

**Report on the exemplary performance test of  
the multi-component emission measuring  
system OPSIS AR 602 Z of OPSIS AB,  
Furulund/Sweden, for the determination of  
phenol and formaldehyde**

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**Institut für Umweltschutz  
und Energietechnik**

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## 1

**ABSTRACT**

At the request of OPSIS GmbH, 50226 Frechen, and with financial support from the state of North Rhine-Westphalia, the TÜV Rheinland, Sicherheit und Umweltschutz GmbH /1/, (Technical Inspectorate of Rhineland, Safety and Environmental Protection Limited) subjected the measuring system OPSIS AR 602 Z to an exemplary performance test in accordance with the Recommendations for Continuously-Operating Emission Measuring Systems and the Test Catalogue. The system operates on the principle of Differential Optical Absorption Spectroscopy (DOAS). We assessed the measurement of phenol and formaldehyde in the measuring range from 0 to 20 mg/m<sup>3</sup>.

The exemplary performance test covers the entire emission measuring system. The tests included laboratory tests and a continuous operation field-test in the purified gas of a plant manufacturing mineral-wool products. The process characteristics were determined both at the laboratory and during the field measurements.

Overall, the measuring system OPSIS AR 602 Z satisfied the Minimum Requirements during the test. We therefore recommend publication as a suitable measuring system for determination of phenol and formaldehyde concentrations in flue gases and waste gases of plants operated under the TA Luft (German Technical Regulations for Air Pollution Control).

We must, however, draw attention to the SO<sub>2</sub> cross sensitivity in formaldehyde measurements. At concentrations of more than 15 mg/m<sup>3</sup> (with a 2 m monitoring path), the permissible values are no longer met.

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/1/ This exemplary performance test was carried out with considerable financial support from the Ministry of Environmental Protection, Regional Planning and Agriculture of North Rhine-Westphalia.

OPSIS GmbH, 50226 Frechen, requested the TÜV Rheinland Sicherheit und Umweltschutz GmbH (Technical Inspectorate of Rhineland, Safety and Environmental Protection Limited) to subject the multi-component emission measuring system OPSIS AR 602 Z to an exemplary performance test with regard to the continuous measurement of phenol and formaldehyde in the flue gas of plants operated under the TA Luft (German Technical Regulations for Air Pollution Control). The system is an **"in-situ"** instrument whose operating principle relies on the fact that the gas to be measured absorbs a light beam in a characteristic wavelength range. The exemplary test was carried out with financial support from the state of North Rhine-Westphalia.

In the course of the exemplary performance test, the measuring system was tested both at the laboratory and in the field. The test results were compared with the Minimum Requirements according to the

"Recommendations for performance testing, installation, calibration and maintenance of measuring systems for continuous emission measurement" issued by the Federal Ministry of Environmental Protection, Nature Conservation and Reactor Safety (BMU circular dated March 1, 1990; IGI 2-556 134/4 GMB1. No. 12; pp. 226/229).

### 3 DESCRIPTION OF THE MEASURING SYSTEM

#### 3.1 Principle of operation and design

##### 3.1.1 Physical fundamentals

A detailed description of the multi-component emission measuring system OPSIS AR 602 Z is given in the manufacturer's User Manual included as an annex to this report. The monitoring system is a photometric measuring instrument. The principle of operation of such instruments is based on the fact that the monitored gas absorbs light in a wavelength range that is characteristic for this gas. Analysis is performed by measuring the absorption on the basis of the relation between the gas concentration and the amount of absorbed light as stated by Beer-Lambert's Law:

$$I_1 = I_0 * e^{-\alpha LC} \quad \text{or} \quad \ln(I_0/I_1) = \alpha LC \quad (0)$$

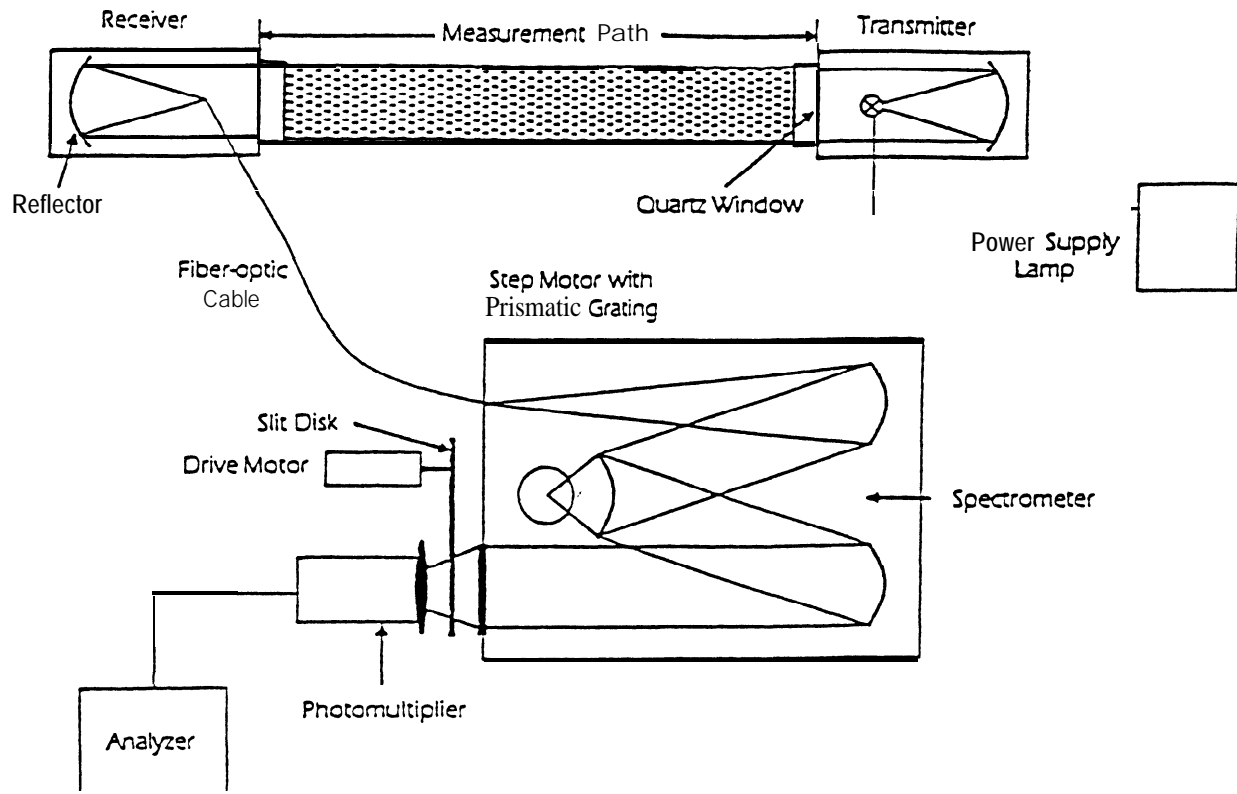
with:

$I_1$ : intensity of the transmitted light  
 $I_0$ : intensity of the emitted light  
 $L$ : length of the monitoring path  
 $c$ : concentration of the monitored gas  
 $\alpha$ : average absorption of the gas in the examined wavelength range

##### 3.1.2 Functional description

A light source emits a highly-concentrated beam of light in the wavelength range between 200 and 2000 nm. This light passes through the medium to be monitored and is focused on the end of a fibre-optic cable.

The light source is a high-pressure xenon lamp with a power input of 150 watts. The lamp is situated in the focal point of a parabolic reflector. The divergence angle of the parallelly emitted light is less than 2 mrad. The light beam penetrates a quartz glass window at the emitter's output.



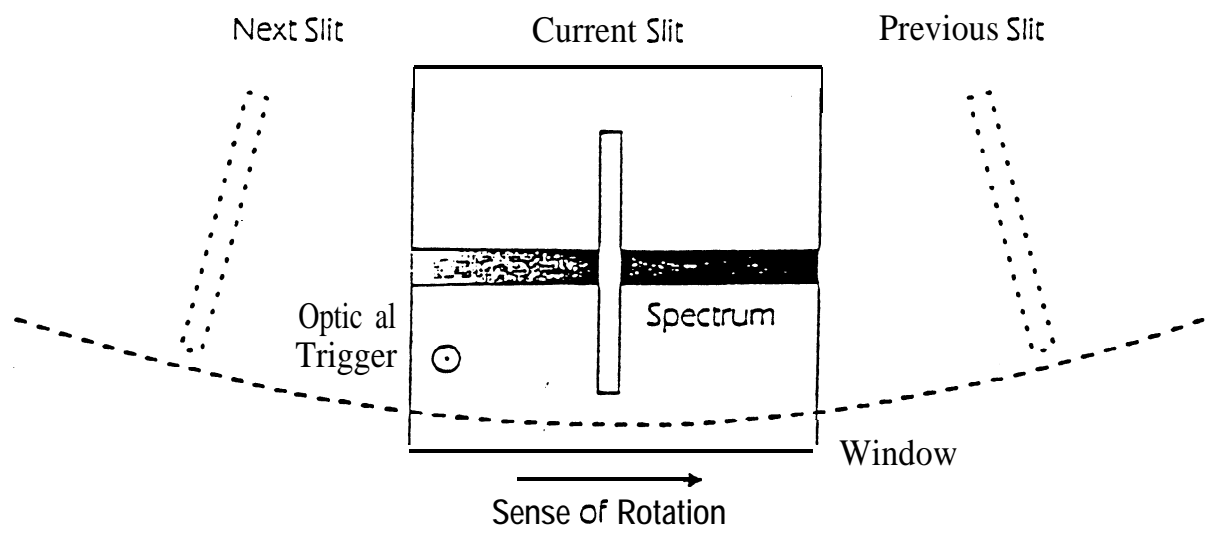
**Figure 3.1:** Functional diagram of the emission measuring system OPSIS AR 602 Z

The optical receiver ER 060 is similar in design to the emitter but with the inlet area of a fibre-optic cable situated in the focal point of the parabolic reflector.

The fibre-optic cable connects the receiver to the analyzer. It has a light-active core diameter of 0.6 mm and transmits light in the range between 200 and 2000 nm.

The analyzer is a grating spectrometer (Czerny-Turner principle with a light path of 0.5 m). The entry slit is replaced by the end of the optical cable. A spectral grating which is moved by means of a stepping motor breaks up the incoming light so that the wavelength range to be analyzed hits the window of one out of a maximum of three photomultipliers. The light is focused on the photomultiplier by a lens in the window.

A slit disk (200 mm in diameter) rotates between the window and the photomultiplier at 300 rpm. 20 slits are etched into this disk. The spacing of the slits is selected so that during one measurement only one slit will pass over the window in front of the photomultiplier (see Figure 3.2). This permits a scanning rate of 100 scans per second.



**Figure 3.2:** Recording the individual spectra

The UV-sensitive photomultiplier has a diameter of 50 mm. The photomultiplier's high voltage is resolved into 4096 steps (12 bits) within the range of 190 to 1100 volts and is set to a new operating point at each measurement. This operating point depends on the light intensity of the light to be measured. The photomultiplier current resulting from each scan operation is converted into a digital signal with an accuracy of 4096 steps (12 bits) by a very fast analog-to-digital converter. The scanned signals are stored in a register which splits up the wavelength range among 1000 channels.

For emission measurements, the integration period for one component is between 3 and 30 seconds. Several thousand scan signals are recorded during this period so that an adequate signal-to-noise ratio is obtained. Brief interruptions of the light beam - in proportion to the measuring period under observation - do not effect the measurement result.

The longer the measuring time, the higher is the signal-to-noise ratio since the scanned signals for each wavelength are added up.



On the basis of the measured values stored in 1000 registers (each register corresponds to a defined wavelength range), the absorption spectrum is approximated by the following method to permit the calculation of the equation

$$\begin{aligned} \ln(I_0/I_1) &= \Delta\alpha L c \\ 0 &= \ln(I_0/I_1) - \Delta\alpha L c \end{aligned} \quad (1)$$

with:

$I_0$ : intensity spectrum of the xenon lamp  
 $I_1$ : measured intensity spectrum  
 $\Delta\alpha$ : differential absorption coefficient  
 $L$ : length of the measurement path  
 $C$ : concentration to be determined

First, the stored raw data spectrum is divided by a previously recorded spectrum of the xenon high-pressure lamp stored in the analyzer. This spectrum was recorded by means of a separate lamp with a fibre-optic cable connecting the lamp and the analyzer either at the laboratory or in the field during the zero point calibration. This step ensures that the wave dependence of the lamp intensity and all changes in the spectrum resulting from the test set-up (e.g. effects resulting from the fibre-optic cable, the light path within the analyzer, the photomultiplier) are taken into account. The result is an absorption spectrum (12) of the flue gas to be measured.

Now, this spectrum is approximated by a polynomial of degree 5. The absorption spectrum 12 is divided by the calculated 5th-degree spectrum to eliminate all wide-band effects within the medium to be measured that might change the light spectrum of the lamp (e.g. light scattering due to dust, etc.). This has no effect on the absorptions of the individual molecules which affect specific lines only. Thus, a differential absorption spectrum 1x is obtained. This is equivalent to  $(I_0/I_1)$  in equation 1.

The logarithm of this quotient is then calculated.

The absorption coefficient  $\alpha(i)$  was determined at the laboratory for each wavelength (with defined concentration, measured  $I_0$ , measured  $I_1$  and known length in a closed vessel).

The concentration to be determined is the concentration at which the following expression is minimized:

$$(\ln I_x(i) - L \cdot c \cdot \Delta\alpha(i))^2 \Rightarrow 0 \quad (2)$$

The standard error of the result is proportional to  $a$ ; the variance is  $\sigma^2$ .

$$\sigma^2 = \sum_i \frac{(\ln I_x(i) - L \cdot c \cdot \Delta\alpha(i))^2}{n - 1}$$

$n$ : Number of channels used

Cross sensitivities to unknown substances having a differential absorption effect in the same wavelength range lead to an increase in the standard error. This standard error is calculated and displayed as a quality criterion for each measured value.

Cross sensitivities to known substances can be minimized by a corresponding modification of the above equation if the differential absorption coefficients are stored in the computer.

In the multi-component system examined by us, a specific wavelength range is set for each component, i.e. each component is measured separately. In exceptional cases, i.e. when two substances are measured in exactly the same spectral range, as for example NO and NH<sub>3</sub>, two components can be measured simultaneously in one wavelength range.

**3.1.3 Specifications of the measuring system**

Type designation	OPSIS AR 602 Z
Manufacturer	OPSIS AR, Furulund/Sweden
Distribution, technical service	OPSIS GmbH, Hauptstrasse 169, 50226 Frechen
Principle of operation	Differential Optical Absorption Spectroscopy (DOAS)
Monitored components	Phenol, formaldehyde
Measuring range	Phenol: 0 to 1000 µg/m <sup>3</sup> Formaldehyde: 0 to 1000 µg/m <sup>3</sup> Measuring ranges freely selectable by software settings
Smallest measuring range tested	Phenol: 0 to 20 µg/m <sup>3</sup> Formaldehyde: 0 to 20 µg/m <sup>3</sup>
Detection limit	Phenol : 0.2 µg/m <sup>3</sup> , 2m monitoring path Formaldehyde: 0.5 µg/m <sup>3</sup> , 2m monitoring path
Minimum measuring time	Phenol : 10 sec. Formaldehyde : 30 sec.
Length of monitoring path	up to 10 m
Measured-value display	Hercules, monochrome graphics
Zero drift	< 2% of the measuring span/month
Sensitivity drift	< 2% of the measuring span/month
Line voltage	230 V AC (± 10%) or 115 V (± 10%)
Power input	110 VA
Dimensions	600 * 440 * 266 (in mm)
Weight	approx. 30 kg
Degree of protection	IP 53
Modem	2400 bauds, full duplex, Hayes compatible
Emitter/Receiver	ER 060
Dimensions (L * W * H)	Emitter : 230 * 200 * 255 (in mm) Receiver: 310 * 165 * 125 (in mm)
Total weight	Emitter: approx. 7.5 kg Receiver: approx. 6.5 kg
Lamp in the emitter/wattage	Xenon high-pressure lamp, 150 watts
Duct connection	1 1/2" male thread
Degree of protection	IP 65

Power supply unit	<b>PS 150</b>
Dimensions (L * W * H)	280 * 115 * 270 (in mm)
Input voltage/current	230 V AC (t 6%, -10 %), 2.5 A max.
Power input	220 VA
Weight	4.5 kg
Degree of protection	IP 65
<b>Multiplexer</b>	<b>MX 024 / HX 004</b>
Dimensions (L * W * H)	400 * 310 * 190 / 370 * 260 * 185 (in mm)
Sequence time	< 5 sec.
Power input	40 watts max.
Inputs	2 * 12 / 2 * 2
outputs	2 * 1
Weight	approx. 15 kg / approx. 7 kg
Degree of protection	IP 65
<b>Mirror box</b>	<b>MB 060</b>
Calibration path	<b>CB 100 / MC 100</b>
<b>Signal manager</b>	<b>IO80</b>
AI 016	16 analog inputs
AO 008	8 analog outputs, max. 3 cards per system
DI 032	32 digital inputs/outputs max.

### 3.3 Reference measuring method

A thermostatted packed-bed cell [1] was used for phenol determination. Formaldehyde testing was performed with test gases from pressure cylinders supplied by Messer-Griesheim, Duisburg.

#### 3.3.1 Sampling and analytical methods for phenol

Test object:	Phenol
Measuring method:	VDI Recommendation 3485, Sheet 1, December 1988
Sampling equipment:	
- sampling probe:	heated
material:	glass/PTFE tubing
- particle filter:	heated by flue gas
material:	quartz wool in filter container of quartz glass
- absorption vessel:	100 ml washing bottles, with fritted glass disks D2; rinsed with aqua regia
- sorbent	caustic lye of soda, $c(\text{NaOH}) = 0.1 \text{ mol/l}$

Two fritted bottles connected in series were filled with 35 ml each.

For storage, the washing bottles were transferred into a glass bottle with lid (PTFE seal) in a clean location and afterwards flushed with the sorbent.

The samples were stored in a refrigerator. At low temperatures, they can be preserved for at least one week.

- sample storage time	2 days max.
- distance between probe intake point and separating element	2.2 m

Analytical determination:

- 3.75 ml of hydrochloric acid,  $c(\text{HCl}) = 1 \text{ mol/l}$ , were added to 37.5 ml of the sample solution: the mixture was then filled up to 50 ml. In accordance with the expected concentration, an aliquot part of the sample was **pipetted** in a 200 ml measuring flask and filled up to a total volume of 50 ml with a mixed solution (750 ml caustic lye of soda  $c(\text{NaOH}) = 0.1 \text{ mol/l}$ ; 75 ml hydrochloric acid  $c(\text{HCl}) = 1 \text{ mol/l}$ ; and 175 ml of distilled water). 15 ml of formaldehyde solution,  $c(\text{HCHO}) \approx 0.5 \text{ g/l}$ , and 20 ml reagent,

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[1] W. Jockel and P. Wilbring (1993), "State of the art of and outlook for automatic emission monitoring of special substances", VDI reports No. 1059, pp. 141 - 160

$c(\text{nitroaniline}) = 0.69 \text{ g/l}$  (1.38 g p-nitroaniline + 310 ml hydrochloric acid,  $c(\text{HCl}) = 1 \text{ mol/l}$ , filled up with distilled water to a total volume of 2 l) were added. 5 drops of the freshly prepared sodium nitrite solution (1 g  $\text{NaNO}_2$  + 9 g  $\text{H}_2\text{O}$ ) were dropped in and shaken until decolorization set in. After addition of 15 ml sodium carbonate  $c(\text{Na}_2\text{CO}_3) = 1 \text{ mol/l}$ , the samples were left to stand for 15 minutes; afterwards, the extinction at 490 nm was measured against water.

- Analysis equipment:

- \* Beckman photometer Model 34
- \* 50 mm cells

- Standards:

Approx. 7 mg of phenol are weighed out and dissolved in 1 l sorbent. Corresponding aliquots are drawn from this solution and filled up with sorbent to 150 ml. After 15 ml of hydrochloric acid have been added, the sample is filled up to 200 ml with distilled water.

**Process characteristics / Quality assurance**

- Influence of attendant substances:

Hydrogen sulphide and **amines** can be removed by means of a filter cartridge (glass balls coated with a saturated solution of silver sulphate in 85% phosphoric acid) during the sampling process.

- Absolute detection limit: 0.007 mg for examination of the entire sample volume

- Quality assurance measures:

The tests were carried out as twin determinations. Each series of measurements included the analysis of standards.

- Measurement uncertainty established for Phenol (U):

Mean value mg/m <sup>3</sup>	u (95%) mg/m <sup>3</sup>	Sampled gas volume l
6.3 *	0.5	30

\* Own twin determinations from 1993

### 3.3.2 Sampling and analytical methods for formaldehyde

Test object: aliphatic aldehydes, specifically formaldehyde  
Measuring method: Directive DIN 3862, Sheet 1, December 1990; MBTH method

Sampling equipment:

- sampling probe: heated  
material: glass
- sampling tube: heated  
material: glass
- particle filter: heated by flue gas  
material: quartz wool in filter container of glass
- absorption vessel: 100 ml washing bottles, with fritted glass disks D2; rinsed with aqua regia
- sorbent: MBTH solution, 0.05%

Two fritted bottles connected in series were filled with 20 ml each.

For storage, the washing bottles were transferred into a glass bottle with lid (PTFE seal) in a clean location and afterwards flushed with the sorbent.

- sample storage time: 1 day max., refrigerated
- distance between the probe intake point and the separating element: 2.2 m

#### Analytical determination:

15 ml of the sample solution were filled into a 25 ml measuring flask: 2 ml of the oxidation solution were added and admixed. After a period of 60 minutes, the samples were filled up with acetone and mixed thoroughly. After a further waiting period of 15 min, the sample was again filled up with acetone to compensate for volume contraction; afterwards, extinction was measured at 628 nm against acetone.

Analysis equipment:

- \* 10 mm cells
- \* Beckman photometer Model 34

Analysis was performed on the basis of a calibration curve. The individual standards for the calibration curve were prepared in accordance with the specification.

**Process characteristics / Quality assurance**

Influence of attendant substances:

- \* No interference was observed for up to 30 mg of sulphur dioxide per m<sup>3</sup> of flue gas.
  - \* The measurement result was not affected by up to 100 mg/m<sup>3</sup> nitrogen dioxide. Staining occurring during the sampling process has no influence on the measurement result if it disappears before the addition of ferric chloride; otherwise, the solutions must be discarded.
  - \* The measurement result was not affected by up to 5000 mg/m<sup>3</sup> of nitric oxide. Turbidity may occur at high concentrations: in this case, the samples must be discarded.
  - \* Hexamethylene-tetramine is hydrolyzed under the process conditions, making the formaldehyde concentrations appear higher than they are.
  - \* Turbidity that does not disappear after the addition of acetone renders photometric measurement impossible. The sample must be discarded.
- Absolute detection limit: 0.001 mg under the process and analysis conditions described above

**Quality assurance measures:**

Each series of measurements was prepared with blank values and standards of different concentrations. The measured values thus obtained were compared with those of the calibration curve.

- Measurement uncertainty (U) established for formaldehyde:

Mean value mg/m <sup>3</sup>	u (95%) mg/m <sup>3</sup>	Sampled gas volume l
2	0.1	20
20	0.2	20



### 3.4 Functional check of the measuring system

Recommended extent of the functional check:

#### **System test**

- \* Visual check of the entire measuring system
- \* Light intensity check for each individual component on the monitor and, if the red fibre-optic cable is used, with a hand-held photometer (intensity < 8000 lux)
- \* Checking the mirrors in emitter and receiver
- \* Cleaning the windows
- \* Checking the purge-air supply
- \* Checking the data recorded by the system for frequent occurrence of negative standard deviations
- \* System check

#### **With the calibration source CA 150:**

- \* For zero calibration, an ozone-free xenon high-pressure lamp must be installed in the calibration light source
- \* Zero point check in accordance with the instructions in the manual
- \* The fibre-optic cable used during measurements on the duct must be used for the calibration as well.

#### **With the calibration path CB 100 or a test path:**

- \* Emitter and receiver are flange-mounted to the calibration or test gas monitoring path. For this purpose, you can either use the units removed from the duct or additional systems.
- \* The fibre-optic cable used during measurements on the duct must be used for the calibration as well.
- \* The light level is adjusted to the light intensity found in the duct.
- \* Zero point, reference point and linearity check ( $Q < 3$  l/min); if the ambient temperatures are low, it may be necessary to use heated gas sampling lines and monitoring paths.
- \* As phenol test gases are not commercially available in pressure cylinders at present, a test gas generator must be used to check the phenol reference point. If such a unit is not available, comparison samples must be drawn from the flue gas duct (calibration).
- \* If applicable, reinstall emitter and receiver on the duct and optimize the light level.

The equipment required for these checks is listed in Annex 9.3 of this report.

## 4 TEST PROGRAM

### 4.1 Laboratory tests

The exemplary performance test was carried out in accordance with the "**Recommendations** concerning the performance testing, installation, calibration and maintenance of measuring systems for continuous emission measurements" issued by the Federal Ministry of Environmental Protection, Nature Conservation and Reactor Safety (BMU circular dated March 1, 1990; IGI 2-556 134/4-GMB1. No. 12, pp. 226/229).

These recommendations specify the following laboratory test program:

- Determination of the instrument characteristic with test gases

- A check of all instrument functions

- A check of the measuring system's cross sensitivity to attendant substances in the flue gas

- A check of the zero point stability in the admissible ambient temperature range

- A check of the reference point stability in the admissible ambient temperature range

- Determination of the influence of line voltage variations on the measuring signal

### 4.2 Field Test

The continuous-operation test was carried out with two identical OPSIS AR 602 Z systems over a period of three months.

Serial numbers of the two units used:

Unit 1: AR 602 Z - D - 081

Unit 2: AR 602 Z - G - 209

The following measuring ranges were selected for the continuous-operation test:

Phenol: 0 to 20 mg/m<sup>3</sup>

Formaldehyd: 0 to 20 mg/m<sup>3</sup>

The following equipment characteristics were established over the test period:

- availability

- maintenance interval

- detection limit

- capability of being calibrated

- stability of the instrument characteristic (zero,

- sensitivity drift)

- reproducibility

**LABORATORY TESTS****5.1 Instrument characteristic check (calibration function)**

The relation between the measured value and the given quantity of the test object was established at the laboratory. For this purpose, various test gas concentrations were prepared. A total of three test series took place. First of all, the calibration factors of the emission measuring system OPSIS AR 602 Z were established in a first series of tests and the system was adjusted by means of internal OPSIS calibration factors (Offset and Span). In the process, each measuring point was verified with the aid of a wet chemical comparison measurement. The instrument characteristic obtained in this way was subsequently verified twice on different days.

**Table 5.1:** Summary of the individual values from the linearity test for phenol

OPSIS AR 602 Z		Measuring range Actual value (n = 2)	Deviation in % of the upper range limit
Specified value mg/m <sup>3</sup>	Actual value mg/m <sup>3</sup>	mA	%
0.0	0.0	4.0	0.0
2.1	2.0	5.6	0.5
4.2	4.3	7.4	-0.5
6.3	6.2	9.0	0.5
8.4	8.3	10.6	0.5
10.5	10.3	12.2	1.0
12.6	12.8	14.2	-1.0
14.7	14.7	15.8	0.0
16.8	16.8	17.4	0.0
18.9	18.8	19.0	0.5
21.0	21.0	20.8	0.0

The given phenol test gas concentrations (x-axis) in mg/m<sup>3</sup> were allocated to the corresponding measuring signals of the analyzer (y-axis) in mA. The characteristic values established by this procedure are listed in Table 5.2.

**Table 5.2:** Characteristic values established during the linearity test for phenol

Measuring range	Number of measured values	a	b	R	Va	Vx
0 to 20 mg/m <sup>3</sup>	11	0.80	3.97	0.9997	0.004	0.09

a = slope of the instrument characteristic (mA / (mg/m<sup>3</sup>) phenol)

b = axis intercept of the instrument characteristic (mA)

R = correlation coefficient

Va = confidence interval of slope a (mA / (mg/m<sup>3</sup>) phenol)

Vx = confidence interval of axis intercept b (mA)

The characteristic values of the instrument characteristic were determined by a linear regression calculation as follows:

$$y = 0.80 * x + 3.97$$

**Table 5.3:** Summary of the individual values from the linearity test for formaldehyde

OPSIS AR 602 Z		Measuring range Actual value (n = 2)	Deviation in % of the upper range limit
Specified value mg/m <sup>3</sup>	Actual value mg/m <sup>3</sup>	mA	%
0.0	0.0	4.0	0.0
1.8	2.1	5.7	1.5
3.7	4.4	7.5	3.5
5.5	6.2	9.0	3.5
7.4	8.0	10.4	3.0
9.2	9.7	11.8	2.5
11.0	11.5	13.2	2.5
12.9	13.2	14.6	1.5
14.7	15.2	16.1	2.5
16.6	17.0	17.6	2.0
18.4	18.4	18.7	0.0

The given formaldehyde test gas concentrations (x-axis) in  $\text{mg}/\text{m}^3$  were allocated to the corresponding measuring signals of the analyzer (y-axis) in  $\text{mA}$ . The characteristic values established by this procedure are listed in Table 5.4.

Table 5.4: Characteristics established during the linearity test for formaldehyde

Measuring range	Number of measured values	a	b	R	Va	Vx
0 to 20 $\text{mg}/\text{m}^3$	11	0.80	4.36	0.9983	0.2	0.01

a = slope of the instrument characteristic ( $\text{mA} / (\text{mg}/\text{m}^3)$  formaldehyde)

b = axis intercept of the instrument characteristic ( $\text{mA}$ )

R = correlation coefficient

Va = confidence interval of slope a ( $\text{mA} / (\text{mg}/\text{m}^3)$  formaldehyde)

Vx = confidence interval of axis intercept b ( $\text{mA}$ )

The characteristic values of the instrument characteristic were determined by a linear regression calculation as follows:

$$y = 0.80 * x + 4.36$$

## 5.2 Determination of the cross sensitivities

The cross sensitivities to attendant substances that are normally present in the flue gas were determined using test gases of known composition.

The following test gases were presented to the Analyzer:

Component		Concentration	
Carbon dioxide	co2	9	vol. % in N2
Carbon monoxide	co	424.5	mg/m3 in N2
Sulphur dioxide	so2	441.5	mg/m3 in N2 for phenol
Sulphur dioxide	so2	15	mg/m3 in N2 for formaldehyde
Nitric oxide	NO	444	mg/m3 in N2
Nitrogen dioxide	NO2	3.8	mg/m3 in synthetic air
Ammonia	NH3	249.5	mg/m3 in N2
Hydrogen chloride	HCl	25	mg/m3 in N2
Moisture	H2O	260	g/m3 in N2
Phenol	C6H5OH	13.9	mg/m3 in N2 for formaldehyde
Formaldehyde	HCHO	9.2	mg/m3 in N2 for phenol

The results listed in Table 5.5 show that the tested measuring system for determination of phenol has no cross sensitivity to other flue gas components in normal concentrations. For formaldehyde, a slight cross sensitivity to nitrogen oxides was observed at the zero point. At the reference point, the measured value reading showed slight negative deviations upon addition of high ammonia concentrations.

The tested measuring system for determination of formaldehyde has a considerable cross sensitivity to SO2. For SO2 concentrations not exceeding 15 mg/m3 (for a 2 m monitoring path), the measuring system's cross sensitivity is within the limits specified by the Minimum Requirements.

**Table 5.5:** The influence of attendant substances on the measurement result

	Deviation in % of the measuring span								
	CO	SO <sub>2</sub>	NO	NO <sub>2</sub>	NH <sub>3</sub>	ACI	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> OH	HCHO
Phenol									
Zero point	co.2	<0.2	<0.2	co.2	<0.2	<0.2	<0.2	-	<0.2
Reference point relative to the measuring span	co.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	-	<0.2
Formaldehyde									
Zero point	<0.2	0.5	0.8	0.6	-1.9	<0.2	<0.2	co.2	-
Reference point relative to the measuring span	<0.2	2.5	<0.2	0.6	-0.9	to.2	co.2	<0.2	

### 5.3 The influence of ambient temperature on the measurement result

The measuring system was tested in the temperature range from -20 °C to +40 °C (ambient temperature) with three test gas concentrations graduated over the measuring range, including zero gas (N<sub>2</sub>). The ambient temperature was varied in an air-conditioned chamber in steps of 10 or 5 °C with the relative humidity of the ambient air at a (relatively) constant level of 60%. Adjustment/calibration of the measuring system was performed with nitrogen and test gas at an initial temperature of 20 °C. The test gas supply and the measuring cell were thermostatted (approx. 60 °C).

The steady-state period for each temperature stage was 60 minutes. Zero gas (N<sub>2</sub>) and test gas were applied at each temperature setting. The results of the temperature test are listed in Tables 5.6 and 5.7.

**Table 5.6:** The influence of ambient temperature on the measuring signal; deviations in % of the upper range limit (= 20 mg/m<sup>3</sup>)

Temperature	°C	-20	-10	0	10	20	30	40
Phenol								
Measured value	mg/m <sup>3</sup>	0.0	0.1	0.1	0.2	0.0	0.0	0.2
Deviation	%	0.5	0.0	0.5	1.0	0.0	0.0	1.0
Formaldehyde								
Measured value	mg/m <sup>3</sup>	-0.1	0.3	0.5	0.3	0.0	0.3	0.6
Deviation	%	-2.0	1.0	1.0	1.5	0.0	1.5	1.5

**Table 5.7** The influence of ambient temperature on the measuring signal; deviations in % of the measuring span  
 c(phenol) = 14.7 mg/m<sup>3</sup> and c(formaldehyde) = 17.3 mg/m<sup>3</sup>  
 Sampling lines and measuring cell heated to approx. 60 °C

Temperature	°C	-20	-10	0	10	20	30	40
Phenol								
Measured value	mg/m <sup>3</sup>	14.2	14.7	14.6	14.7	14.7	14.8	15.1
Deviation	%	-2.0	0.0	-0.7	0.0	0.0	0.7	2.0
Formaldehyde								
Measured value	mg/m <sup>3</sup>	16.9	17.3	17.1	17.5	17.3	17.9	17.5
Deviation	%	-2.3	0.0	-1.2	1.2	0.0	1.2	2.3

The Minimum Requirements permit the following change in the measuring signals for a 10 °C change in ambient temperature:

Zero point	± 2% of the upper range limit
Sensitivity	± 4% of the measuring span

The tested **system** satisfies the Minimum Requirements for phenol and formaldehyde.



#### 5.4 The influence of line voltage variations on the measuring signal

To determine the influence of line voltage variations on the measurement result, an isolating transformer was used to vary the power supply in the voltage range from -15% to +10% of 230 volts in steps of 5%. The influence of the voltage variation was examined for phenol with zero gas (N<sub>2</sub>) and at 14.7 mg/m<sup>3</sup> in the measuring range of 0 to 20 mg/m<sup>3</sup>. The measurement series were performed twice; the results are the maximum deviations listed in Table 5.8.

**Table 5.8:** The influence of line voltage variations on the measuring signal for phenol

Line voltage V	Zero point		Reference point	
	Measured value mg/m <sup>3</sup>	Deviation in % of the measuring range	Measured value mg/m <sup>3</sup>	Deviation in % of the measuring range
195.5	0.0	0.0	14.3	-2.0
207.0	0.0	0.0	14.7	0.0
218.5	0.0	0.0	14.7	0.0
230.0	0.0	0.0	14.7	0.0
241.5	0.1	0.5	14.7	0.0
253.0	0.0	0.0	14.7	0.0
264.5	0.1	0.5	14.6	0.5

The Minimum Requirements permit the following changes in the measuring signals:

Zero point       $\pm 2\%$  of the upper range limit  
Sensitivity      $\pm 4\%$  of the measuring span

The influence of line voltage variations was also examined for formaldehyde both with zero gas (N<sub>2</sub>) and at 17.3 mg/m<sup>3</sup> in the measuring range from 0 to 20 mg/m<sup>3</sup>. The measurement series were performed twice; the results are the maximum deviations listed in Table 5.9.

**Table 5.9:** The influence of line voltage variations on the measuring signal for formaldehyde

Line voltage V	Zero point		Reference point	
	Measured value mg/m <sup>3</sup>	Deviation in % of the measuring range	Measured value mg/m <sup>3</sup>	Deviation in % of the specified value
195.5	0.4	2.0	17.6	1.7
207.0	0.3	1.5	17.6	1.7
218.5	0.4	2.0	16.9	-2.3
230.0	0.0	0.0	17.3	0.0
241.5	0.4	2.0	17.8	2.9
253.0	0.4	2.0	16.8	-2.9
264.5	0.0	0.0	16.8	-2.9

The Minimum Requirements permit the following changes in the measuring signals:

Zero point       $\pm 2\%$  of the upper range limit  
Sensitivity       $\pm 4\%$  of the measuring span

The tested system satisfies the Minimum Requirements for formaldehyde.

#### 5.5        **The influence of relative air humidity, liquid-water content of the air, vibrations and service position**

The influence of relative air humidity was not specifically examined. In view of the instrument's design and construction, it can, however, be assumed that it is not sensitive to air humidity as long as the temperature does not drop below the dew point. The analyzer should be protected against splash water by installation in a cabinet.

During the continuous-operation test, the instruments were exposed to vibrations and shocks **occurring** at the test site. We observed no perceptible effects on the performance of the instruments. Nevertheless, care should be taken to select an installation site where the analyzer is exposed to a minimum of vibration and shock.

The manufacturer does not give specific instructions concerning the **analyzer's** service position: it is obvious from the unit's design. Emitter and receiver must be flange-mounted to the duct in accordance with the manufacturer's instructions.

#### 5.6        **The influence of light-beam drift on the measuring signal**

In order to determine the effects of light-beam drift at the laboratory, zero and reference point measurements were performed with and without light-beam drift. For this purpose, the fixing mechanism between the receiver and the monitoring path was removed enabling the receiver to be rotated round its axis.

With zero or reference gas flowing through the monitoring path, the receiver was rotated round its axis to make the light beam drift in an angular range of  $\pm 0.3^\circ$  (in steps of  $0.1^\circ$ ) in the horizontal and in the vertical direction. To measure the directional dependence, the measuring signal was first recorded at a deviation of  $0^\circ$  and the emitter was then rotated in the horizontal and in the vertical direction in angular steps of  $0.1^\circ$ .

For phenol, the deviations at the zero point were less than 0.2 % of the upper range limit and the maximum deviations at the reference point (14.7 mg/m<sup>3</sup>) were less than 0.5% of the display range. For formaldehyde, the maximum deviations found during the test were -1.6% at the zero point and -1.7% at the reference point (17.3 mg/m<sup>3</sup>).

## CONTINUOUS OPERATION FIELD-TEST

The Minimum Requirements stipulate a continuous operation field-test of at least three months **wich** should be carried out in one place if possible. During this period, the measuring system under examination must be operated under real-life conditions allowing the test results to be applied to comparable operating conditions.

The continuous-operation test was carried out in a plant manufacturing mineral wool products. The sampling point was in a circular, vertical duct after the scrubber. The duct had a diameter of 2 m and the gas was flowing upwards. The flue gas temperature was about 40 °C. Conditions at the sampling point varied from slightly positive to slightly negative pressure. The two OPSIS systems and the sampling connector for the comparison measurements were situated in a straight line above each other.

The performance test for phenol and formaldehyde was started on June 15, 1993. After an operating period of about 4 weeks, the test for formaldehyde had to be aborted because the measuring system could not meet the detection limits and zero point tolerances in the field test. The test for phenol was successfully completed after three months without any problems. The two measuring systems were then taken back to the manufacturer where they were optimized for formaldehyde measurements. After a supplementary test at the laboratory, the field test for formaldehyde was resumed on November 1, 1993, and completed on January 31, 1994. All calibration and maintenance work during this time was carried out by personnel of the Technical Inspectorate (TÜV) or by the manufacturer's service personnel under supervision.

Overall, the field measurements were carried out (phenol in the first, formaldehyde in the second attempt) without major problems with two identical OPSIS AR 602 Z measuring systems. During the three-months field test, measurement of the flue-gas moisture content was also activated with varying measuring times. The values output by the OPSIS measuring system were converted to standard state **"wet"** by OPSIS' internal 1080 signal manager to which the duct temperature and pressure values had been supplied. All measurement results were condensed to **half-hourly** mean values and continuously recorded over the entire duration of the continuous-operation test.

Two complete measuring systems were used during the **continuous-operation** test. Each of them comprised the following components:

- Analyzer OPSIS AR 602 Z
- Emitter and receiver (ER 060)
- Power supply unit (PS 150)
- Fibre-optic cable, 5m (OF6 OR)
- Analog input card (AI 016)
- Analog output card (AO 008)
- Calibration unit CA 150 with luxmeter, fibre-optic cable (OFR OR), 5 m

The measured data were stored on the **analyzer's** built-in hard disk. To generate the half-hourly mean values, the data recorded by the Analyzer were processed by the software included in the supply package. For a time, an additional data recorder with an integration period of 30 minutes was used as well.

At the beginning and at the end of the performance tests in the mineral wool plant, the system parameters were adjusted and/or checked with the aid of the calibration equipment. During the continuous-operation test, the calibration source CA 150 and the calibration path CB 100 were used to check the zero points. Furthermore, calibration measurements were performed both at the beginning and at the end of the continuous operation test.

## 6.1 Dead and response times

According to the VDI Recommendation 2449, Sheet 2, the dead time is the period between a sudden change in the state variable and the rise of the measured value to 10% of the value of the step response to be expected. The rise time is the time, after a sudden change in the state variable, of the rise of the measured value from 10% to 90% of the expected step response. The response time is the sum of the dead and the rise time.

For the "in-situ" measuring system OPSIS AR 602 Z, the dead time cannot be determined in this way. The measuring system will normally measure several flue gas components in sequence. As a general rule, the detection limit decreases as the measuring time for an individual component is increased, because the signal-to-noise ratio is improved. Table 6.1 lists the minimum measuring times established by the TÜV Rheinland in the course of performance tests or other test measurements to date.

If four components were activated in a system for plant monitoring in accordance with the TA Luft (German Technical Regulations for Air Pollution Control), a possible measuring cycle would take 60 seconds. A further 30 seconds (on average) per measuring cycle must be added for spectrometer adjustments. Thus, the total time for one measuring cycle is about 90 sec.

Due to the measuring principle, the maximum dead time or 90% time in case of sudden concentration changes in the flue gas duct will be 150 sec.

**Table 6.1:** Minimum measuring times for tested components of the measuring system OPSIS AR 602 Z

Component	Minimum measuring range tested	Unit	Minimum measuring time [s]	Comments
Sulphur dioxide	0 to 80	mg/m <sup>3</sup>	30 3	Performance Test Report TÜV Rheinland 936/800009 of Aug. 8, 1991 tested on the occasion of the exemplary performance test for mercury (0)
Nitric oxide	0 to 150	mg/m <sup>3</sup>	30 10	Performance Test Report TÜV Rheinland 936/804002/Hg of Feb. 25, 1994 Performance Test Report TÜV Rheinland 936/800009 of Aug. 8, 1991 tested on the occasion of the exemplary performance test for mercury (0)
Nitrogen dioxide	0 to 20	mg/m <sup>3</sup>	30 5	Performance Test Report TÜV Rheinland 936/800009 of Aug. 8, 1991 tested on the occasion of the exemplary performance test for mercury (0)
Ammonia	0 to 20	mg/m <sup>3</sup>	30	Performance Test Report TÜV Rheinland 936/804002/Hg of Feb. 25, 1994
	0 to 10	mg/m <sup>3</sup>	10	Performance Test Report TÜV Rheinland 936/800010 of May 27, 1992
Water	0 to 30	vol. %	30	Performance Test Report TÜV Rheinland 936/804002/NH <sub>3</sub> of Feb. 25, 1994
	0 to 30	vol. %	10	Performance Test Report TÜV Rheinland 936/800010/2 of March 1, 1993 tested on the occasion of the exemplary performance test for phenol and formaldehyde
Phenol	0 to 20	mg/m <sup>3</sup>	10	936/802011 of Feb. 25, 1994 tested on the occasion of the exemplary performance test for phenol and formaldehyde
Formaldehyde	0 to 20	mg/m <sup>3</sup>	30	936/802011 of Feb. 25, 1994 tested on the occasion of the exemplary performance test for phenol and formaldehyde
Metallic mercury	0 to 150	µg/m <sup>3</sup>	10	936/802011 of Feb. 25, 1994 Performance Test Report TÜV Rheinland 936/804002/Hg of Feb. 25, 1994

For components that are not listed here but can nevertheless be activated in the system, the manufacturer normally recommends a minimum measuring time of 30 sec.

## 6.2 Analysis function of the measuring system

The analysis function was prepared with the aid of manual comparison measurements. For this purpose, the measured value reading of the instrument was compared with the concentration in the flue gas determined with the comparison measurement method. The sampling point for the comparison measurements was situated approx. 0.3 m above the measuring axes of the two OPSIS AR 602 Z units. The comparison measurement methods used are described in Chapter 3.3.

The statistical evaluation of the measurement results which took the form of a regression analysis showed that the relation established by calibration between the concentrations in the flue gas determined with the comparison method  $y$  (mg/m<sup>3</sup>) and the instrument reading  $x$  (mA) can be described by the following linear equation:

$$y = a + b * x$$

The statistical evaluation includes the calibration curves with their upper and lower confidence limits for the mean values as well as the two tolerance limits for individual concentration values.

The tolerance limits specify the range within which the gas concentrations of an individual measured value (half-hourly mean value) may lie. According to definition, the tolerance limits state that 95% of all measured values will lie within this range with a significance level of 5%.

The following calibration measurements were performed for the component phenol:

Calibration at the beginning of the continuous-operation test

(Table 6.2 and Figures 6.1 and 6.2)

Calibration at the end of the continuous-operation test

(Table 6.3 and Figures 6.3 and 6.4).

The individual values are listed in Annex 9.4.



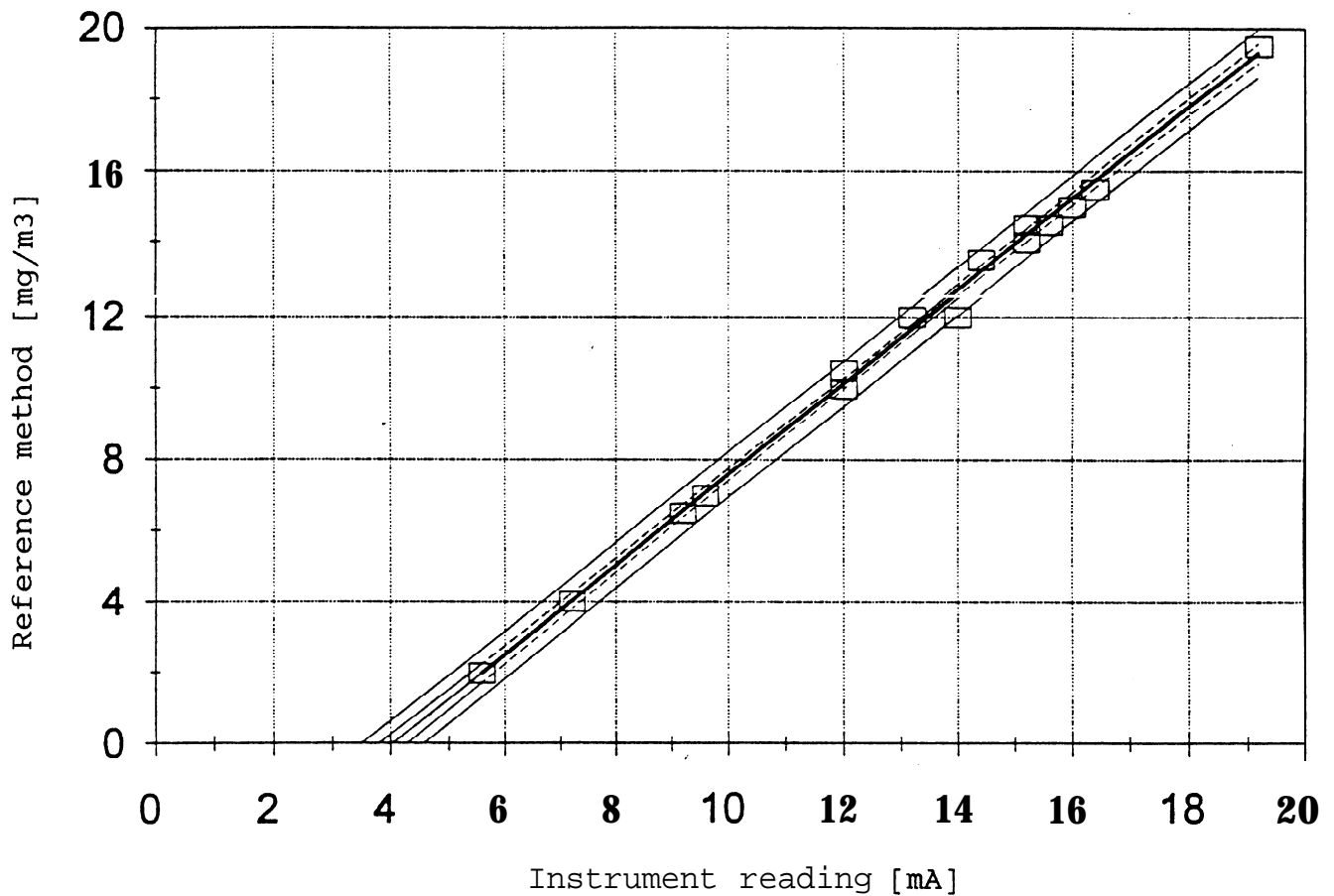
**Table 6.2:** Results of the regression analyses for phenol performed at the beginning of the continuous-operation test

	Unit 081	Unit 209
Number of measured values	16	16
Measuring range (mg/m <sup>3</sup> )	0 - 20	0 - 20
Mean value of the instrument reading (mA)	13.1	13.0
Mean value of the reference method (mg/m <sup>3</sup> ) for wet flue gas in standard state	11.4	11.4
Slope of the regression line (mg/m <sup>3</sup> ) / mA	1.27	1.26
Ordinate offset of the regression line (mg/m <sup>3</sup> )	-5.2	-5.0
Correlation coefficient	0.9962	0.9961

**Table 6.3:** Results of the regression analyses for phenol performed at the end of the continuous-operation test

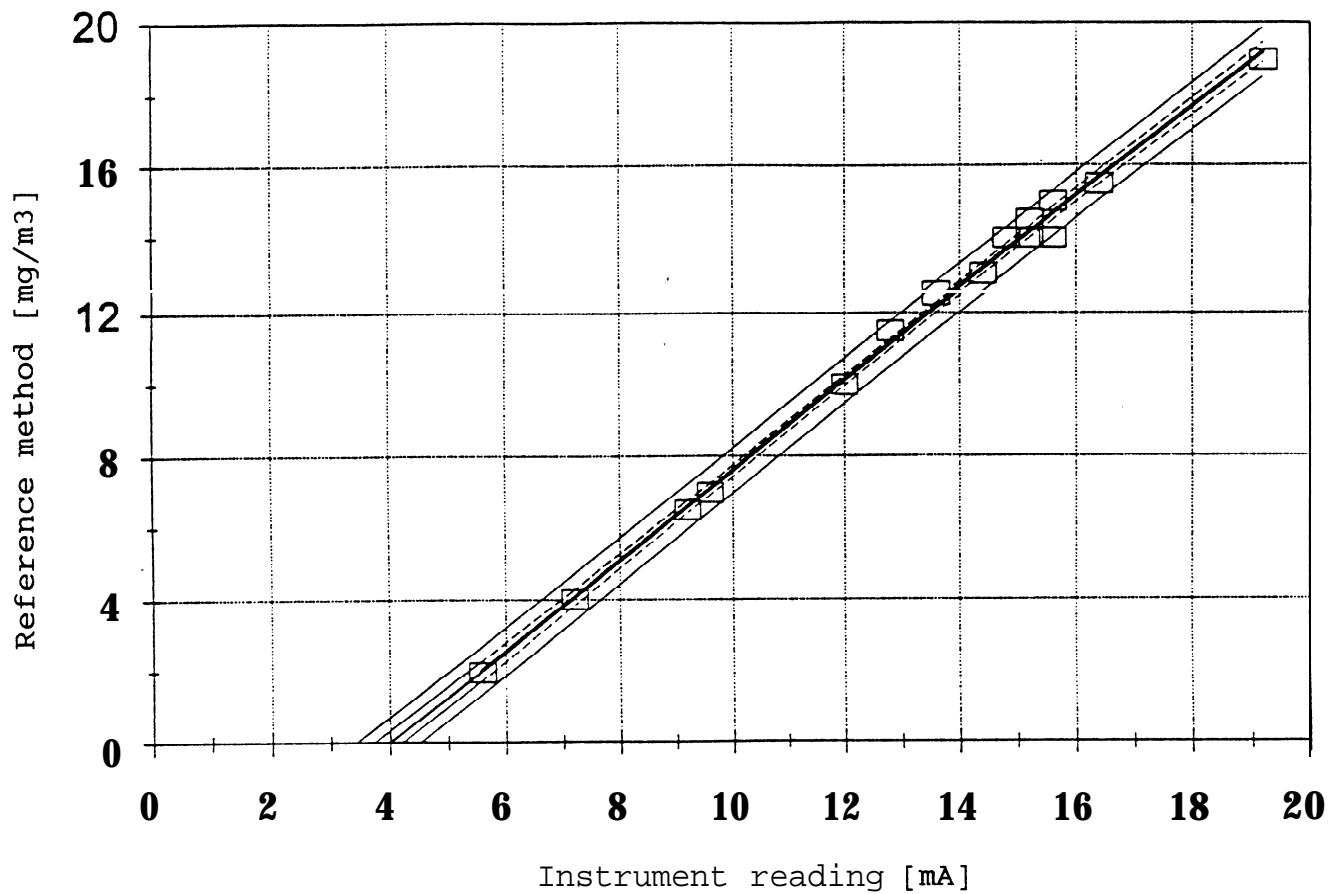
	Unit 081	Unit 209
Number of measured values	16	16
Measuring range (mg/m <sup>3</sup> )	0 - 20	0 - 20
Mean value of the instrument reading (mA)	12.8	12.8
Mean value of the reference method (mg/m <sup>3</sup> ) for wet flue gas in standard state	11.0	11.0
Slope of the regression line (mg/m <sup>3</sup> ) / mA	1.25	1.24
Ordinate offset of the regression line (mg/m <sup>3</sup> )	-5.1	-4.9
Correlation coefficient	0.9951	0.9941

The listed concentrations refer to wet flue gas in standard state.



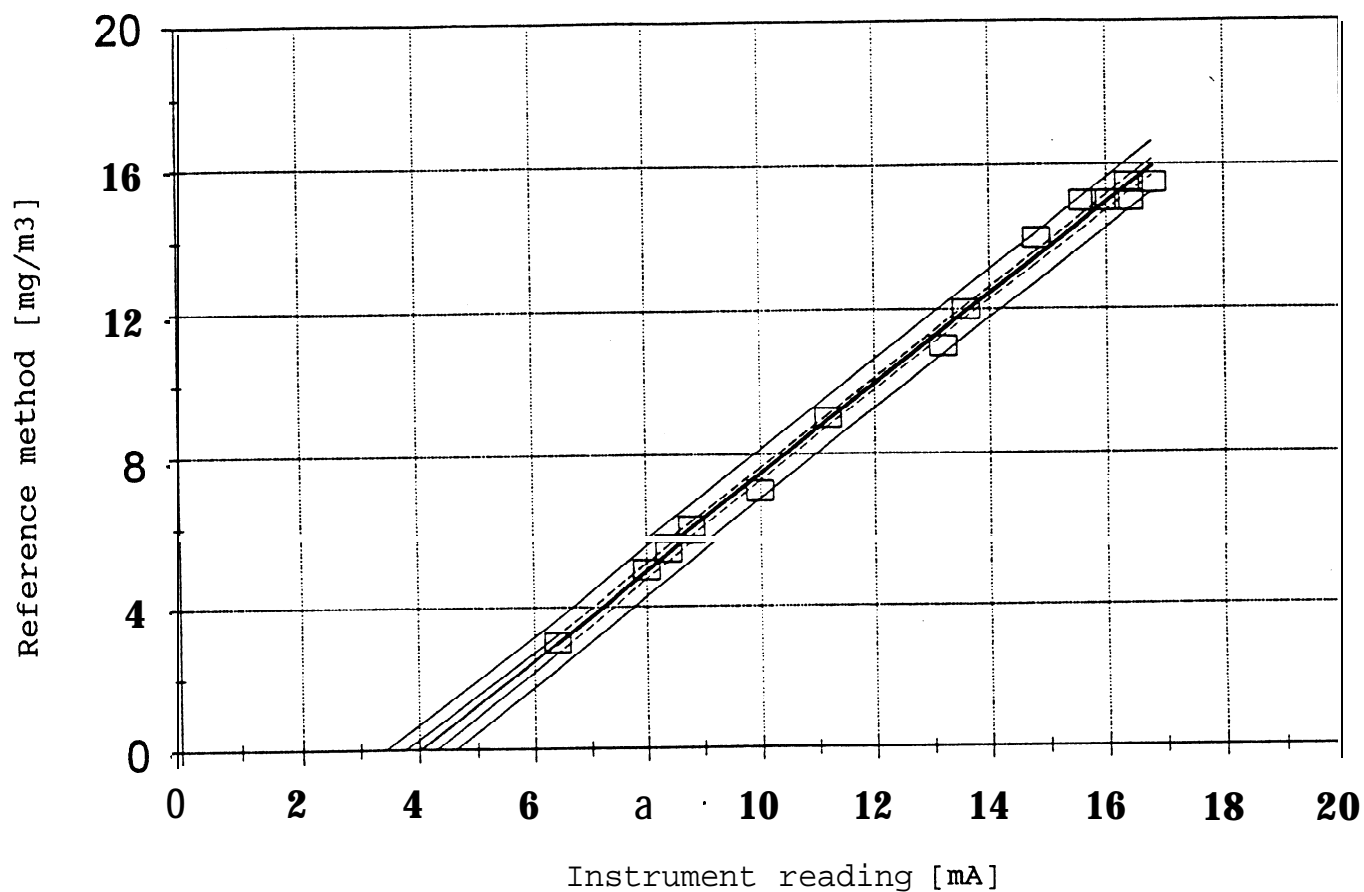
**Figure 6.1:** Calibration curve (analysis function) at the beginning of the exemplary performance test

Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m<sup>3</sup> phenol  
Tested criterion: Relation between the Unit 081 and the comparison method  
Test site: Purified gas of a mineral wool plant



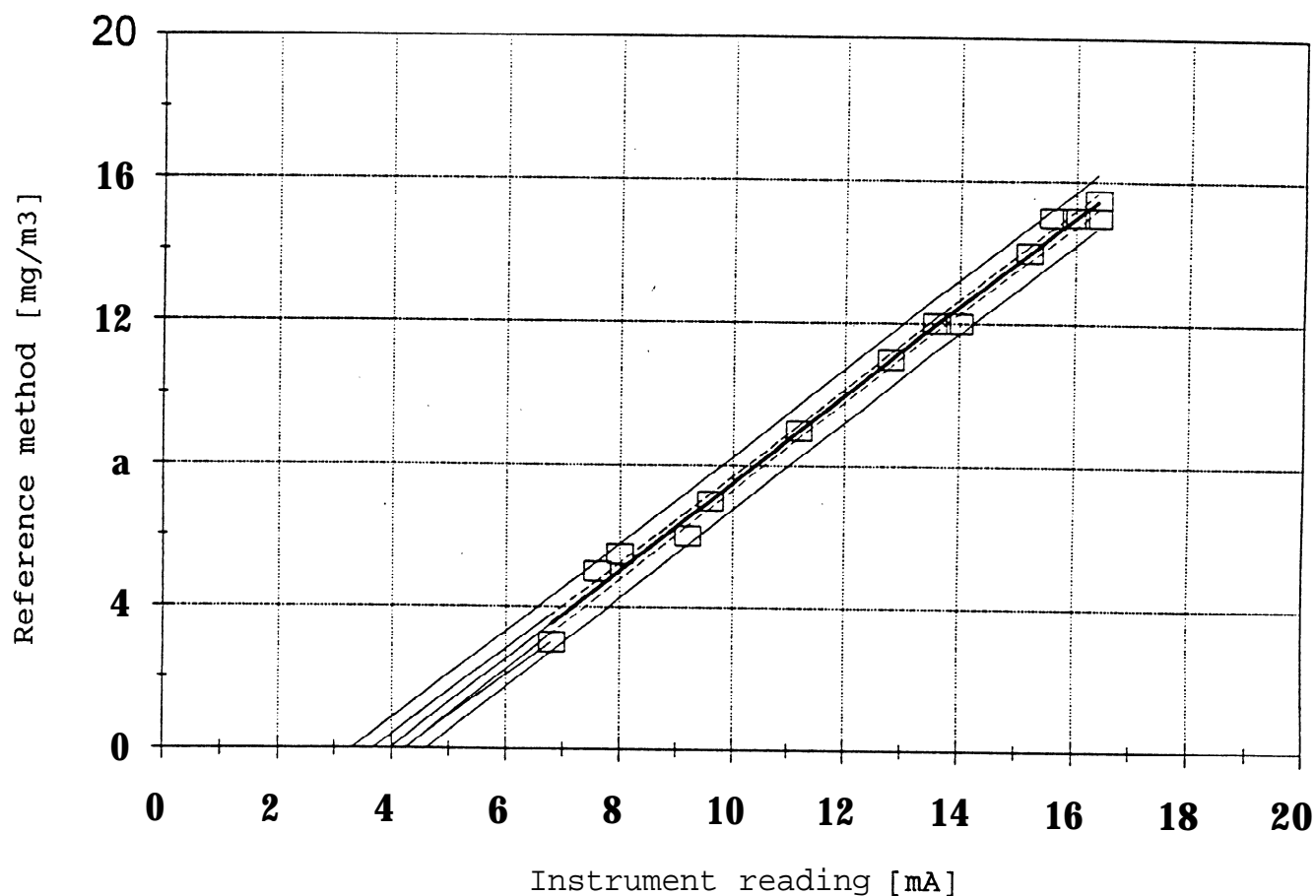
**Figure 6.2:** Calibration curve (analysis function) at the beginning of the exemplary performance test

Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m<sup>3</sup> phenol  
Tested criterion: Relation between the Unit 209 and the comparison method  
Test site: Purified gas of a mineral wool plant



**Figure 6.3:** Calibration curve (analysis function) at the end of the exemplary performance test

Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m<sup>3</sup> phenol  
Tested criterion: Relation between the Unit 081 and the comparison method  
Test site: Purified gas of a mineral wool plant



**Figure 6.4:** Calibration curve (analysis function) at the end of the exemplary performance test

Manufacturer: OPSIS AB  
 Measuring system: OPSIS AR 602 Z  
 Measuring range: 0 - 20 mg/m<sup>3</sup> phenol  
 Tested criterion: Relation between the Unit 209 and the comparison method  
 Test site: Purified gas of a mineral wool plant

The following calibration measurements were carried out for the component formaldehyde:

Calibration at the beginning of the continuous operation test (Table 6.4 and Figures 6.5 and 6.6)

Calibration at the end of the continuous operation test (Table 6.5 and Figures 6.7 and 6.8).

The individual values are listed in Annex 9.4.

In view of the small bandwidth of the formaldehyde values in continuous operation, the number of comparison measurements was kept to the minimum ( $n=30$ ).

An indirect plausibility check of the calibration curves can, however, be derived from the laboratory tests conducted to establish the instrument characteristic and the cross sensitivities and from the reproducibility tests (with addition of test gas). From the results of these tests, it is to be expected that the analysis function for formaldehyde can be prepared over the entire measuring range from 0 to 20 mg/m<sup>3</sup> in a real-life flue gas matrix as well.

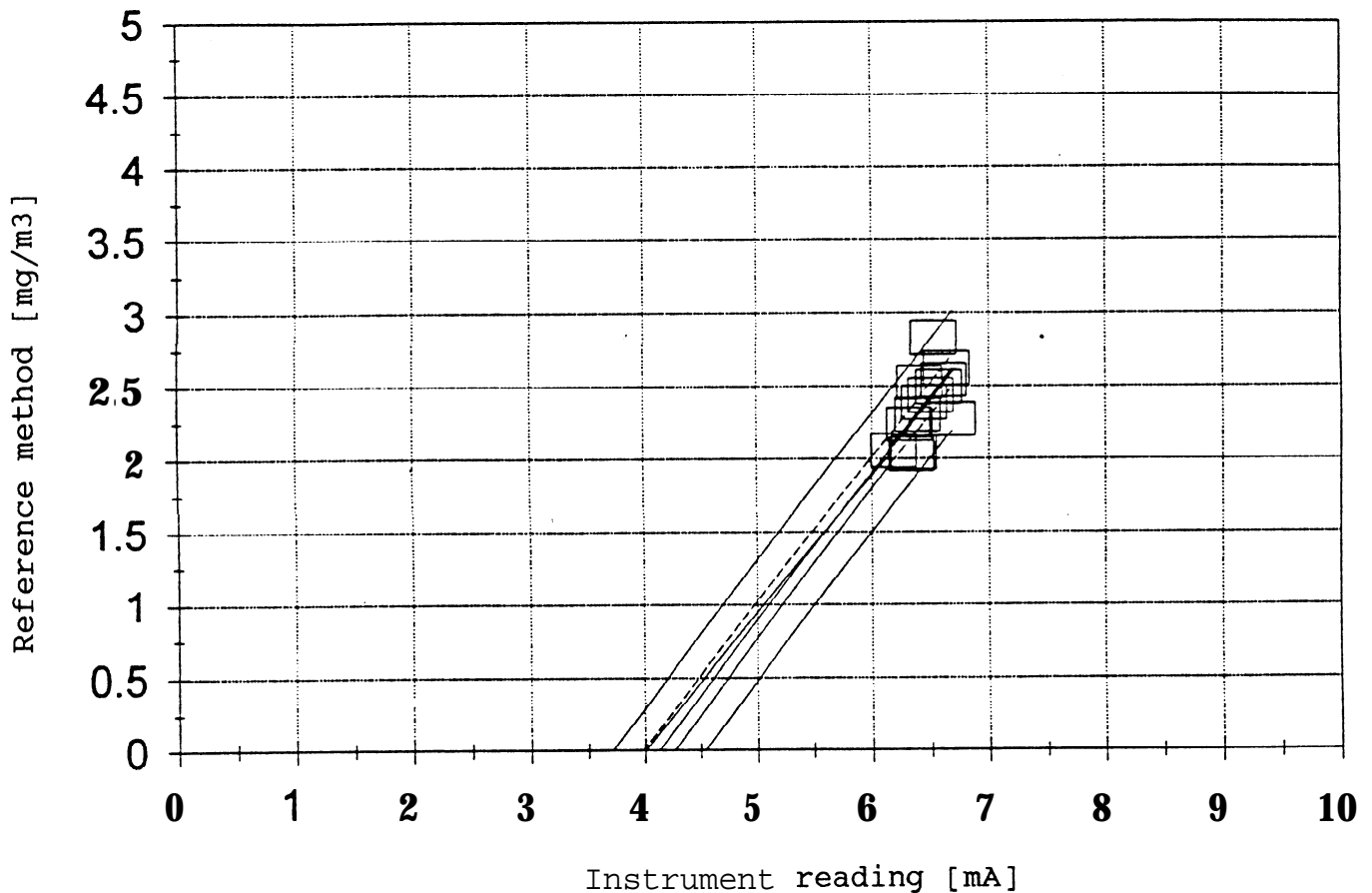
**Table 6.4:** Results of the regression analyses for formaldehyde performed at the beginning of the continuous-operation test

	Unit 081	Unit 209
Number of measured values	15	15
Measuring range (mg/m <sup>3</sup> )	0 - 20	0 - 20
Mean value of the instrument reading (mA)	5.9	5.3
Mean value of the reference method (mg/m <sup>3</sup> ) for wet flue gas in standard state	1.8	1.7
Slope of the regression line (mg/m <sup>3</sup> ) / mA	1.02	1.29
Ordinate offset of the regression line (mg/m <sup>3</sup> )	-4.21	-5.12
Correlation coefficient	0.991	0.994

**Table 6.5:** Results of the regression analyses for formaldehyde performed at the end of the continuous-operation test

	Unit 081	Unit 20
Number of measured values	15	15
Measuring range (mg/m <sup>3</sup> )	0 - 20	0 - 20
Mean value of the instrument reading (mA)	5.4	5.3
Mean value of the reference method (mg/m <sup>3</sup> ) for wet flue gas in standard state	1.5	1.6
Slope of the regression line (mg/m <sup>3</sup> ) / mA	1.06	1.23
Ordinate offset of the regression line (mg/m <sup>3</sup> )	-4.2	-4.9
Correlation coefficient	0.982	0.959

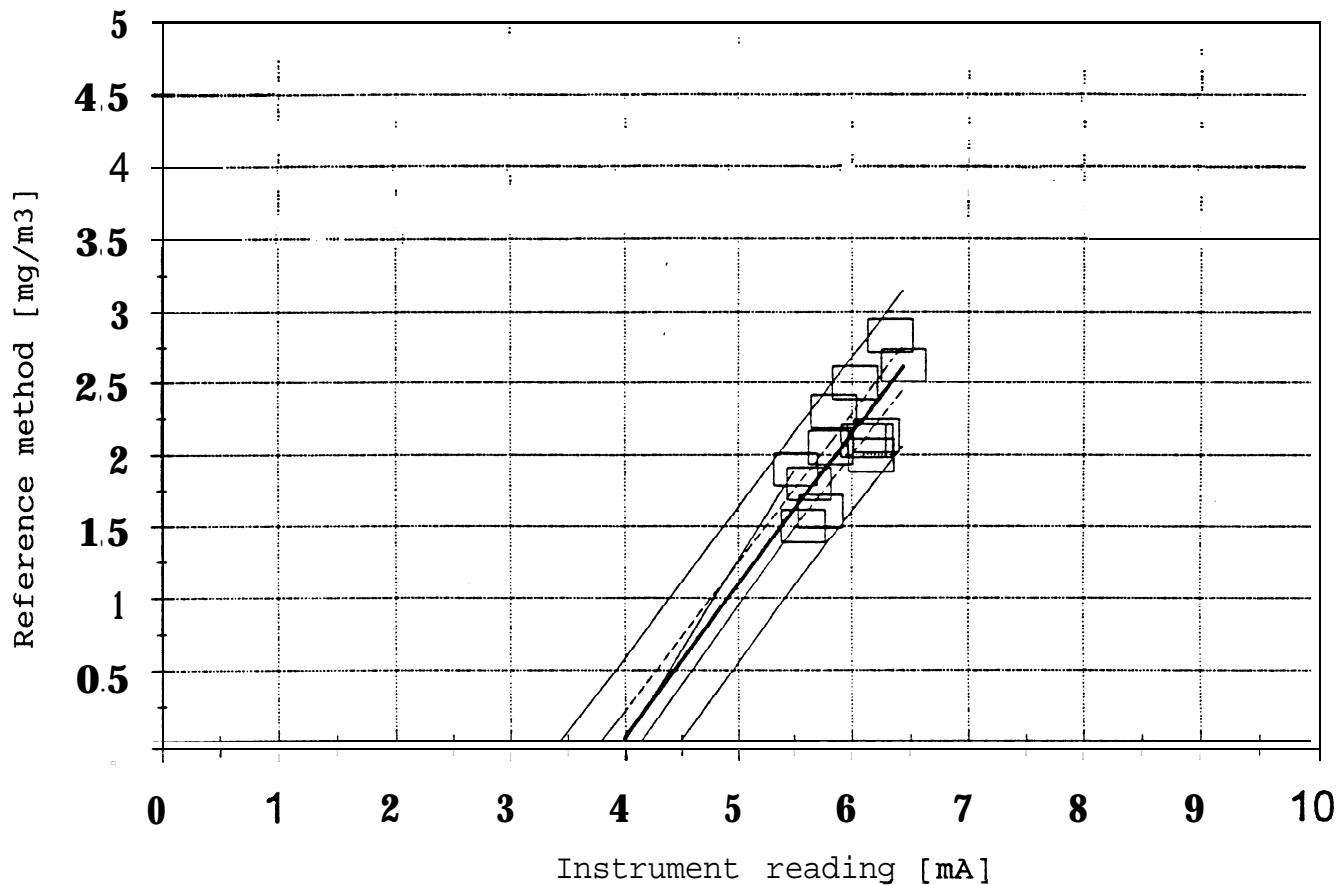
The listed concentrations refer to wet flue gas in standard state.



**Figure 6.5:** Calibration curve (analysis function) at the beginning of the exemplary performance test

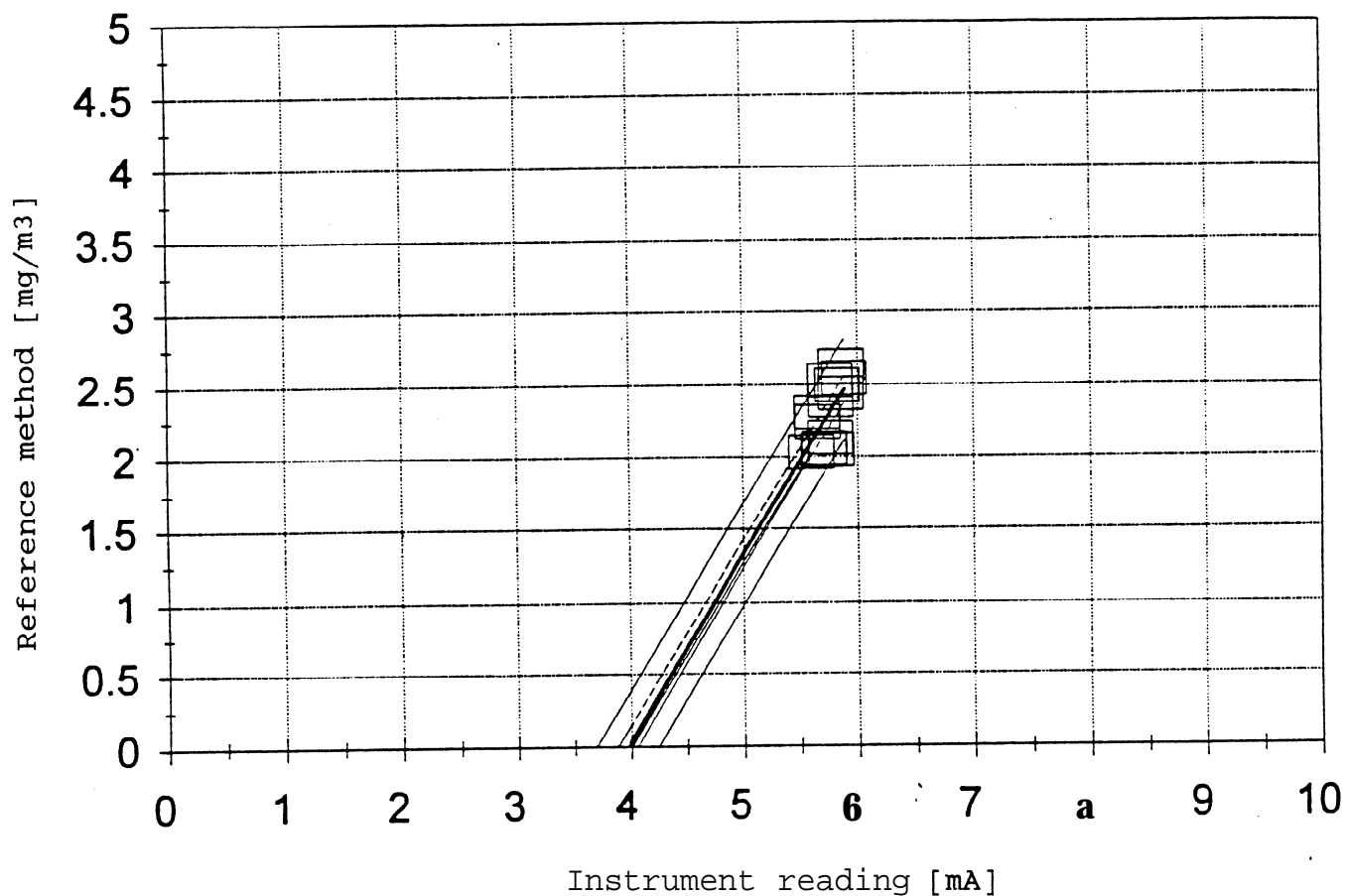
Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m3 formaldehyde  
Tested criterion: Relation between the Unit 081 and the comparison method  
Test site: Purified gas of a mineral wool plant





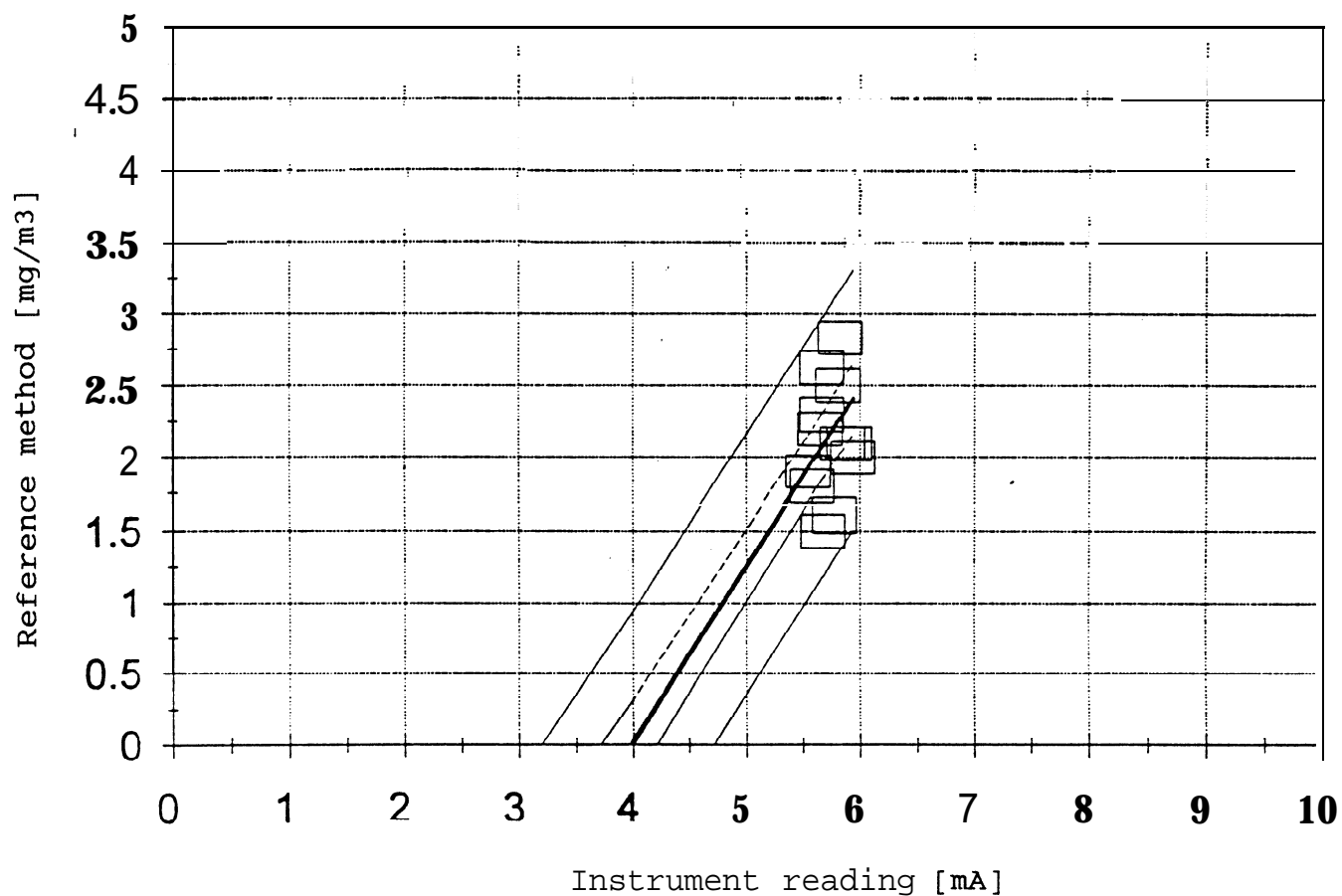
**Figure 6.6:** Calibration curve (analysis function) at the beginning of the exemplary performance test

Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m<sup>3</sup> formaldehyde  
Tested criterion: Relation between the Unit 209 and the comparison method  
Test site: Purified gas of a mineral wool plant



**Figure 6.7:** Calibration curve (analysis function) at the end of the exemplary performance test

Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m3 formaldehyde  
Tested criterion: Relation between the Unit 081 and the comparison method  
Test site: Purified gas of a mineral wool plant



**Figure 6.8:** Calibration curve (analysis function) at the end of the exemplary performance test

Manufacturer: OPSIS AB  
Measuring system: OPSIS AR 602 Z  
Measuring range: 0 - 20 mg/m<sup>3</sup> formaldehyde  
Tested criterion: Relation between the Unit 209 and the comparison method  
Test site: Purified gas of a mineral wool plant

### 6.3 Determination of the detection limits

The detection limits for phenol were determined both in the course of the continuous-operation test and during the laboratory tests. The results are listed in Table 6.6. For the individual values, refer to Annex 9.1. The tests were carried out on a 2 m monitoring path (duct diameter at the measuring point).

**Table 6.6** Detection limits for phenol (2 m monitoring path), measuring range 0 to 20 mg/m<sup>3</sup>

		Unit 081	Unit 209
Number of values	n	30	30
Mean value of blank readings	mg/m <sup>3</sup>	0.0	0.0
Standard deviation	mg/m <sup>3</sup>	0.06	0.05
Detection limit	mg/m <sup>3</sup>	0.2	0.2
Detection limit	% of upper range limit	1.0	1.0

The detection limits for formaldehyde were also determined in the course of the continuous-operation test and during the laboratory tests. The results are listed in Table 6.7. For the individual values, refer to Annex 9.1. The tests were carried out on a 2 m monitoring path (duct diameter at the measuring point).

**Table 6.7** Detection limits for formaldehyde (2 m monitoring path), measuring range 0 to 20 mg/m<sup>3</sup>

		Unit 081	Unit 209
Number of values	n	30	30
Mean value of blank readings	mg/m <sup>3</sup>	0.0	0.0
Standard deviation	mg/m <sup>3</sup>	0.13	0.16
Detection limit	mg/m <sup>3</sup>	0.4	0.5
Detection limit	% of upper range limit	2.0	2.5

#### 6.4 Reproducibility of the instrument reading

For the reproducibility check, the data recorded during the continuous-operation tests were used as half-hourly mean values divided into three classes; the values were selected by the random sampling procedure that is customary for performance tests.

Table 6.8 lists the reproducibility data for phenol: the individual values are listed in Annex 9.2. Figure 6.9 shows a graphical representation of the twin determinations with the two units.

**Table 6.8** Results of the reproducibility check for phenol

Sampling criterion	Number of value pairs	R'	R
Class I (0 - 6.6 mg/m <sup>3</sup> )	50	27	81
Class II (6.6 - 13.3 mg/m <sup>3</sup> )	50	30	44
Class III (13.3 - 20 mg/m <sup>3</sup> )	50	63	63
Classes I, II and III	150	58	58

R' - relative to the upper class limit

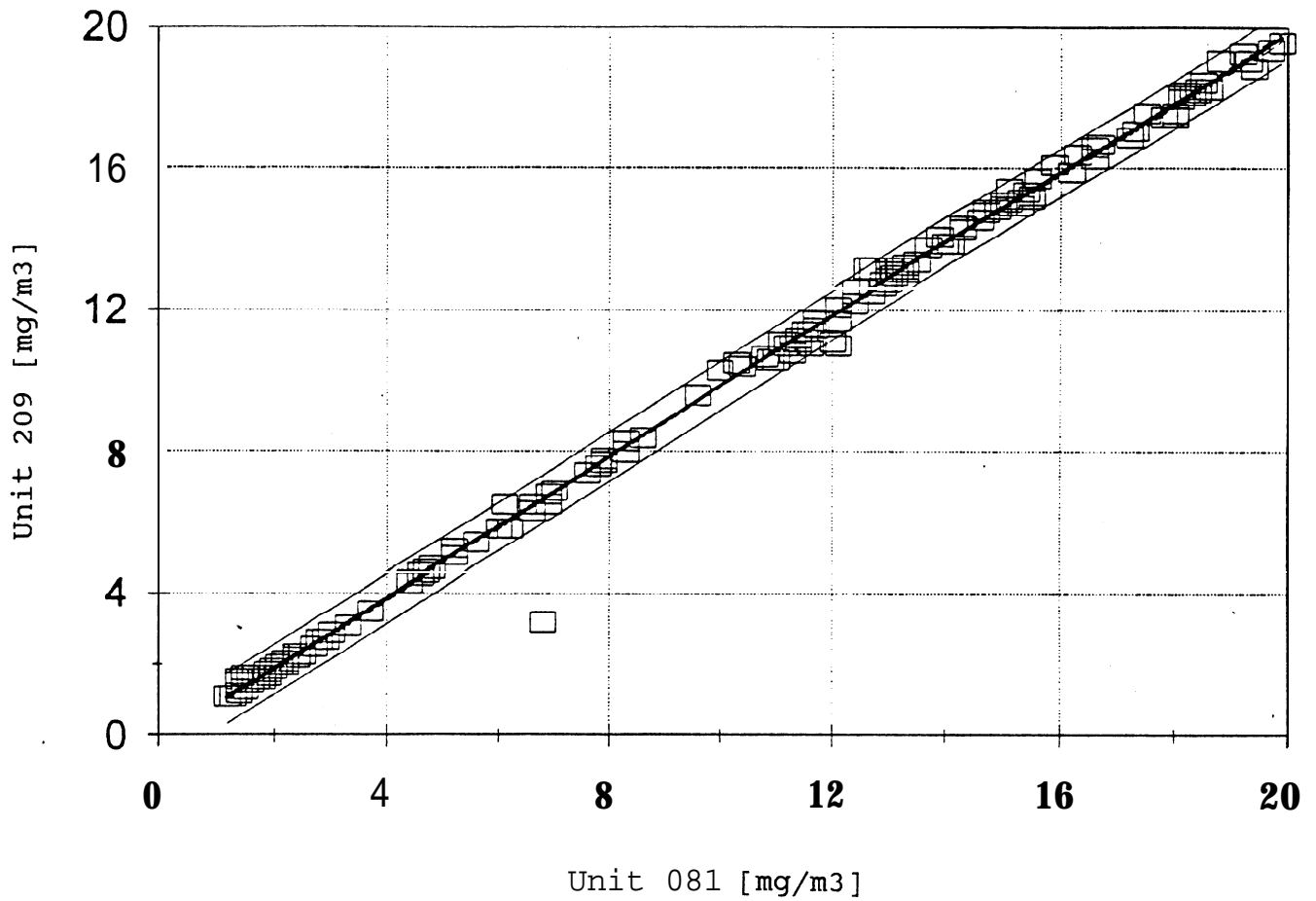
R - relative to the upper range limit

Reproducibility  $R = \text{upper limit} / (s * t)$

with upper limit = upper range or upper class limit respectively

s - standard deviation established by twin determinations

t - test quantity of Student's distribution at 95% certainty



**Figure 6.9:** Phenol  
Reproducibility for OPSIS AR 602 Z - Units 081/209

Legend:      ——— confidence interval of the calibration curve  
             ——— tolerance band for individual values

Table 6.9 lists the reproducibility data for formaldehyde: the individual values are listed in Annex 9.2. Figure 6.10 shows a graphical representation of the twin determinations with the two units.

As mentioned before, all individual values measured during the field test were below 6 mg/m<sup>3</sup>; therefore, additional measurements with test gases were performed at the laboratory to improve the information content of the results.

**Table 6.9** Results of the reproducibility check for phenol

Sampling criterion	Number of value pairs	R'	R
Class I (0 - 6.6 mg/m <sup>3</sup> )	50	14	44
Class II (6.6 - 13.3 mg/m <sup>3</sup> )	50	25	37
Class III (13.3 - 20 mg/m <sup>3</sup> )	50	29	29
Classes I, II and III	150	36	36

R' - relative to the upper class limit

R - relative to the upper range limit

Reproducibility R = upper limit / (s \* t)

with upper limit = upper range or upper class limit respectively

s - standard deviation established by twin determinations

t - test quantity of Student's distribution at 95% certainty

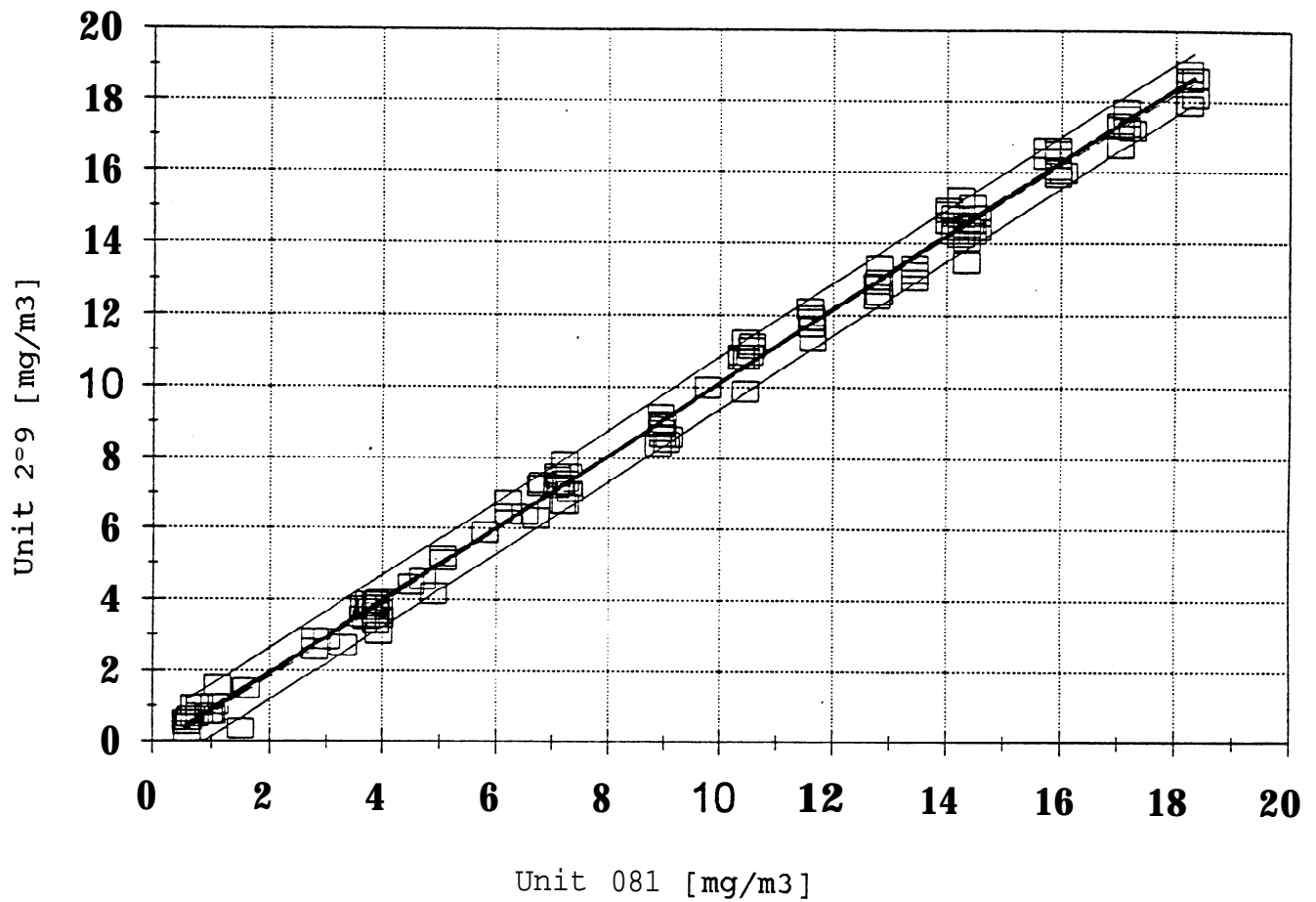


Figure 6.10: Formaldehyde  
Reproducibility for OPSIS AR 602 Z - Units 081/209

Legend: — confidence interval of the calibration curve  
— tolerance band for individual values



## 6.5 Zero and reference point stability

The zero points of the two units were checked regularly on the occasion of the checks carried out every 2 weeks. The following results were found for phenol:

- for Unit 081 and Unit 209 at the zero point:
  - \* < 1 % of the upper range limit

Readjustment of the zero point did not become necessary during the entire test period.

No reference point check was carried out in the field because mobile test gas generators for phenol were not available. At the end of the field test, the units were taken to the laboratory for zero and reference point checks. The shifts both in the zero and in the reference point were found to be below 2 % of the upper range limit.

For formaldehyde the following results were found on the occasion of the bi-weekly checks:

- for Unit 081 and Unit 209 at the zero point
  - \* < 1 % of the upper range limit

After a period of about 2 months, the zero point for formaldehyde had to be recalibrated. The reference point was checked about 2 weeks before the last calibration. At that time, the shifts observed were +2.3 % for Unit 081 and -3.3% for Unit 209, i.e. within the admissible tolerance limits. Therefore, readjustment was not performed.

## 6.6 Maintenance interval

In the course of the continuous operation field-test a maintenance interval of 1 month was established for the components phenol and formaldehyde. The following maintenance work has to be carried out after this period:

- \* visual check of the entire measuring system
- \* light intensity check for each component on the monitor and, if the red fibre-optic cable is being used, with a hand-held photometer (intensity < 8000 lux)
- \* checking the mirrors in the emitter and the receiver
- \* cleaning the windows
- \* checking the purge air supply
- \* checking the data recorded by the system for frequent occurrence of negative standard deviations
- \* system check
- \* an ozone-free xenon high-pressure lamp must be installed in the calibration source CA 150 for zero point checks
- \* zero point check in accordance with the instructions given in the manual

Dust on the windows does not affect the measurement results since the resulting decrease in the light intensity is electronically compensated for. Also, the dust spectrum does not interfere with the molecular absorption spectrum of the gas.

Nevertheless, the windows should be cleaned if the light intensity drops to less than 50% of the value reached at the time of installation. The light intensity can be read on the monitor any time. Further, a signal can be assigned to the light intensity to activate an alarm as soon as it drops below a freely selectable level.

## 6.7 Availability

As stipulated by the Minimum Requirements, the measuring systems must have an availability of 90%; it should be better than 95% during the performance test. The availability is the period during which the system provides useful data for assessing a plant's emission levels.

The availabilities established in the course of the **continuous-operation** test are listed in Tables 6.10 and 6.11.

**Table 6.10:** Availability of the two OPSIS AR 602 Z systems for phenol during the continuous-operation test

	Unit 081	Unit 209
Total operating time	2148 h = 100%	2184 h = 100%
Time for checks and maintenance	30 h = 1.4%	30 h = 1.4%
Service work	20 h = 0.9%	20 h = 0.9%
Down-time due to malfunction	0 h	0 h
Available measuring time	2154 h = 97.7%	2154 h = 97.7%

**Table 6.11:** Availability of the two OPSIS AR 602 Z systems for formaldehyde during the continuous-operation test

	Unit 081	Unit 209
Total operating time	2148 h = 100%	2184 h = 100%
Time for checks and maintenance	50 h = 2.3%	50 h = 2.3%
Service work	20 h = 0.9%	20 h = 0.9%
Down-time due to malfunction	16 h = 0.7%	20 h = 0.9%
Available measuring time	2098 h = 96.1%	2094 h = 95.9%

# COMPARISON BETWEEN THE TEST RESULTS AND THE MINIMUM REQUIREMENTS

Minimum requirement	Test result	Evaluation
1.1.1		
The performance test is to be carried out in accordance with the definition of the VDI Recommendation 2449, Sheet 1, of Oct. 1970, the DIN-ISO standard 6879 of Jan. 1984 and the DIN standard 43745 of Feb. 1975.	The performance test was carried out in accordance with the said recommendations and standards. The continuous operation test took place in a mineral-wool plant from June 15 to September 15, 1993, for the component phenol and from November 1, 1993, to January 31, 1994, for the component formaldehyde.	satisfied
1.1.2		
Compliance with the minimum requirements should be verified by means of a continuous operation test of at least three months within the scope of the performance test. As far as possible, the continuous operation test should be carried out in one place over an uninterrupted period of time. Only in exceptional cases may shorter test operation periods in different places be taken into account for the continuous operation test.	The test was carried out in one place.	satisfied
1.1.3		
During the performance test, the relation between the instrument reading and the value of the measured object in the flue gas determined by means of a reference method as mass concentration or volumetric flow, for example, should be established by regression calculation (analysis function).	The calibration was carried out with 32 comparison measurements for phenol and 30 comparison measurements for formaldehyde. There is a statistically established relation between the instrument reading and the phenol or formaldehyde content of the flue gas.	satisfied
1.1.4		
The measuring system must be provided with a facility offering security against unauthorized or unintentional adjustment changes.	Owing to its mode of operation, the measuring system does not permit any unauthorized or unintentional adjustment changes. Furthermore, operator control is secured by means of a password and a detachable operator keyboard.	satisfied

Minimum requirement	Test result	Evaluation
1.1.5		
The zero point of the instrument reading should be situated at approx. 10 % or 20 % of the full-scale reading, the reference point should be situated at approx. 70 %.	The zero point was situated at approx. 4 mA (20 % of the instrument display range) during the test; it is, however, freely selectable via the menu. The reference point is determined by the selected test gas concentration.	satisfied
1.1.6		
The measuring systems should be designed in such a way that the display range can be adjusted to the respective measurement tasks. Normally, the most sensitive display range should be 2.5 to 3 times the value of the stipulated emission limit.	The measuring range of the measuring system OPSIS AR 602 Z is freely selectable for each component via computer menu.	satisfied
1.1.7		
The measuring systems should have a measured value output for connection of an additional display or recording unit.	Up to 24 analog outputs (4 - 20 mA) can be programmed in the tested measuring system (e.g. measured value, light intensity, etc.)	satisfied
1.1.8		
The measuring systems should be able to communicate their current operating status (readiness for operation, maintenance, fault) to a subsequent evaluation unit by means of a status signal.	Installation of an external status signal transmitter in an analog output is possible without any problems. Fault messages can be communicated via interfaces.	satisfied
1.1.9		
The measuring system should have a minimum availability of 90% in continuous operation; during the performance test, the availability should be 95%. (The availability describes the period of time during which useful measured values are obtained for evaluating the monitored plant's emissions. )	The availability was established for both measuring systems. The value established for phenol was 97.4 %; for formaldehyde it was 96.1 and 95.9 % respectively.	satisfied
1.1.10		
The maintenance interval of the measuring system must be established and stated.	The maintenance interval of the measuring system was established in the course of the continuous operation test. A maintenance interval of 4 weeks is recommended.	satisfied

Minimum requirement	Test result	Evaluation
<hr/>		
1.1.11		
<p>The reproducibility <math>R = \frac{\bar{x}}{U}</math></p> <p>(<math>\bar{x}</math> upper limit of the measuring range; <math>U</math> uncertainty range in accordance with the VDI Recommendation 2449, Sheet 1) is to be established by means of twin determinations. For this purpose, measurements with two similar measuring systems are to be carried out in the same place.</p>	<p>The reproducibilities were established by means of twin determinations. For this purpose, measurements with two similar OPSIS AR 602 Z measuring systems were carried out in the same place.</p>	satisfied
<hr/>		
1.1.12		
<p>The performance test covers the entire measuring system including sampling, sample preparation and data recording or data output. The manufacturer's manual is to be included in the performance test.</p>	<p>The entire OPSIS AR 602 Z measuring system comprising an emitter, a receiver, an analyzer with monitor and keyboard, a modem and a recorder was examined during the continuous operation test to which the measuring system was subjected.</p>	satisfied
<hr/>		
1.1.13		
<p>The minimum requirements should be complied with under the rated conditions of use listed below in accordance with DIN 43745 of Feb. 1975, Installation Category II:</p> <p>a) line voltage b) relative air humidity c) liquid-water content of the air d) vibrations e) service position</p>	<p>a) The effect of line voltage fluctuations on the measuring signal was within the admissible tolerance limits both for phenol and for formaldehyde,</p> <p>The following individual values were established: At the <u>zero point</u>: 0 to 0.5 % for phenol 0 to 2.0 % for formaldehyde At the <u>reference point</u>: -2.0 to 0.5 % for phenol -2.9 to 2.9 % for formaldehyde</p> <p>b) t c) The OPSIS monitoring path (emitter, receiver, power supply unit) is splash-water proof. Effects of the relative air humidity on the system's serviceability could not be detected.</p> <p>d) Vibrations were not detected to have any effect on the system operation during the continuous operation test.</p> <p>e) The emitter and receiver of the OPSIS AR 602 Z measuring system must be mounted to the flue gas duct in a horizontal position.</p>	<p>satisfied</p> <p>satisfied</p> <p>satisfied</p>

Minimum requirement	Test result	Evaluation
1.1.14		
If the measuring systems are equipped with facilities for automatic function testing and readjustment, these facilities must be included in the performance test. A status signal should be given if the automatic correction goes beyond an adjustment range of $\pm 6\%$ of the display range.	The OPSIS AR 602 Z measuring system has no facilities for automatic function testing and readjustment.	n.a.
1.1.15		
Multi-component measuring systems must comply with the requirements for each individual component and must be tested accordingly.	The multi-component measuring system OPSIS AR 602 Z complies with the requirements for all tested components.	satisfied
1.3.2.3		
The interference effect of light-beam drift must be stated. Option: In the angular range of $\pm 0.3^\circ$ , the interference effect should not exceed 2% of the display range.	The interference was established at the laboratory. For phenol, the max. interference at the zero point was 0.2% of the upper range limit; at the reference point it was $< 0.5\%$ . For formaldehyde, a max. deviation of -1.6% of the upper range limit was found at the zero point and a deviation of -1.7% at the reference point.	satisfied
1.4		
Gaseous emissions		
1.4.1		
General		
1.4.1.1		
The detection limit of the measuring systems should not exceed 2 % of the most sensitive display range.	With a monitoring path of 2 m, the measuring system's detection limit was 0.2 mg/m <sup>3</sup> $\approx$ 1 % of the display range for phenol and  0.5 mg/m <sup>3</sup> $\approx$ 2.5% of the display range for formaldehyde	satisfied  satisfied with certain qualifications

Minimum requirement	Test result	Evaluation
1.4.1.2		
The ambient temperature range rating is t5 °C to t 35 °C. It should reach -10 °C and +55 °C in accordance with the DIN standard 43745 of February 1975, Installation Category II.	The emitter, receiver and monitoring path of the measuring system were tested in an air-conditioned chamber. Analyzer, monitor, keyboard and recorder were located outside the air-conditioned chamber at room temperature. The manufacturer specifies 30 °C as the upper temperature limit for the analyzer AR 602 Z (refer to the operator's manual),	satisfied
1.4.1.3		
The variation in the zero point reading should not exceed $\pm 2\%$ of the display range for a 10 K variation in the ambient temperature within the allowable temperature limits. Zero point variations resulting from variations in the temperature of the measured medium must be compensated for by suitable measures.	The zero point deviations for phenol and formaldehyde were within the admissible tolerance limits during the tests in the air-conditioned chamber.	satisfied
1.4.1.4		
The variation in the reference point reading resulting from the temperature-dependence of the system's sensitivity should not exceed $\pm 2\%$ of the specified value for a 10 K variation in the ambient temperature within the allowable temperature limits. Reference point variations resulting from variations in the temperature of the measured medium must be compensated for by suitable measures.	The reference point deviations for phenol and formaldehyde were within the admissible tolerance limits during the tests in the air-conditioned chamber.	satisfied



Minimum requirement	Test result	Evaluation
1.4.1.5		
The interference effect of cross sensitivities to attendant substances present in the measured medium in mass concentrations which are typical for flue gases must not exceed $\pm 2\%$ of the display range. If this requirement cannot be met, the effect of the interfering component in question must be taken into account by suitable measures.	For phenol, no detectable cross sensitivities to the tested attendant substances in the flue gas were observed. For formaldehyde, a slight cross sensitivity to nitrogen oxides can be observed at the zero point. At the reference point, the instrument reading shows slight negative deviations upon addition of high ammonia concentrations. For formaldehyde, the tested measuring system had a pronounced cross sensitivity to SO <sub>2</sub> . For this reason, the SO <sub>2</sub> concentrations must not exceed 15 mg/m <sup>3</sup> (for a 2 m monitoring path).	satisfied
1.4.1.6		
The response time (90% time) of the measuring system, including the sampling system, should not exceed 200 seconds.	The tested measuring system measures directly in the flue-gas duct (in-situ). When measuring four components, the maximum 90% time is 150 seconds.	satisfied
1.4.1.7		
The variation in the zero point reading over time should not exceed $\pm 2\%$ of the display range within the maintenance interval.	The variation of the zero point reading over time was established at the laboratory and during the continuous operation test. It was < 1 % of the upper range limit.	satisfied
1.4.1.8		
The variation in the reference point reading over time resulting from a variation in sensitivity should not exceed $\pm 4\%$ of the display range within the maintenance interval.	The variation of the reference point reading over time was < 2% for phenol and < 4% for formaldehyde at the reference point.	satisfied

Minimum requirement	Test result	Evaluation
<hr/>		
1.4.1.9		
In terms of material and heating, sampling and sampling preparation operations must be conceived in such a way that satisfactory solid matter filtering is achieved and conversion as well as carry-over effects resulting from adsorption and desorption phenomena are avoided as far as possible.	The tested measuring system measures directly in the flue-gas duct (in-situ measurement). Thus, no sampling and sampling preparation operations are required with this measuring system.	satisfied
<hr/>		
1.4.1.10		
The reproducibility should not be below a value of 30.	During the continuous operation test, the reproducibility was 58 for phenol and 36 for formaldehyde .	satisfied
<hr/>		

## 8. SUMMARY

At the request of OPSIS GmbH, 50226 Frechen, and with financial support from the state of North Rhine-Westphalia (Ministry of Environmental Protection, Regional Planning and Agriculture), the TÜV Rheinland, Sicherheit und Umweltschutz GmbH (Technical Inspectorate of Rhineland, Safety and Environmental Protection Limited), subjected the measuring system OPSIS AR 602 Z to an exemplary performance test. The components to be assessed were phenol and formaldehyde. The test was carried out in accordance with the Minimum Requirements: the continuous-operation test took place in the purified gas of a mineral wool plant.

In view of the positive test results, publication as a performance-tested measuring system is recommended as follows:

Multi-component measuring system  
OP SIS AR 602 Z for phenol and formaldehyde

Manufacturer : OPSIS AD, Furulund/Sweden

Distribution OPSIS GmbH, Frechen

Suitability: For plants producing mineral wool

Minimum measuring range  
during the performance test: Phenol : O-20 mg/m<sup>3</sup>  
Formaldehyde : O-20 mg/m<sup>3</sup>

Note: When measuring formaldehyde, the SO<sub>2</sub> concentrations must not exceed 15 mg/m<sup>3</sup> (for a 2 m monitoring path).  
The detection limit for formaldehyde is 2.5% of the upper range limit: this can be tolerated in practical application.  
The analyzer may only be operated at a max. temperature of 30 °C.  
If the measuring system is used to measure four components, for example, the time needed for one measuring and calculation cycle is approx. 90 sec. The dead time and 90% time is reached after the second measuring cycle, i.e. 150 sec., at the latest.  
The analyzer may only be operated up to a temperature of 30 °C max.  
On the occasion of the annual function test, the analysis function must be checked by wet chemical comparison methods as long as no test gases are available.

Cologne  
June 6, 1994  
936-dr.wil-za

Dr. P. Wilbring

- Annex 9.1:** Individual values for determining the threshold of measurement and the detection limit
- Annex 9.2:** Individual values for determining reproducibility
- Annex 9.3:** Apparatus and equipment for functional testing and maintenance
- Annex 9.4:** Individual values from the calibration measurements
- Annex 9.5:** OPSIS Manuals

**Annex 9.1:**        Individual values for determining the threshold of  
measurement and the detection limit

**Table 1:** Zero points for the determining the detection limit  
Monitoring path 2.0 m - test gas nitrogen, field test  
Unit 081

Number	mg/m3	mA
1	0	4.0
2	0.1	4.1
3	0	4.0
4	0	4.0
5	0.1'	4.1
6	0.2	4.2
7	0	4.0
8	0	4.0
9	0.1	4.1
10	0.1	4.1
11	0.2	4.2
12	0	4.0
13	0.1	4.1
14	0	4.0
15	0.1	4.1
16	0.1	4.1
17	0	4.0
18	0.1	4.1
19	0.1	4.1
20	0	4.0
21	0	4.0
22	0	4.0
23	0.1	4.1
24	-0.1	3.9
25	0	4.0
26	0	4.0
27	0	4.0
28	0.1	4.1
29	0.1	4.1
30	0	4.0

Table 1: Zero points for the determining the detection limit  
Monitoring path 2.0 m - test gas nitrogen, field test  
Unit 209

Number	mg/m3	mA
1	0.3	4.2
2	0.2	4.2
3	0.1	4.1
4	0.2	4.2
5	0.1'	4.1
6	0.1	4.1
7	0.2	4.2
8	0.2	4.2
9	0.2	4.2
10	0.2	4.2
11	0.1	4.1
12	0.1	4.1
13	0.1	4.1
14	0.1	4.1
15	0.1	4.1
16	0	4.0
17	-0.1	3.9
18	-0.2	3.8
19	0	4.0
20	-0.2	3.8
21	0	4.0
22	-0.2	3.8
23	-0.1	3.9
24	0	4.0
25	0.1	4.1
26	-0.1	3.9
27	0	4.0
28	0.1	4.1
29	0	4.0
30	0	4.0

**Annex 9.2: Individual values for determining reproducibility**



Table 1: Reproducibility of the instrument reading  
Measured values of Class I for phenol 0 - 6.6 mg/m<sup>3</sup>

instrument reading		Instrument reading	
Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>	Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>
1.2	1.1	2.2	2.1
1.3	1.1	2.4	2.3
1.4	1.6	2.4	2.2
1.4	1.2	2.4	2.2
1.4	1.5	2.5	2.3
1.4	1.2	2.7	2.5
1.5	1.6	2.7	2.5
1.5	1.5	2.8	2.7
1.5	1.7	2.9	2.7
1.5	1.3	3.0	2.9
1.6	1.7	3.3	3.1
1.6	1.5	3.7	3.5
1.7	2.7	4.4	4.3
1.7	1.6	4.6	4.5
1.7	1.6	4.7	4.6
1.8	1.6	4.8	4.7
1.9	1.7	4.8	4.7
1.9	1.7	5.2	5.0
1.9	1.8	5.2	5.2
1.9	1.8	5.6	5.4
2.0	1.9	6.0	5.8
2.1	2.0	6.1	6.5
2.2	2.1	6.2	5.8
2.2	2.0	6.6	6.3
2.2	2.0	6.6	6.5

Table 2: Reproducibility of the instrument reading  
Measured values of Class II for phenol 6.6 - 13.3 mg/m<sup>3</sup>

Instrument reading		Instrument reading	
Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>	Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>
6.8	3.2	11.5	11.4
6.9	6.5	11.6	11.0
6.9	6.8	11.6	11.4
7.0	6.9	11.7	11.7
7.6	7.4	11.7	11.5
7.8	7.6	12.0	11.1
7.9	7.8	12.1	11.0
7.9	7.7	12.1	12.1
8.3	8.3	12.1	11.7
8.3	8.0	12.1	11.7
8.6	8.4	12.4	12.2
9.6	9.6	12.4	12.5
10.0	10.3	12.6	13.1
10.3	10.5	12.7	12.5
10.4	10.4	12.7	13.1
10.8	10.7	12.9	12.7
10.9	10.6	13.0	13.0
11.0	10.6	13.0	13.1
11.1	11.1	13.0	12.8
11.2	11.0	13.1	12.9
11.3	11.0	13.2	13.1
11.3	10.8	13.2	13.1
11.3	11.0	13.3	13.0
11.4	11.2	13.3	13.2
11.4	11.1	13.3	13.1

**Table 3:** Reproducibility of the instrument reading  
Measured values of Class III for phenol  
13.3 - 20.0 mg/m<sup>3</sup>

Instrument reading		Instrument reading	
Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>	Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>
13.5	13.3	16.2	15.9
13.7	13.7	16.3	16.4
13.9	14.0	16.6	16.3
14.0	13.8	16.6	16.6
14.0	13.8	16.7	16.7
14.1	13.8	17.2	16.9
14.3	14.3	17.3	17.1
14.3	14.2	17.5	17.6
14.6	14.5	17.8	17.5
14.6	14.5	18.0	17.5
14.7	14.7	18.0	17.6
14.7	14.8	18.1	18.0
14.7	14.7	18.1	18.1
14.9	14.8	18.2	18.2
15.0	14.9	18.3	18.1
15.0	15.0	18.4	18.3
15.1	15.4	18.4	18.2
15.1	15.0	18.5	18.5
15.3	14.9	18.6	18.3
15.3	15.1	18.8	19.1
15.4	15.3	19.2	19.3
15.5	15.1	19.3	19.1
15.5	15.2	19.4	18.9
15.6	15.7	19.7	19.4
15.9	16.1	19.9	19.6

Table 4: Reproducibility of the instrument reading  
Measured values of Class I for formaldehyde  
0 - 6.6 mg/m<sup>3</sup>

Instrument reading		Instrument reading	
Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>	Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>
0.6	0.6	3.7	3.9
0.6	0.5	3.8	3.7
0.6	0.3	3.8	3.7
0.6	0.5	3.8	3.6
0.6	0.6	3.9	3.9
0.6	0.7	3.9	3.4
0.7	0.7	3.9	3.8
0.7	1.0	3.9	3.9
0.8	1.0	3.9	3.3
0.8	1.0	3.9	3.9
0.8	0.8	3.9	3.8
1.0	0.8	3.9	3.1
1.0	0.8	3.9	3.7
1.1	1.1	3.9	4.0
1.1	1.6	3.9	3.5
1.5	0.4	4.5	4.4
1.6	1.5	4.7	4.6
2.8	2.6	4.9	4.2
2.8	2.9	5.1	5.2
3.0	2.9	5.1	5.1
3.3	2.7	5.8	5.9
3.6	3.5	6.2	6.4
3.7	3.8	6.2	6.8
3.7	3.4	6.5	6.4
3.7	3.7	6.6	6.3

Table 5: Reproducibility of the instrument reading  
Measured values of Class II for formaldehyde  
6.6 - 13.3 mg/m<sup>3</sup>

Instrument reading		Instrument reading	
Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>	Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>
6.8	7.2	9.8	10.0
6.8	7.3	10.4	10.9
7.1	7.2	10.4	10.8
7.1	7.6	10.4	9.9
7.1	7.5	10.4	11.3
7.1	7.2	10.5	10.8
7.1	7.3	10.5	10.9
7.1	7.2	10.6	11.1
7.2	7.3	10.6	11.2
7.2	6.7	11.6	12.2
7.2	7.9	11.6	11.7
7.2	7.3	11.6	11.9
7.2	6.7	11.6	12.0
7.3	7.2	11.6	11.3
7.3	7.6	11.6	11.7
7.3	7.1	12.8	12.5
8.9	8.4	12.8	12.9
8.9	9.2	12.8	13.0
8.9	8.9	12.8	12.6
8.9	9.0	12.8	12.6
9.0	8.8	12.8	13.4
9.0	8.6	12.8	12.6
9.0	9.1	13.3	13.2
9.0	8.5	13.3	13.0
9.1	8.6	13.3	13.3

Table 6: Reproducibility of the instrument reading  
Measured values of Class III for formaldehyde  
13.3 - 20.0 mg/m<sup>3</sup>

Instrument reading		Instrument reading	
Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>	Unit 081 mg/m <sup>3</sup>	Unit 209 mg/m <sup>3</sup>
14.0	14.9	14.5	14.8
14.0	15.0	15.7	16.4
14.0	14.6	15.7	16.7
14.1	14.6	15.9	16.1
14.1	14.8	15.9	16.7
14.1	14.3	15.9	16.6
14.1	14.4	15.9	16.0
14.2	14.2	15.9	16.7
14.2	14.4	15.9	16.4
14.2	14.8	15.9	15.9
14.2	14.4	15.9	16.7
14.2	14.8	16.0	16.0
14.2	15.3	17.0	16.7
14.3	14.5	17.0	17.3
14.3	13.5	17.0	17.4
14.3	14.6	17.1	17.3
14.3	14.1	17.1	17.8
14.3	14.4	17.1	17.6
14.3	14.4	17.2	17.2
14.4	14.6	18.2	17.9
14.4	14.3	18.2	18.7
14.4	15.1	18.2	18.9
14.4	14.6	18.2	18.6
14.4	14.4	18.3	18.7
14.5	14.4	18.3	18.1

**Annex 9.3:       Apparatus and equipment for function testing and  
                  maintenance**

Apparatus and equipment required for function testing and maintenance\*:

- F - a monitoring path 1 m in length and with an internal diameter of 60 mm
- M - a calibration source, comprising
  - \* a calibration light source (OPSIS, CA 150)
  - \* a lamp, Type B, Hamamatsu L 2274 (ozone-free)
  - \* a measuring cell
  - \* a fibre-optic cable, identical with the cable used during measurements
- M, F - test gas cylinder with valve for zero point checks
- M, F - PTFE connecting hose
- M, F - flow meter for a range of 0 to 5 l/min
- M, F - hand-held photometer (OPSIS accessory)

\* (maintenance M, function testing F)



#### **Annex 9.4:        Individual values from the calibrations**

**Table 1:** Calibration at the beginning of the performance test for phenol, **Unit 081**

Convetional method mg/m <sup>3</sup>	Instrument reading mA
2.0	5.6
4.0	7.2
6.5	9.2
7.0	9.6
10.0	12.0
10.5	12.0
12.0	14.0
12.0	13.2
13.5	14.4
14.0	15.2
14.5	15.6
14.5	15.2
14.5	15.2
15.0	16.0
15.5	16.4
19.5	19.2

**Table 2:** Calibration at the end of the performance test for phenol, **Unit 081**

Convetional method mg/m <sup>3</sup>	Instrument reading mA
3.0	6.5
5.0	8.0
5.5	8.2
6.0	8.8
7.0	10.0
9.0	11.4
11.0	13.1
12.0	13.6
12.0	13.9
14.0	15.3
15.0	15.6
15.0	15.8
15.0	16.3
15.5	16.5
15.5	16.3
15.0	16.4

**Table 3:** Calibration at the beginning of the performance test for phenol, Unit 209

Conventional method mg/m <sup>3</sup>	Instrument reading mA
2.0	5.6
4.0	7.2
6.5	9.2
7.0	9.6
10.0	12.0
10.0	12.0
11.5	12.8
12.5	13.6
13.0	14.4
14.0	14.8
14.5	15.2
14.0	15.2
14.0	15.6
15.0	15.6
15.5	16.4
19.5	19.2

**Table 4:** Calibration at the end of the performance test for phenol, Unit 209

Conventional method mg/m <sup>3</sup>	Instrument reading mA
3.0	6.8
5.0	7.6
5.5	8.0
6.0	9.2
7.0	9.6
9.0	11.2
11.0	12.8
12.0	13.6
12.0	14.0
14.0	15.2
15.0	15.6
15.0	16.0
15.0	16.0
15.5	16.4
15.5	16.4
15.0	16.4

**Table 5:** Calibration at the beginning of the performance test for formaldehyde, **Unit 081**

Conventional method mg/m <sup>3</sup>	Instrument reading mA
2.1	6.2
2.2	6.3
2.0	6.3
2.0	6.4
2.3	6.4
2.5	6.4
2.4	6.4
2.4	6.5
2.8	6.5
2.5	6.6
2.5	6.6
2.6	6.6
2.3	6.7

**Table 6:** Calibration at the end of the performance test for formaldehyde, **Unit 081**

Conventional method mg/m <sup>3</sup>	Instrument reading mA
1.9	5.5
1.5	5.6
1.8	5.6
1.6	5.7
2.1	5.8
2.3	5.8
2.5	6.0
2.1	6.1
2.1	6.2
2.0	6.2
2.1	6.2
2.8	6.3
2.6	6.4

**Table 7:** Calibration at the beginning of the performance test for formaldehyde, **Unit 209**

Conventional method mg/m <sup>3</sup>	Instrument reading mA
2.0	5.6
2.3	5.6
2.2	5.7
2.0	5.7
2.1	5.7
2.5	5.8
2.1	5.8
2.4	5.8
2.0	5.8
2.5	5.8
2.4	5.9
2.6	5.9
2.5	5.9

**Table 4:** Calibration at the end of the performance test for formaldehyde, **Unit 209**

Conventional method mg/m <sup>3</sup>	Instrument reading mA
1.9	5.6
1.8	5.6
2.2	5.6
2.6	5.7
2.3	5.7
1.5	5.7
1.6	5.8
2.5	5.8
2.8	5.8
2.8	5.8
2.1	5.8
2.1	5.9
2.0	5.9

**Annex 9.5: OPSIS Manuals**