Long-term drift at span level”

[No. 8.5.4 of EN 14625, statement dated 17th November 2011 page 27 onwards]

The Spanish institute “Instituto de Salud Carlos III” determined this test item to be non-compliant with the requirements of test standards in its summary of the evaluation of the existing test reports (“EVALUATION OF TYPE APPROVAL REPORT 2010”) for the Model 49i AMS.

As part of the necessary supplementary tests of the AMS due to the new coating of the measuring cell, the test was repeated in accordance with the standards in 2011. The test results were documented and presented in the statement dated 17th November 2011. The results obtained are considered accordingly in the calculation of total uncertainty.

This complies with the minimum requirements.

7. Update of total uncertainty calculation in accordance with Annex E of Standard EN 14625

The calculation of total uncertainty was updated based on the new version of Standard EN 14625, Annex E.

The performance criteria according to EN 14625 (Version 2012) are completely fulfilled.

Table 1: Expanded uncertainty from the results of the laboratory test for system 1 (SN 1 + SN 0529812870)

Measuring device:	Thermo Fisher Scientific Model 49i				Serial number:	Gerät 1	
Measured component:	O3				1h-Alert threshold:	120	nmol/mol

No.	Performance characteristic	Performance criterion	Result	Partial uncertainty		Square of partial uncertainty
1	Repeatability standard deviation at zero	≤ 1.0 nmol/mol	0.100	$u_{r,z}$	0.03	0.0007
2	Repeatability standard deviation at 1h-limit value	≤ 3.0 nmol/mol	0.100	$u_{r,lh}$	0.03	0.0007
3	"lack of fit" at 1h-limit value	≤ 4.0% of meas. value	1.500	$u_{l,lh}$	1.04	1.0800
4	Sensitivity coefficient of sample gas pressure at 1h-limit value	≤ 2.0 nmol/mol/kPa	0.100	u_{gp}	1.04	1.0800
5	Sensitivity coefficient of sample gas temperature at 1h-limit value	≤ 1.0 nmol/mol/K	0.054	u_{gt}	0.56	0.3149
6	Sensitivity coefficient of surrounding temperature at 1h-limit value	≤ 1.0 nmol/mol/K	-0.230	u_{st}	-1.59	2.5392
7	Sensitivity coefficient of electrical voltage at 1h-limit value	≤ 0.30 nmol/mol/V	0.020	u_V	0.30	0.0885
8a	Interferent H_20 with 21 mmol/mol	≤ 10 nmol/mol (Zero)	-0.980	u_{H2O}	-1.07	1.1427
		≤ 10 nmol/mol (Span)	-1.640			
8b	Interferent Toluene with 0,5 µmol/mol	≤ 5.0 nmol/mol (Zero)	0.100	$u_{int,pos}$ or $u_{int,neg}$	0.79	0.6280
		≤ 5.0 nmol/mol (Span)	0.970			
8c	Interferent Xylene with 0,5 µmol/mol	≤ 5.0 nmol/mol (Zero)	0.100			
		≤ 5.0 nmol/mol (Span)	0.940			
9	Averaging effect	≤ 7.0% of meas. value	3.150	u_{av}	2.18	4.7628
18	Difference sample/calibration port	≤ 1%	0.000	$u_{\Delta sc}$	0.00	0.0000
21	Uncertainty of test gas	≤ 3%	2.000	u_{cg}	1.20	1.4400

Combined standard uncertainty	u_c	3.6163	nmol/mol
Expanded uncertainty	U	7.2326	nmol/mol
Relative expanded uncertainty	W	6.03	%
Maximum allowed expanded uncertainty	W_{req}	15	%

Table 2: Expanded uncertainty from the results of the laboratory and field tests for system 1 (SN 1 + SN 0529812870)

Measuring device:	Thermo Fisher Scientific Model 49i					Serial number:	Gerät 1	
Measured component:	O3					1h-Alert threshold:	120	nmol/mol

No.	Performance characteristic	Performance criterion		Result	Partial uncertainty		Square of partial uncertainty	
1	Repeatability standard deviation at zero	≤	1.0 nmol/mol	0.100	$u_{r,z}$	0.03	0.0007	
2	Repeatability standard deviation at 1h-limit value	≤	3.0 nmol/mol	0.100	$u_{r,lh}$	not considered, as ur,lh = 0,02 < ur,f	-	
3	"lack of fit" at 1h-limit value	≤	4.0% of meas. value	1.500	$u_{l,lh}$	1.04	1.0800	
4	Sensitivity coefficient of sample gas pressure at 1h-limit value	≤	2.0 nmol/mol/kPa	0.100	u_{gp}	1.04	1.0800	
5	Sensitivity coefficient of sample gas temperature at 1h-limit value	≤	1.0 nmol/mol/K	0.054	u_{gt}	0.56	0.3149	
6	Sensitivity coefficient of surrounding temperature at 1h-limit value	≤	1.0 nmol/mol/K	-0.230	u_{st}	-1.59	2.5392	
7	Sensitivity coefficient of electrical voltage at 1h-limit value	≤	0.30 nmol/mol/V	0.020	u_V	0.30	0.0885	
8a	Interferent H_20 with 21 mmol/mol	≤	10 nmol/mol (Zero)	-0.980	u_{H2O}	-1.07	1.1427	
		≤	10 nmol/mol (Span)	-1.640				
8b	Interferent Toluene with 0.5 µmol/mol	≤	5.0 nmol/mol (Zero)	0.100	$u_{int,pos}$	0.79	0.6280	
		≤	5.0 nmol/mol (Span)	0.970				
8c	Interferent Xylene with 0.5 µmol/mol	≤	5.0 nmol/mol (Zero)	0.100	or			
		≤	5.0 nmol/mol (Span)	0.940	$u_{int,\ neg}$			
9	Averaging effect	≤	7.0% of meas. value	3.150	u_{av}	2.18	4.7628	
10	Reproducibility standard deviation under field conditions	≤	5.0% of 3 month average	0.826	$u_{r,f}$	0.99	0.9825	
11	Long term drift at zero level	≤	5.0 nmol/mol	1.000	$u_{d,l,z}$	0.58	0.3333	
12	Long term drift at 1h-limit value	≤	5.0% of max. of cert. range	1.450	$u_{d,l,lh}$	1.00	1.0092	
18	Difference sample/calibration port	≤	1%	0.000	$u_{\Delta sc}$	0.00	0.0000	
21	Uncertainty of test gas	≤	3%	2.000	u_{cg}	1.20	1.4400	

Combined standard uncertainty	u_c	3.9245	nmol/mol
Expanded uncertainty	U	7.8490	nmol/mol
Relative expanded uncertainty	W	6.54	%
Maximum allowed expanded uncertainty	W_{req}	15	%

Table 3: Expanded uncertainty from the results of the laboratory test for system 2 (SN 2 + Pilot 1)

Measuring device:	Thermo Fisher Scientific Model 49i					Serial number:	Gerät 2	
Measured component:	O3					1h-Alert threshold:	120	nmol/mol

No.	Performance characteristic	Performance criterion		Result	Partial uncertainty		Square of partial uncertainty
1	Repeatability standard deviation at zero	≤	1.0 nmol/mol	0.100	$u_{r,z}$	0.03	0.0007
2	Repeatability standard deviation at 1h-limit value	≤	3.0 nmol/mol	0.100	$u_{r,lv}$	0.03	0.0007
3	"lack of fit" at 1h-limit value	≤	4.0% of meas. value	1.600	$u_{l,lv}$	1.11	1.2288
4	Sensitivity coefficient of sample gas pressure at 1h-limit value	≤	2.0 nmol/mol/kPa	0.090	u_{gp}	0.94	0.8748
5	Sensitivity coefficient of sample gas temperature at 1h-limit value	≤	1.0 nmol/mol/K	0.003	u_{gt}	0.03	0.0010
6	Sensitivity coefficient of surrounding temperature at 1h-limit value	≤	1.0 nmol/mol/K	-0.290	u_{st}	-2.01	4.0368
7	Sensitivity coefficient of electrical voltage at 1h-limit value	≤	0.30 nmol/mol/V	0.030	u_V	0.45	0.1992
8a	Interferent H_20 with 21 mmol/mol	≤	10 nmol/mol (Zero)	-0.800	u_{H2O}	-0.99	0.9819
		≤	10 nmol/mol (Span)	-1.570			
8b	Interferent Toluene with 0,5 µmol/mol	≤	5.0 nmol/mol (Zero)	0.070	$u_{int,pos}$	0.43	0.1864
		≤	5.0 nmol/mol (Span)	0.540	or		
8c	Interferent Xylene with 0,5 µmol/mol	≤	5.0 nmol/mol (Zero)	0.040			
		≤	5.0 nmol/mol (Span)	0.500	$u_{int,\ neg}$		
9	Averaging effect	≤	7.0% of meas. value	3.760	u_{av}	2.61	6.7860
18	Difference sample/calibration port	≤	1%	0.000	u_{Dsc}	0.00	0.0000
21	Uncertainty of test gas	≤	3%	2.000	ucg	1.20	1.4400

Combined standard uncertainty	u_c	3.9669	nmol/mol
Expanded uncertainty	U	7.9338	nmol/mol
Relative expanded uncertainty	W	6.61	%
Maximum allowed expanded uncertainty	W_{req}	15	%

Table 4: Expanded uncertainty from the results of the laboratory and field tests for system 2 (SN 2 + Pilot 1)

Measuring device:	Thermo Fisher Scientific Model 49i					Serial number:	Gerät 2	
Measured component:	O3					1h-Alert threshold:	120	nmol/mol

No.	Performance characteristic	Performance criterion		Result	Partial uncertainty		Square of partial uncertainty	
1	Repeatability standard deviation at zero	≤	1.0 nmol/mol	0.100	$u_{r,z}$	0.03	0.0007	
2	Repeatability standard deviation at 1h-limit value	≤	3.0 nmol/mol	0.100	$u_{r,lh}$	not considered, as ur,lh = 0,02 < ur,f	-	
3	"lack of fit" at 1h-limit value	≤	4.0% of meas. value	1.600	$u_{l,lh}$	1.11	1.2288	
4	Sensitivity coefficient of sample gas pressure at 1h-limit value	≤	2.0 nmol/mol/kPa	0.090	u_{gp}	0.94	0.8748	
5	Sensitivity coefficient of sample gas temperature at 1h-limit value	≤	1.0 nmol/mol/K	0.003	u_{gt}	0.03	0.0010	
6	Sensitivity coefficient of surrounding temperature at 1h-limit value	≤	1.0 nmol/mol/K	-0.290	u_{st}	-2.01	4.0368	
7	Sensitivity coefficient of electrical voltage at 1h-limit value	≤	0.30 nmol/mol/V	0.030	u_V	0.45	0.1992	
8a	Interferent H_20 with 21 mmol/mol	≤	10 nmol/mol (Zero)	-0.800	u_{H2O}	-0.99	0.9819	
		≤	10 nmol/mol (Span)	-1.570				
8b	Interferent Toluene with 0.5 µmol/mol	≤	5.0 nmol/mol (Zero)	0.070	$u_{int,pos}$	0.43	0.1864	
		≤	5.0 nmol/mol (Span)	0.540				
8c	Interferent Xylene with 0.5 µmol/mol	≤	5.0 nmol/mol (Zero)	0.040	or			
		≤	5.0 nmol/mol (Span)	0.500	$u_{int,\ neg}$			
9	Averaging effect	≤	7.0% of meas. value	3.760	u_{av}	2.61	6.7860	
10	Reproducibility standard deviation under field conditions	≤	5.0% of 3 month average	0.826	$u_{r,f}$	0.99	0.9825	
11	Long term drift at zero level	≤	5.0 nmol/mol	1.040	$u_{d,l,z}$	0.60	0.3605	
12	Long term drift at 1h-limit value	≤	5.0% of max. of cert. range	-1.480	$u_{d,l,lh}$	-1.03	1.0514	
18	Difference sample/calibration port	≤	1%	0.000	u_{Asc}	0.00	0.0000	
21	Uncertainty of test gas	≤	3%	2.000	u_{cg}	1.20	1.4400	

Combined standard uncertainty	u_c	4.2579	nmol/mol
Expanded uncertainty	U	8.5159	nmol/mol
Relative expanded uncertainty	W	7.10	%
Maximum allowed expanded uncertainty	W_{req}	15	%

TÜV RHEINLAND
ENERGIE UND UMWELT GMBH

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-11120-02-00

Addendum

Addendum zum Eignungsprüfbericht der Messeinrichtung Modell 49i der Firma Thermo Fisher Scientific für die Komponente Ozon zu dem TÜV-Bericht 936/21203248/B1 vom 05.01.2006 sowie zur Stellungnahme vom 17.01.2011

Bericht-Nr.: 936/21221382/A1
Köln, 29.03.2014

teu-service@de.tuv.com

Die TÜV Rheinland Energie und Umwelt GmbH ist mit der Abteilung Immissionsschutz
für die Arbeitsgebiete:

- Bestimmung der Emissionen und Immissionen von Luftverunreinigungen und Geruchsstoffen;
- Überprüfung des ordnungsgemäßen Einbaus und der Funktion sowie Kalibrierung kontinuierlich arbeitender Emissionsmessgeräte einschließlich Systemen zur Datenauswertung und Emissionsfernüberwachung;
- Feuerraummessungen;
- Eignungsprüfung von Messeinrichtungen zur kontinuierlichen Überwachung der Emissionen und Immissionen sowie von elektronischen Systemen zur Datenauswertung und Emissionsfernüberwachung
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- Bestimmung der Emissionen und Immissionen von Geräuschen und Vibrationen, Bestimmung von Schallleistungspegeln und Durchführung von Schallmessungen an Windenergieanlagen

nach DIN EN ISO/IEC 17025 akkreditiert.

Die Akkreditierung ist gültig bis 22-01-2018. DAkkS-Registriernummer: D-PL-11120-02-00.

TÜV Rheinland Energie und Umwelt GmbH
D-51105 Köln, Am Grauen Stein, Tel: 0221 806-5200, Fax: 0221 806-1349

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Kurzfassung

Das folgende Addendum enthält Anmerkungen zu der Messeinrichtung Thermo Fisher Scientific Modell 49i für die Komponente Ozon sowie eine Beurteilung der Messeinrichtung im Hinblick auf Einhaltung der Anforderungen gemäß der Richtlinie DIN EN 14625 in der Version 2012.
Die Messeinrichtung Thermo Fisher Scientific Modell 49i wurde eignungsgeprüft und wie folgt bekanntgegeben:

- Modell 49i für O_3 mit Bekanntmachung des Umweltbundesamtes vom 21. Februar 2006 (BAnz. S. 2653, Kapitel IV Nummer 3.2)

Die Prüfung der Messeinrichtung Modell 49i wurde damals so gestaltet, dass die Prüfungen redundant gemäß den Mindestanforderungen der Richtlinie VDI 4202 Blatt 1 sowie der entsprechenden europäischen Richtlinie EN 14625 (Version 2005) ausgewertet und dokumentiert wurden.
Mittlerweile wurde die Europäische Richtlinie DIN EN 14625 einer Revision unterzogen und in der neuen Version im Dezember 2012 wiederveröffentlicht. Im Rahmen der Revision wurden u.a. auch Mindestanforderungen für die Eignungsprüfung überarbeitet. Es gilt daher die Einhaltung der Anforderungen gemäß der aktuellen Richtlinie DIN EN 14625 (Ausgabe Dezember 2012) auf Basis der vorhandenen Prüfergebnisse zu überprüfen.

Für die Messeinrichtung Model 49i wurden in 2011 zusätzlich im Zuge der Bewertung der Typ1-Änderung „Neubeschichtung der Messzelle“ umfangreiche Nachprüfungen gemäß der Richtlinie EN 14625 durchgeführt. Die in diesem Rahmen gewonnenen Prüfergebnisse werden daher ebenfalls für die Beurteilung der Messeinrichtung im Hinblick auf Einhaltung der Anforderungen gemäß der Richtlinie DIN EN 14625 in der Version 2012 dieser Messeinrichtung herangezogen. Die entsprechende Änderungsmitteilung erfolgte wie folgt:

- Model 49i für O_3 mit Bekanntmachung des Umweltbundesamtes vom 23. Februar 2012 (BAnz. S. 920, Kapitel V Mittteilung 1), Stellungnahme vom 17. November 2011

Da die Basisprüfung der Messeinrichtung und die Auswertung der Daten aus diesem Feldtest sowohl nach den Mindestanforderungen der VDI 4202 Blatt 1 als auch nach der DIN EN 14625 (Version 2005) hin ausgewertet und im Prüfbericht dokumentiert wurden, sind im Rahmen der Überführung der Messeinrichtung in das Zertifiziersystem der EN 15267 Fragen aufgetreten.

Im folgenden Addendum zum Eignungsprüfbericht soll auf diese Punkte erläuternd eingegangen werden und gleichzeitig die Einhaltung der Anforderungen gemäß der aktuellen Richtlinie DIN EN 14625 (Ausgabe Dezember 2012) für die Messeinrichtung Thermo Fisher Scientific Modell 49i für die Komponente Ozon überprüft und dokumentiert werden.

Das Addendum wurde im März 2014 dahingehend überarbeitet, dass das bislang mit 4 Wochen aufgeführte Kontrollintervall nun gemäß Richtlinie DIN EN 14625 auf 3 Monate korrigiert wird. Gemäß Richtlinie DIN EN 14625 ist das Kontrollintervall die Zeitspanne, in der die Drift innerhalb des Leistungskriteriums für die Langzeitdrift liegt. Das Kontrollintervall von 3 Monaten gemäß Richtlinie DIN EN 14625 konnte sowohl in der Erstprüfung (Prüfbericht 936/21203248/B1 vom 05. Januar 2006) wie auch in den umfangreichen Nachuntersuchungen (Stellungnahme vom 17. November 2011) ermittelt werden, da in beiden Feldtests keine unzulässigen Driften beobachtet wurden. Die Tabelle unter Punkt 1 des Addendums wurde daraufhin korrigiert und das Addendum unter der Berichtsnummer 936/21221382/A1 aktualisiert.

Dieses Addendum ist nach seiner Veröffentlichung fester Bestandteil des TÜV Rheinland Prüfberichtes der Nummer 936/21203248/B1 sowie der Stellungnahme vom 17.01.2011 und wird im Internet unter www.qal1.de einsehbar sein.

Inhaltsverzeichnis

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1. Übersicht über die Ergebnisse der Prüfungen der Messeinrichtung Modell 49i gemäß Richtlinie DIN EN 14625 (Ausgabe Dezember 2012)

Die nachfolgende Tabelle gibt einen Überblick über die gemäß Richtlinie DIN EN 14625 (Ausgabe Dezember 2012) zu prüfenden Leistungskenngrößen, die Leistungskriterien sowie die erzielten Testergebnisse (Basis: Prüfbericht 936/21203248/B1 vom 05. Januar 2006 und Stellungnahme vom 17. November 2011). Darüber hinaus explizit wird auf Änderungen in den Anforderungen zwischen der Richtlinienversion aus 2005 und der aktuellen Version aus 2012 hingewiesen. In den nachfolgenden Kapiteln erfolgt eine entsprechende Stellungnahme zu diesen Punkten. Zusätzlich wurde die Unsicherheitsberechnung auch auf den Stand der aktuellen Richtlinienversion aus 2012 aktualisiert.

Leistungskenngröße	Leistungskriterium	Testergebnis	Erfüllt	Erfüllung dokumentiert in
8.4.5 Wiederholstandardabweichung bei Null	≤ 1,0 nmol/mol	S_{rz} Gerät 0529812870: 0,1 ppb S_{rz} Gerät Pilot 1: 0,1 ppb	ja	Stellungnahme vom 17. November 2011
8.4.5 Wiederholstandardabweichung bei Konzentration c_t	≤ 3,0 nmol/mol	$S_{r,ct}$ Gerät 0529812870: 0,1 ppb $S_{r,ct}$ Gerät Pilot 1: 0,1 ppb	ja	Stellungnahme vom 17. November 2011 + Siehe Punkt 2
8.4.6 „lack of fit“ (Abweichung von der linearen Regressionsfunktion)	Größte Abweichung von der linearen Regressionsfunktion ≤ 4 % des Messwerts Abweichung bei Null ≤ 5,0 nmol/mol	r_z Gerät 0529812870: ZP -0,14 ppb r_{max} Gerät 0529812870: SP -2,5 % r_z Gerät Pilot 1: ZP -0,20 ppb r_{max} Gerät Pilot 1: SP -2,7 %	ja	Stellungnahme vom 17. November 2011
8.4.7 Empfindlichkeitskoeffizient des Probegasdrucks	≤ 2,0 nmol/mol/kPa	b_{gp} Gerät 1: 0,10 ppb/kPa b_{gp} Gerät 2: 0,09 ppb/kPa	ja	936/21203248/B1 vom 05. Januar 2006
8.4.8 Empfindlichkeitskoeffizient der Probegastemperatur	≤ 1,0 nmol/mol/K	b_{gt} Gerät 0529812870: 0,054 ppb/K b_{gt} Gerät Pilot 1: 0,003 ppb/K	ja	Stellungnahme vom 17. November 2011
8.4.9 Empfindlichkeitskoeffizient der Umgebungstemperatur	≤ 1,0 nmol/mol/K	b_{st} Gerät 0529812870: -0,23 ppb/K b_{st} Gerät Pilot 1: -0,29 ppb/K	ja	Stellungnahme vom 17. November 2011
8.4.10 Empfindlichkeitskoeffizient der elektrischen Spannung	≤ 0,30 nmol/mol/V	b_v Gerät 1: 0,02 ppb/V b_v Gerät 2: 0,03 ppb/V	ja	936/21203248/B1 vom 05. Januar 2006 + Siehe Punkt 3
8.4.11 Störkomponenten bei Null und Konzentration ct	H_2O ≤ 10 nmol/mol Toluol ≤ 5,0 nmol/mol Xylol ≤ 5,0 nmol/mol	H_2O Gerät 1: ZP -0,98 ppb / SP -1,64 ppb Gerät 2: ZP -0,80 ppb / SP -1,57 ppb Toluol Gerät 1: ZP 0,10 ppb / SP 0,97 ppb Gerät 2: ZP 0,07 ppb / SP 0,54 ppb	ja	936/21203248/B1 vom 05. Januar 2006 + Siehe Punkt 4

Leistungskenngröße	Leistungskriterium	Testergebnis	Erfüllt	Erfüllung dokumentiert in
		Xylol: Gerät 1: ZP 0,10 ppb / SP 0,94 ppb Gerät 2: ZP 0,04 ppb / SP 0,50 ppb		
8.4.12 Mittelungseinfluss	≤ 7,0 % des Messwerts	E_{av} Gerät 0529812870: 3,15 % E_{av} Gerät Pilot 1: 3,76 %	ja	Stellungnahme vom 17. November 2011
8.4.13 Differenz zwischen Proben-/ Kalibiereingang	≤ 1,0 %	ΔX_{SC} Gerät 1: ---- ΔX_{SC} Gerät 2: ----	nicht anwendbar	936/21203248/B1 vom 05. Januar 2006
8.4.3 Einstellzeit (Anstieg)	≤ 180 s	t_r Gerät 0529812870: max. 65 s t_r Gerät Pilot 1: max. 63 s	ja	Stellungnahme vom 17. November 2011
8.4.3 Einstellzeit (Abfall)	≤ 180 s	t_f Gerät 0529812870: max. 61 s t_f Gerät Pilot 1: max. 61 s	ja	Stellungnahme vom 17. November 2011
8.4.3 Differenz zwischen Anstiegs- und Abfallzeit	≤ 10 s	t_d Gerät 1: 5 s t_d Gerät 2: 5 s	ja	ja, siehe Punkt 5
8.5.6 Kontrollintervall	3 Monate oder weniger, wenn der Hersteller eine kürzere Zeitspanne angibt, aber nicht weniger als 2 Wochen.	Gerät 1: 3 Monate Gerät 2: 3 Monate	ja	936/21203248/B1 vom 05. Januar 2006
8.5.7 Verfügbarkeit des Messgeräts	> 90 %	A_a Gerät 1: 98 % A_a Gerät 2: 98 %	ja	936/21203248/B1 vom 05. Januar 2006
8.5.5 Wiederholstandardabweichung unter Feld-Bedingungen	≤ 5,0 % des Durchschnitts eines 3-Monatszeitraums	$S_{r,f}$ Gerät 0529812870: 0,826 % $S_{r,f}$ Gerät Pilot 1: 0,826 %	ja	Stellungnahme vom 17. November 2011
8.5.4 Langzeitdrift bei Null	≤ 5,0 nmol/mol	$D_{l,z}$ Gerät 0529812870: 1,00 ppb $D_{l,z}$ Gerät Pilot 1: 1,04 ppb	ja	Stellungnahme vom 17. November 2011
8.5.4 Langzeitdrift beim Spanniveau	≤ 5,0 % des Maximums des Zertifizierungsbereiches	$D_{l,s}$ Gerät 0529812870: max. 1,45 % $D_{l,s}$ Gerät Pilot 1: max. -1,48 %	ja	Stellungnahme vom 17. November 2011 + Siehe Punkt 6
8.4.4 Kurzzeitdrift bei Null	≤ 2,0 nmol/mol über 12 h	$D_{s,z}$ Gerät 1: 0,06 ppb $D_{s,z}$ Gerät 2: -0,08 ppb	ja	936/21203248/B1 vom 05. Januar 2006
8.4.4 Kurzzeitdrift beim Spanniveau	≤ 6,0 nmol/mol über 12 h	$D_{s,s}$ Gerät 1: -1,34 ppb $D_{s,s}$ Gerät 2: 0,29 ppb	ja	936/21203248/B1 vom 05. Januar 2006
8.4.14 Verweilzeit im Messgerät	≤ 3 s	ca 2,9 s	ja	Stellungnahme vom 17. November 2011

2. Stellungnahme zum Prüfpunkt „Wiederholstandardabweichung bei der Konzentration c_t“

[Nr. 8.4.5 der DIN EN 14625, Stellungnahme vom 17. November 2011 ab Seite 10]

Das spanische Institut „Instituto de Salud Carlos III“ hat diesen Prüfpunkt in seiner Zusammenstellung der Auswertung der existierenden Prüfberichte („EVALUATION OF TYPE APPROVAL REPORT 2010“) für die Messeinrichtung Modell 49i als abweichend zu den Vorgaben der Prüfrichtlinien gekennzeichnet.

Im Zuge der notwendigen Nachprüfungen der Messeinrichtung wegen der neu beschichteten Messzelle, wurde die Prüfung in 2011 richtlinienkonform wiederholt. Die Dokumentation und Darstellung der Prüfergebnisse erfolgte in der Stellungnahme vom 17. November 2011. Die ermittelten Ergebnisse werden bei der Ermittlung der Gesamtunsicherheit entsprechend berücksichtigt.

Damit werden die Mindestanforderungen erfüllt.

3. Stellungnahme zum Prüfpunkt „Empfindlichkeitskoeffizient der elektrischen Spannung“

[Nr. 8.4.10 der DIN EN 14625, Prüfbericht 936/21203248/B1 ab Seite 66]

Bei der Prüfung der Messeinrichtung Modell 49i kann für diesen Prüfpunkt eine minimale Abweichung im Spanniveau zu den Vorgaben der Richtlinie EN 14625 festgestellt werden. Statt bei der vorgeschriebenen Prüfkonzentration im Bereich von 70 % - 80 % des Zertifizierungsbereichs (entspricht 175 ppb – 200 ppb) wurde die Prüfung lediglich bei ca. 163 ppb (entspricht ca. 65 % des Zertifizierungsbereichs) und damit formal bei einem zu niedrigen Spanniveau durchgeführt.

Die Beurteilung des Empfindlichkeitskoeffizienten der Spannung ist jedoch rein fachlich auch bei diesem Prüfgaslevel repräsentativ möglich sein. Die gefundenen Werte von max. 0,03 ppb/V liegen zudem weit unterhalb der Mindestanforderung von 0,30 ppb/V. Bei der Ermittlung der Messunsicherheit wird darüber hinaus das zu niedrige Prüfgaslevel ebenfalls berücksichtigt. Vor diesem Hintergrund ist das ermittelte Ergebnis als repräsentativ anzusehen.

4. Stellungnahme zum Prüfpunkt „Störkomponenten bei Null und bei der Konzentration c_t“

[Nr. 8.4.11 der DIN EN 14625, Prüfbericht 936/21203248/B1 ab Seite 56]

Das spanische Institut „Instituto de Salud Carlos III“ hat diesen Prüfpunkt in seiner Zusammenstellung der Auswertung der existierenden Prüfberichte („EVALUATION OF TYPE APPROVAL REPORT 2010“) für die Messeinrichtung Model 49i als abweichend zu den Vorgaben der Prüfrichtlinien gekennzeichnet.

Als Diskrepanz zu den Vorgaben der Richtlinie EN 14625 kann an dieser Stelle eine Abweichung im Spanniveau festgestellt werden. Statt der vorgeschriebenen 120 ppb (1h-Alarmschwelle) wurde die Prüfung bei ca. 175 ppb O_3 (= 70 % ZB) und damit formal bei einem zu hohen Spanniveau durchgeführt.

Die Beurteilung des Einflusses von Störkomponenten sollte jedoch rein fachlich auch bei diesem Prüfgaslevel repräsentativ möglich. Bei der Ermittlung der Messunsicherheit wird darüber hinaus das zu hohe Prüfgaslevel für jede Störkomponente ebenfalls berücksichtigt. Vor diesem Hintergrund ist das ermittelte Ergebnis als repräsentativ anzusehen.

5. Stellungnahme zum Prüfpunkt „Differenz zwischen Anstiegs- und Abfallzeit“

[Nr. 8.4.3 der DIN EN 14625, Stellungnahme vom 17. November 2011 ab Seite 6]

Im Rahmen der Revision der Richtlinie DIN EN 14625 wurde die Mindestanforderung für den Prüfpunkt „Differenz zwischen Anstiegs- und Abfallzeit“ insofern geändert, dass die Anforderung von ≤10 % relative Differenz oder 10 s, je nachdem, welcher Wert größer ist (Version 2005) auf lediglich die Anforderung von ≤10 s (Version 2012) eingeschränkt wurde.
Die im Rahmen der Eignungsprüfung ermittelten Differenzen zwischen Anstiegs- und Abfallzeit liegen für O_3 bei 5 s (Gerät 0529812870) bzw. 5 s (Gerät Pilot 1).
Damit werden die Mindestanforderungen der Richtlinie DIN EN 14625 auch in der Version aus 2012 erfüllt.

6. Stellungnahme zum Prüfpunkt „Langzeitdrift beim Spanniveau“

[Nr. 8.5.4 der DIN EN 14625, Stellungnahme vom 17. November 2011 ab Seite 27]

Das spanische Institut „Instituto de Salud Carlos III“ hat diesen Prüfpunkt in seiner Zusammenstellung der Auswertung der existierenden Prüfberichte („EVALUATION OF TYPE APPROVAL REPORT 2010“) für die Messeinrichtung Modell 49i als abweichend zu den Vorgaben der Prüfrichtlinien gekennzeichnet.

Im Zuge der notwendigen Nachprüfungen der Messeinrichtung wegen der neu beschichteten Messzelle, wurde die Prüfung in 2011 richtlinienkonform wiederholt. Die Dokumentation und Darstellung der Prüfergebnisse erfolgte in der Stellungnahme vom 17. November 2011. Die ermittelten Ergebnisse werden bei der Ermittlung der Gesamtunsicherheit entsprechend berücksichtigt.

Damit werden die Mindestanforderungen erfüllt.

7. Update der Gesamtunsicherheitsberechnung gemäß Annex E der Richtlinie DIN EN 14625

Die Ermittlung der Gesamtunsicherheit wurde auf Basis der neuen Version der Richtlinie DIN EN 14625, Annex E aktualisiert.

Die Leistungskriterien nach DIN EN 14625 (Version 2012) werden in vollem Umfang erfüllt.

Tabelle 1: Erweiterte Unsicherheit aus den Ergebnissen der Laborprüfung für Gerät 1 (SN 1 + SN 0529812870)

Messgerät:	Thermo Fisher Scientifc Modell 49i				Seriennummer:	Gerät 1	
Messkomponente:	O3				1h-Grenzwert Alarmschwelle:	120	nmol/mol

Nr.	Leistungskenngröße	Anforderung	Ergebnis	Teilunsicherheit		Quadrat der Teilunsicherheit	
1	Wiederholstandardabweichung bei Null	≤ 1,0 nmol/mol	0,100	$u_{r,z}$	0,03	0,0007	
2	Wiederholstandardabweichung beim 1h-Grenzwert	≤ 3,0 nmol/mol	0,100	$u_{r,1h}$	0,03	0,0007	
3	"lack of fit" beim 1h-Grenzwert	≤ 4,0% des Messwertes	1,500	$u_{l,1h}$	1,04	1,0800	
4	Änderung des Probengasdrucks beim 1h-Grenzwert	≤ 2,0 nmol/mol/kPa	0,100	u_{gp}	1,04	1,0800	
5	Änderung der Probengastemperatur beim 1h-Grenzwert	≤ 1,0 nmol/mol/K	0,054	u_{gt}	0,56	0,3149	
6	Änderung der Umgebungstemperatur beim 1h-Grenzwert	≤ 1,0 nmol/mol/K	-0,230	u_{st}	-1,59	2,5392	
7	Änderung der el. Spannung beim 1h-Grenzwert	≤ 0,30 nmol/mol/V	0,020	u_V	0,30	0,0885	
8a	Störkomponente H20 mit 21 mmol/mol	≤ 10 nmol/mol (Null)	-0,980	u_{H2O}	-1,07	1,1427	
		≤ 10 nmol/mol (Span)	-1,640				
8b	Störkomponente Toluol mit 0,5 µmol/mol	≤ 5,0 nmol/mol (Null)	0,100	$u_{int,pos}$	0,79	0,6280	
		≤ 5,0 nmol/mol (Span)	0,970				
8c	Störkomponente Xylol mit 0,5 µmol/mol	≤ 5,0 nmol/mol (Null)	0,100	oder			
		≤ 5,0 nmol/mol (Span)	0,940	$u_{int,neg}$			
9	Mittelungsfehler	≤ 7,0% des Messwertes	3,150	u_{av}	2,18	4,7628	
18	Differenz Proben-/Kalibriergaseingang	≤ 1,0%	0,000	$u_{\Delta sc}$	0,00	0,0000	
21	Unsicherheit Prüfgas	≤ 3,0%	2,000	u_{cg}	1,20	1,4400	

Kombinierte Standardunsicherheit	u_c	3,6163	nmol/mol
Erweiterte Unsicherheit	U	7,2326	nmol/mol
Relative erweiterte Unsicherheit	W	6,03	%
Maximal erlaubte erweiterte Unsicherheit	W_{req}	15	%

Tabelle 2: Erweiterte Unsicherheit aus den Ergebnissen der Labor- und Feldprüfungen für Gerät 1 (SN 1 + SN 0529812870)

Messgerät:	Thermo Fisher Scientifc Modell 49i					Seriennummer:	Gerät 1	
Messkomponente:	O3					1h-Grenzwert Alarmschwelle:	120	nmol/mol
Nr.	**Leistungskenngröße**	**Anforderung**		**Ergebnis**	**Teilunsicherheit**		**Quadrat der Teilunsicherheit**	
1	Wiederholstandardabweichung bei Null	≤	1,0 nmol/mol	0,100	$u_{r,z}$	0,03	0,0007	
2	Wiederholstandardabweichung beim 1h-Grenzwert	≤	3,0 nmol/mol	0,100	$u_{r,lh}$	nicht berücksichtigt, da ur,lh = 0,02 < ur,f	-	
3	"lack of fit" beim 1h-Grenzwert	≤	4,0% des Messwertes	1,500	$u_{l,lh}$	1,04	1,0800	
4	Änderung des Probengasdrucks beim 1h-Grenzwert	≤	2,0 nmol/mol/kPa	0,100	u_{gp}	1,04	1,0800	
5	Änderung der Probengastemperatur beim 1h-Grenzwert	≤	1,0 nmol/mol/K	0,054	u_{gt}	0,56	0,3149	
6	Änderung der Umgebungstemperatur beim 1h-Grenzwert	≤	1,0 nmol/mol/K	-0,230	u_{st}	-1,59	2,5392	
7	Änderung der el. Spannung beim 1h-Grenzwert	≤	0,30 nmol/mol/V	0,020	u_V	0,30	0,0885	
8a	Störkomponente H20 mit 21 mmol/mol	≤	10 nmol/mol (Null)	-0,980	u_{H2O}	-1,07	1,1427	
		≤	10 nmol/mol (Span)	-1,640				
8b	Störkomponente Toluol mit 0,5 µmol/mol	≤	5,0 nmol/mol (Null)	0,100	$u_{int,pos}$	0,79	0,6280	
		≤	5,0 nmol/mol (Span)	0,970	oder			
8c	Störkomponente Xylol mit 0,5 µmol/mol	≤	5,0 nmol/mol (Null)	0,100				
		≤	5,0 nmol/mol (Span)	0,940	$u_{int,\ neg}$			
9	Mittelungsfehler	≤	7,0% des Messwertes	3,150	u_{av}	2,18	4,7628	
10	Vergleichspräzision unter Feldbedingungen	≤	5,0% des Mittels über 3 Mon.	0,826	$u_{r,f}$	0,99	0,9825	
11	Langzeitdrift bei Null	≤	5,0 nmol/mol	1,000	$u_{d,l,z}$	0,58	0,3333	
12	Langzeitdrift beim 1h-Grenzwert	≤	5,0% des Max. des Zert.bereichs	1,450	$u_{d,l,lh}$	1,00	1,0092	
18	Differenz Proben-/Kalibriergaseingang	≤	1,0%	0,000	$u_{\Delta sc}$	0,00	0,0000	
21	Unsicherheit Prüfgas	≤	3,0%	2,000	u_{cg}	1,20	1,4400	
					Kombinierte Standardunsicherheit	u_c	3,9245	nmol/mol
					Erweiterte Unsicherheit	U	7,8490	nmol/mol
					Relative erweiterte Unsicherheit	W	6,54	%
					Maximal erlaubte erweiterte Unsicherheit	W_{req}	15	%

Tabelle 3: Erweiterte Unsicherheit aus den Ergebnissen der Laborprüfung für Gerät 2 (SN 2 + Pilot 1)

Messgerät:	Thermo Fisher Scientifc Modell 49i				Seriennummer:	Gerät 2	
Messkomponente:	O3				1h-Grenzwert Alarmschwelle:	120	nmol/mol

Nr.	Leistungskenngröße	Anforderung	Ergebnis	Teilunsicherheit		Quadrat der Teilunsicherheit	
1	Wiederholstandardabweichung bei Null	≤ 1,0 nmol/mol	0,100	$u_{r,Z}$	0,03	0,0007	
2	Wiederholstandardabweichung beim 1h-Grenzwert	≤ 3,0 nmol/mol	0,100	$u_{r,lv}$	0,03	0,0007	
3	"lack of fit" beim 1h-Grenzwert	≤ 4,0% des Messwertes	1,600	$u_{l,lv}$	1,11	1,2288	
4	Änderung des Probengasdrucks beim 1h-Grenzwert	≤ 2,0 nmol/mol/kPa	0,090	u_{gp}	0,94	0,8748	
5	Änderung der Probengastemperatur beim 1h-Grenzwert	≤ 1,0 nmol/mol/K	0,003	u_{gt}	0,03	0,0010	
6	Änderung der Umgebungstemperatur beim 1h-Grenzwert	≤ 1,0 nmol/mol/K	-0,290	u_{st}	-2,01	4,0368	
7	Änderung der el. Spannung beim 1h-Grenzwert	≤ 0,30 nmol/mol/V	0,030	u_V	0,45	0,1992	
8a	Störkomponente H20 mit 21 mmol/mol	≤ 10 nmol/mol (Null)	-0,800	u_{H2O}	-0,99	0,9819	
		≤ 10 nmol/mol (Span)	-1,570				
8b	Störkomponente Toluol mit 0,5 µmol/mol	≤ 5,0 nmol/mol (Null)	0,070	$u_{int,pos}$			
		≤ 5,0 nmol/mol (Span)	0,540	oder	0,43	0,1864	
8c	Störkomponente Xylol mit 0,5 µmol/mol	≤ 5,0 nmol/mol (Null)	0,040				
		≤ 5,0 nmol/mol (Span)	0,500	$u_{int,\ neg}$			
9	Mittelungsfehler	≤ 7,0% des Messwertes	3,760	u_{av}	2,61	6,7860	
18	Differenz Proben-/Kalibriergaseingang	≤ 1,0%	0,000	u_{Dsc}	0,00	0,0000	
21	Unsicherheit Prüfgas	≤ 3,0%	2,000	ucg	1,20	1,4400	

Kombinierte Standardunsicherheit	u_c	3,9669	nmol/mol
Erweiterte Unsicherheit	U	7,9338	nmol/mol
Relative erweiterte Unsicherheit	W	6,61	%
Maximal erlaubte erweiterte Unsicherheit	W_{req}	15	%

Tabelle 4: Erweiterte Unsicherheit aus den Ergebnissen der Labor- und Feldprüfungen für Gerät 2 (SN 2 + Pilot 1)

Messgerät:	Thermo Fisher Scientifc Modell 49i					Seriennummer:	Gerät 2	
Messkomponente:	O3					1h-Grenzwert Alarmschwelle:	120	nmol/mol
Nr.	**Leistungskenngröße**	**Anforderung**		**Ergebnis**	**Teilunsicherheit**		**Quadrat der Teilunsicherheit**	
1	Wiederholstandardabweichung bei Null	≤	1,0 nmol/mol	0,100	$u_{r,z}$	0,03	0,0007	
2	Wiederholstandardabweichung beim 1h-Grenzwert	≤	3,0 nmol/mol	0,100	$u_{r,lh}$	nicht berücksichtigt, da ur,lh = 0,02 < ur,f	-	
3	"lack of fit" beim 1h-Grenzwert	≤	4,0% des Messwertes	1,600	$u_{l,lh}$	1,11	1,2288	
4	Änderung des Probengasdrucks beim 1h-Grenzwert	≤	2,0 nmol/mol/kPa	0,090	u_{gp}	0,94	0,8748	
5	Änderung der Probengastemperatur beim 1h-Grenzwert	≤	1,0 nmol/mol/K	0,003	u_{gt}	0,03	0,0010	
6	Änderung der Umgebungstemperatur beim 1h-Grenzwert	≤	1,0 nmol/mol/K	-0,290	u_{st}	-2,01	4,0368	
7	Änderung der el. Spannung beim 1h-Grenzwert	≤	0,30 nmol/mol/V	0,030	u_V	0,45	0,1992	
8a	Störkomponente H20 mit 21 mmol/mol	≤	10 nmol/mol (Null)	-0,800	u_{H2O}	-0,99	0,9819	
		≤	10 nmol/mol (Span)	-1,570				
8b	Störkomponente Toluol mit 0,5 µmol/mol	≤	5,0 nmol/mol (Null)	0,070	$u_{int,pos}$			
		≤	5,0 nmol/mol (Span)	0,540	oder	0,43	0,1864	
8c	Störkomponente Xylol mit 0,5 µmol/mol	≤	5,0 nmol/mol (Null)	0,040				
		≤	5,0 nmol/mol (Span)	0,500	$u_{int,\ neg}$			
9	Mittelungsfehler	≤	7,0% des Messwertes	3,760	u_{av}	2,61	6,7860	
10	Vergleichspräzision unter Feldbedingungen	≤	5,0% des Mittels über 3 Mon.	0,826	$u_{r,f}$	0,99	0,9825	
11	Langzeitdrift bei Null	≤	5,0 nmol/mol	1,040	$u_{d,l,z}$	0,60	0,3605	
12	Langzeitdrift beim 1h-Grenzwert	≤	5,0% des Max. des Zert.bereichs	-1,480	$u_{d,l,lh}$	-1,03	1,0514	
18	Differenz Proben-/Kalibriergaseingang	≤	1,0%	0,000	$u_{\Delta sc}$	0,00	0,0000	
21	Unsicherheit Prüfgas	≤	3,0%	2,000	u_{cg}	1,20	1,4400	
					Kombinierte Standardunsicherheit	u_c	4,2579	nmol/mol
					Erweiterte Unsicherheit	U	8,5159	nmol/mol
					Relative erweiterte Unsicherheit	W	7,10	%
					Maximal erlaubte erweiterte Unsicherheit	W_{req}	15	%