RAP-139

Report on the Suitability Tests for Benzene of the Multi-Constituent Ambient Air Concentration Measuring System OPSIS AR 502Z

TÜV Report no. 936/807014/C, TÜV Ambient Pollution Control
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Report on the Suitability Tests for Benzene of the Multi-Constituent Ambient Air Concentration Measuring System OPSIS AR 502Z marketed by OPSIS AB, Furulund / Sweden

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Summary

On behalf of OPSIS AB of Furulund / Sweden, TÜV Immissionsschutz und Energiesysteme GmbH has conducted suitability tests of the OPSIS AR 502Z ambient air concentration measuring system for benzene in accordance with the Guidelines for Continuous Ambient Air Concentration Measurements [1 through 4]. This measuring system operates on the differential optical absorption spectroscopy (DOAS) principle.

The investigations conducted comprised both laboratory and field testing. The field tests were carried out in a large parking lot area in Cologne, using a measuring path length of 300 meters. An air-conditioned container accommodating the measuring systems and calibration measuring paths was placed directly alongside the receivers. The benzene measuring range examined was 0 - 300 µg/m³. A reference value of 10 µg/m³ was adopted. In the course of the field tests, the SO_2, O_3 and NO_2 constituents were measured continuously along with the benzene concentration for part of the testing period.

The suitability tests revealed that the system meets the minimum requirement conditions.

TÜV Immissionsschutz and Energiesysteme GmbH therefore proposes that the system be announced as a suitability-tested measuring device for the continuous measurement of outdoor/ambient air benzene concentrations.

TABLE OF CONTENTS

I. Objective

At the request of OPSIS AB of Furulund / Sweden, TÜV Immissionsschutz und Energiesysteme GmbH carried out suitability tests of the OPSIS AR 502Z measuring system in accordance with the Guidelines for Continuous Ambient Air Concentration Measurements.

The measuring system operates on the DOAS principle and is designed to determine the benzene concentration in outdoor air.

II. Description of the measuring system

In terms of its hardware and software configuration, the OPSIS AR 502Z measuring system is essentially identical to the versions previously tested for SO_2, NO_2 and ozone. As a rule, the foregoing constituents can be measured concurrently to previously established quality standards.

For the benzene measurements, however, it was necessary to introduce a number of improvements. These comprised the following:

- Increase in the spectral resolution of the grid employed

  For this purpose the grid utilized in the analyzer was modified so as to exhibit exactly the same resolution as was previously used for the SO_2, NO_2 and ozone measurements, while also exhibiting a clearly increased resolution for the benzene level analysis.

  This hardware modification evidently called for appropriate software changes. These were carried such that the evaluation technology for SO_2, NO_2 and ozone could be used as before. For benzene the analysis was focussed on a narrower spectral range, adapted to match the increased resolution. This made it possible, specifically, to achieve a clearly reduced cross-sensitivity to other organic constituents and ozone. In addition, the dependence of the measuring signal on the oxygen concentration as a function of the light path was successfully eliminated.

- Introduction of a transmitter/receiver feedback loop for automatic light path optimization

  Stable and reproducible benzene measurements require a high light level, apart from light conditions of maximum uniformity. Light intensity variations caused by environmental factors (e.g., beam deflections due to sunlight incident from one side only) often gave rise to implausible measurements because the light intensity deviated from its optimum level. By inserting a feedback loop between the transmitter and receiver it was possible to implement an automatic system optimizing function that is performed at periodic intervals and produces a marked improvement in measurement quality.

It should be noted here that the abovementioned light level problems may well be specific to the field test location. Due to the soil structure (the parking lot is erected on a former landfill site), the stability of the concrete columns cannot surpass a certain level. Under optimum site conditions the feedback loop may therefore prove dispensable.

- Introduction of the FC 150 calibration and adjustment device

The high light intensity required for the benzene measurements imposed the need to eliminate the multiplexer from the light path. This meant that the calibrating rig previously used for the periodic automatic control of the zero and reference points had to be abandoned as well. However, since such an automatic control system is a mandatory Minimum Requirement, OPSIS has developed the FC 150 calibration and adjustment device.

Fig. 1 Exterior view of the receiver with integrated FC 150 system

The FC 150 unit is bolted to the receiver (refer to Fig. 1). It comprises a high-pressure xenon lamp of the same type as that used in the transmitter. The FC 150 is capable of blocking out the transmitter light while injecting its own light output instead. This makes it possible to generate a zero signal that utilizes all measuring system components except the transmitter. Problems associated with additional light waveguides and other optical components are thus effectively excluded.

This configuration additionally comprises a flow cell fitted permanently in the receiver. This cell remains in the light path both during the "normal" measurement and for the calibration measurements, thereby contributing further to a significant reduction of potential error sources.

Since the flow measuring cell can generally be used in the normal measuring mode as well, the user is able to perform "offset calibrations" or to evaluate the effects of cross-sensitivity constituents during normal measurements.

II.1 Measuring principle

This measuring system belongs to the category of photometric measuring devices. The measuring function of this type of system is based on the absorption of light by the sample gas in the wavelength ranges that are characteristic of that particular gas. The result of the absorption measurement is evaluated in terms of the correlation between the gas concentration and the amount of light absorbed, following the Lambert-Beer law:

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

where

I_1 : intensity of light received
I_0 : intensity of light emitted from source
L : measuring path length
C : concentration of gas to be measured
α : average absorption of this gas in the examined wavelength range

A functional sketch of the OPSIS AR 502Z measuring system is given in Fig. 2.

II. 2 Design and functions of the measuring system

A light source emits a highly focused light beam in the 200 to 2000 nm wavelength range. This light beam traverses the sample medium before being focused onto the end of an optical fiber waveguide.

The light source is a high-pressure xenon lamp with a power consumption of 150 W. This lamp is mounted in the focus of a parabolic mirror. The light emitted in a parallel pattern has a beam angle of less than 2 mrad and passes through a quartz glass window at the transmitter output.

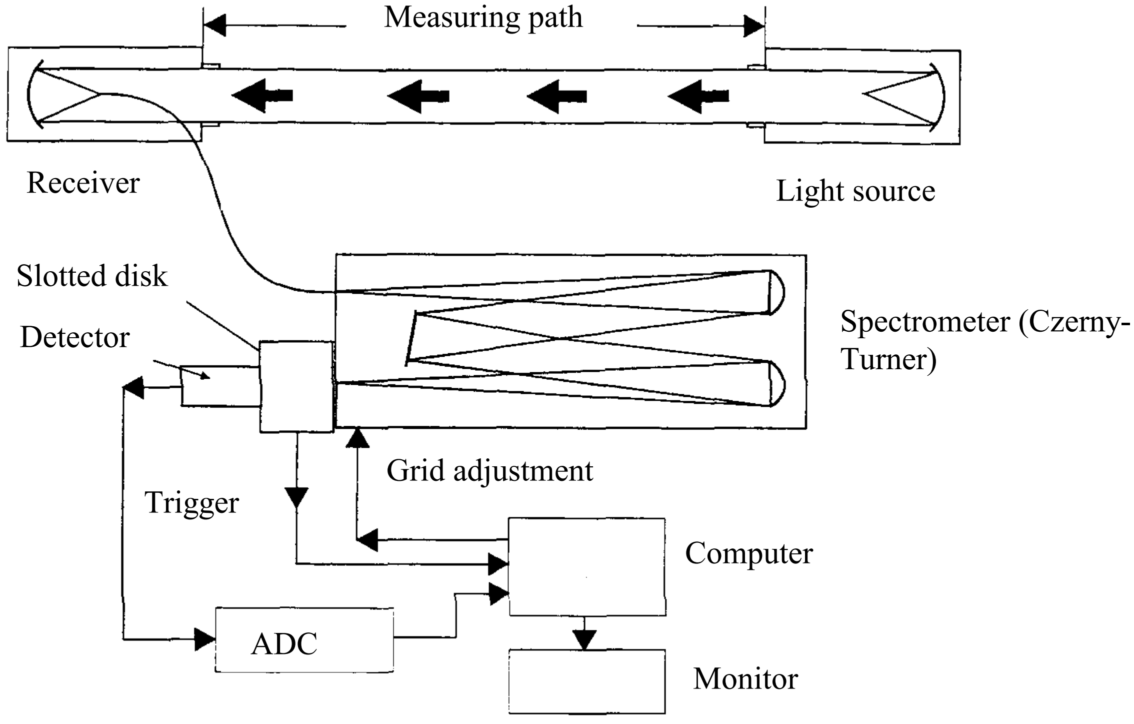

Fig. 2: Functional sketch of the OPSIS AR 502Z Measuring System

The optical design of the light receiver resembles that of the transmitter, except that the light inlet orifice of an optical waveguide is located in the focus of the parabolic mirror.

The optical waveguide connects the analyzer with the receiver. It has a 0.6 mm diameter light-active core and is permeable to light in the 200 to 2000 nm wavelength range.

The analyzer is a grid spectrometer operating on the Czerny-Turner principle, with a 0.5 m long light path. In place of its input slot, the end of the optical waveguide enters the system. A spectral grid moved by a stepper motor splits the incoming beam in such a manner that the wavelength range under analysis hits the window of one of a maximum of three photomultiplier detectors. The light is focused on the photo-multiplier by a lens in the window.

Between the window and the photomultiplier, a slotted disc measuring 200 mm in diameter revolves with a speed of 300 r.p.m. A total of 20 slots are etched into this disc; they are spaced to ensure that only a single slot will move over the window before the photomultiplier at any given time (Fig. 3). This design allows a total of 100 scans per second.

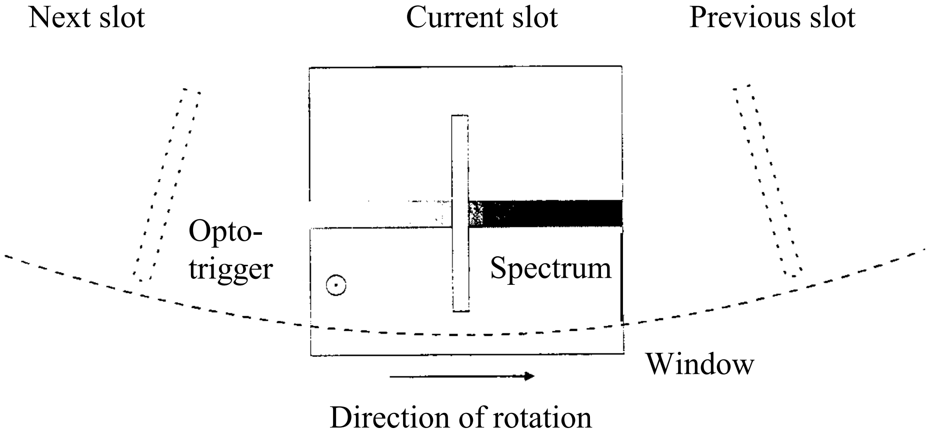

Fig. 3: Individual spectrum scanning

The UV-sensitive photomultiplier has a diameter of 50 mm. Its high voltage output is resolved into 4096 steps (12 bits) over a 190 V to 1100 V range and set to a new operating point for every measurement. This operating point depends on the intensity of the light to be measured. The photomultiplier current obtained from each scan is converted into a digital signal by a high-speed analog/digital converter with a precision of 4096 steps (12 bits). These scan signals are stored in a register spreading the wavelength range into a total of 1000 channels.

The integration time per constituent varies between 30 and 60 seconds. Since the system will record several thousand scan signals during this period, a sufficiently high signal-to-noise ratio is obtained. Interruptions of the light beam which are transient in relation to the measuring period considered will not affect the measurement result.

The signal-to-noise ratio increases with the measuring time since the scanned signals are added for each wavelength.

From the measured values stored in the 1,000 registers (each of which corresponds to a defined wavelength range), the absorption spectrum is approximated by the following trick so that the equation

$$\ln (I_0/I_1) = \Delta\alpha * L * C$$

$$0 = \ln (I_0/I_1) = \Delta\alpha * L * C$$

can be calculated, where

I_0 : intensity range of the xenon lamp
I_1 : measured intensity range
$\Delta\alpha$: differential absorption coefficient
L : measuring path length
c : concentration to be determined

The raw data spectrum written into memory is initially divided by a pre-recorded spectrum of the high-pressure xenon lamp that is stored in the analyzer. This spectrum was stored in memory either in the laboratory or on-site during zero adjustment, using a separate lamp and optical waveguide to connect this lamp to the analyzer. This process ensures that the wavelength-dependence of the lamp's output intensity and all changes in the spectrum caused by the measuring set-up (e.g., influences due to the optical waveguide, the light path inside the analyzer and/or the photomultiplier) are duly taken into account. The result is an absorption spectrum of the exhaust gas to be measured (I_2).

This spectrum is now approximated by means of a 5th degree polynomial. As we divide the absorption spectrum I_2 by the computed 5th degree spectrum, all broadband influences changing the light spectrum of the lamp in the medium under measurement (e.g., light diffraction due to dust, etc.) are eliminated. The absorption levels of individual molecules which concern only certain lines are not affected by this process. The result is a differential absorption spectrum I_x, which corresponds to (I_0/I_1) in equation (1). As a next step, the logarithm of this quotient is computed.

The absorption coefficient $\alpha(i)$ was determined in the laboratory for each separate wavelength (using a defined concentration, measured I_0, measured I_1, and a known path length in a sealed cell). The concentration to be determined is that for which the following expression assumes its lowest value:

$$(\ln lx(i) - L * c * \Delta\alpha(i))^2 ==> 0$$

The standard error of the result is proportional to σ, where σ^2 is the variance.

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

where n = number of channels used

Cross-sensitivities due to unknown substances causing differential absorption in the same wavelength range will increase the standard error. The latter is calculated and displayed for each measured value as a quality criterion.

Cross-sensitivities to known substances can be minimized by modifying the above equation, provided that the differential absorption coefficients are stored in the computer.

In the multi-constituent system examined in this suitability test, a specific wavelength range is set for each constituent, i.e., each constituent is individually measured. In exceptional cases, such as when two substances are analyzed in exactly the same spectral range (e.g., NO and NH_3), the two constituents can be measured simultaneously in the same wavelength range.

III. Test program

III.1 Test implementation notes

The system under test operates with an open measuring path. The test for compliance with the Minimum Requirements is designed for ambient air concentration measuring systems equipped with a sampling device. A measuring path of 300 meters cannot be appropriately simulated on a laboratory scale. The actual tests were therefore performed with short, sealed flow cells into which the test gases were admitted in high concentrations from pressurized gas cylinders. The different concentrations in the calibration measuring set-up that are required for individual parts of the test were produced by using flow cells of different length (1 to 900 mm). For some tests, up to three of these cells were placed in the calibrating rig in series. Dilution errors could thus be avoided. Fig. 4 shows a typical set-up as used in the laboratory tests and calibration process.

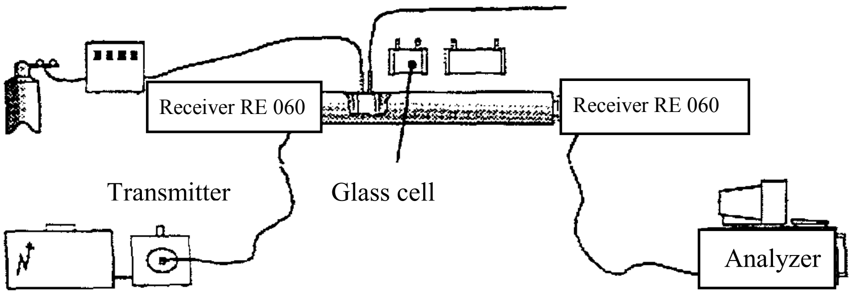

Fig. 4 Typical laboratory test arrangement

For some tests, moreover, the configuration shown in Fig. 5 was employed. This is a combination of the RE 150 receiver with the lamp / flow cell combination FC 150.

The FC 150 system is a receiver expansion module. A flow cell and light source are integrated into the receiver unit. This light source is then used for the calibration measurements instead of the transmitter's light output. For this purpose, the receiver light is blocked and the appropriate light input is fed to the receiver via a system of mirrors. An automatic light level optimizing function will then ensure that the light is focused on the end of the waveguide in the best possible manner. Following a successful optimization, measuring can be commenced.

For this purpose the flow cell built into the receiver is flushed with zero air. Once the zero point is set, it is possible to apply various sample gas concentrations for testing of the system's linearity and drift behaviour.

One key advantage of this configuration, compared with the set-up illustrated in Fig. 4, lies in the possible elimination of a multiplexer and additional optical waveguides not used for the actual measuring function. The sum of these benefits adds up to a significantly increased light yield and hence, more stable measurements.

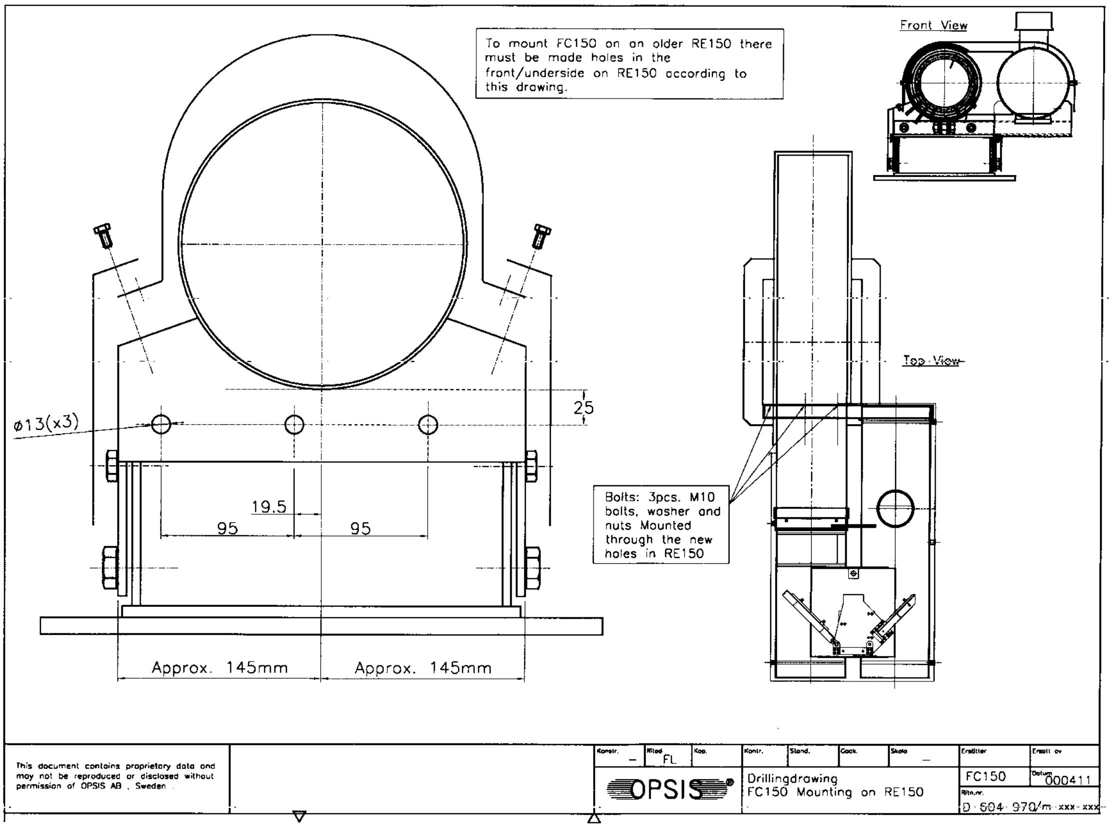

Fig. 5: Calibration measuring path in the receiver, consisting of RE 150 and FC 150

III. 2 Laboratory tests

Laboratory testing was conducted with two identical OPSIS AR 502Z type systems bearing the serial numbers 460 and 461, respectively. In accordance with the current Guidelines [1-4], the following laboratory test program was carried out:

- Verification of all equipment functions
- Determination of the equipment characteristic using test gas
- Determination of the detection limit
- Repeatability determination
- Determination of the measuring system's cross-sensitivity to accompanying substances in the measured gas
- Testing of the zero and reference point stability within the permissible ambient temperature range
- Determination of the impact of test gas temperature changes

- Determination of the impact of mains voltage fluctuations on the measuring signal
- Determination of dead times & transient recovery times
- Determination of the system's calibration capability

The laboratory tests were conducted mainly with the test set-up described in Fig. 4. Departures from this configuration are described under the individual test items.

III.3 Field test

The field test is currently being carried out in a large parking lot area in Cologne. For the endurance tests the measuring systems were installed in an air-conditioned measuring container. The transmitters and receivers of the identical measuring systems were placed on concrete columns at a distance of 300 m. The systems used were the following:

System 1 : serial No. 460
System 2 : serial No. 461

The endurance test was started on April 1, 2000. Measurement data are now available for a four-month period.

Throughout the endurance test, the systems were set as follows:

Measuring range 1: 0 ... 300 µg/m³ = 4 ... 20 mA

The envisaged field test program is as follows:

- Functional test of general equipment functions
- Functional test of measuring systems at the start and end of the field test
- Determination of detection limits
- Determination of dead time and transient recovery time
- Determination of repeatability
- Determination of zero and reference point drift
- Determination of the maintenance interval
- Determination of availability rate
- Comparative tests with a benzene reference measuring unit (GC)
- Comparative tests using passive collectors placed at three points over the measuring path
- Examination of the dependence of indicated values on the relative air humidity

The integration time for the constituent, benzene, was set to 120 seconds throughout the field test. Apart from benzene, SO_2, NO_2 and O_3 were measured concurrently with an integration time of 30 seconds each. This gives a net cycle time of 210 seconds for the measurement alone. To this one must add the times for internal system adjustments, light path optimization steps and computing processes. These times add up to an average of approx. 15 s per measuring cycle.

The resulting maximum cycle time is equal to 225 s. This implies that each constituent is determined approx. 8 times for each half-hour average. The determination of half-hour averages will therefore be ensured even when the measuring system is operating to full capacity. Needless to say, this will also be the case if longer measuring periods such as hourly or annual averages are considered.

The software allows a variation of cycle times between cycles. The measuring system can be programmed, for instance, to omit the benzene measurement in every third measuring cycle. The measuring frequency for the other constituents would thus be increased accordingly (e.g., to 10 times per half hour).

IV Test results

IV.1 Minimum requirements on continuous ambient air concentration measuring systems in suitability tests

IV.1.1 General notes

IV.1.1.1 Normative conditions

> Suitability testing is to be conducted in compliance with the terminological definitions of the VDI Guideline 2449, Sheet 1 (October 1970 edition). The equipment version / design features of the system shall be documented by the test institute.

The suitability test was conducted in compliance with the abovementioned guidelines. The equipment version / design features of the system were documented.

Evaluation: The minimum requirement is met.

VI.1.1.2 Equipment modifications

> The manufacturer of a suitability-tested system shall be required to notify the test institute forthwith of any modifications made on this system. The test institute shall decide, on the basis of the documents submitted, whether these modifications warrant a re-test of the modified equipment type.

The manufacturer has been informed in writing that any modifications made to the system shall be reported to the test institute.

Evaluation: The minimum requirements is met.

IV.1.1.3 Test location

> The suitability tests shall be conducted such that the minimum requirements are met under conditions of practical use. To the extent to which it is expedient and necessary to determine certain parameters both in the laboratory and through field tests, both test results shall be indicated.

To the extent to which this proved necessary, individual portions of the tests were carried out both in the laboratory and in the field. For details refer to the relevant sub-paragraphs.

Evaluation: The minimum requirement is met.

IV.1.1.4 Field test duration

> In the suitability tests, compliance with minimum requirements is to be demonstrated by an endurance test of at least 3 months' duration. The design of the endurance test is to be adapted to the type of suitability validation sought (e.g., for stationary use in a monitoring system and/or for mobile use).

The endurance test was carried out at a single test location, starting on 1 April 2000. As of this date, the measuring systems remained in continuous operation for a period of four months. The measuring system was tested for stationary use. Its mobile application, although generally possible with the tested equipment version, would nevertheless be disproportionately complex and costly. The system was not tested for mobile use.

The two OPSIS measuring systems were operated in parallel with a single-point Type GC 855 gas chromatograph for BTX sourced from Spectras Co.

This measuring system was installed jointly with the OPSIS analyzers in the same air-conditioned measuring container as the OPSIS units. The sampling point for the reference measuring unit was located at the end of the OPSIS measuring path, between the two light paths. All three measuring systems were operated simultaneously and in parallel. The measurements recorded were instantly compressed into half-hour averages. Fig. 6 is a graphic chart of the half-hour averages recorded over a four-week (summer) interval.

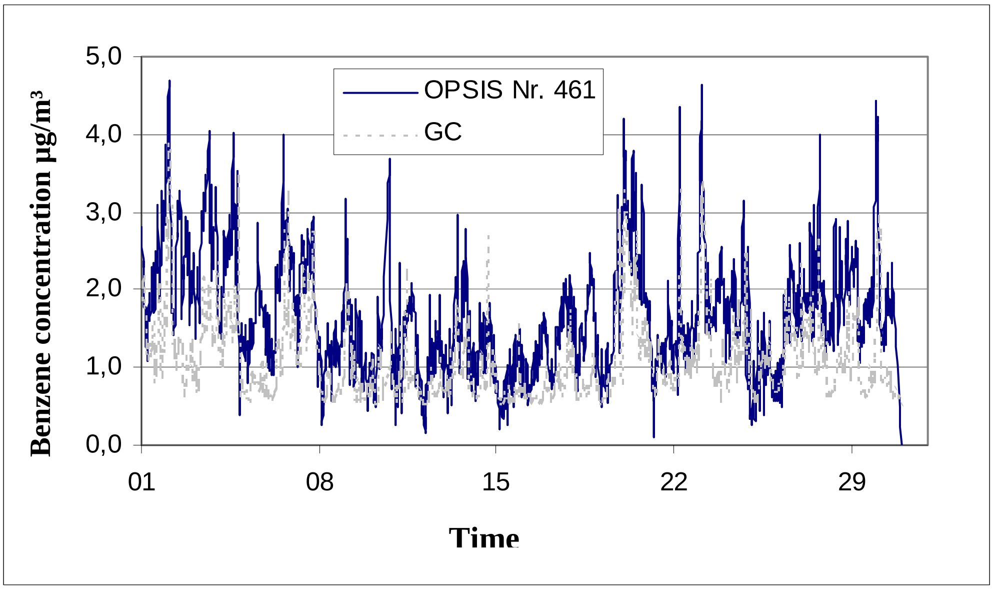

Fig. 6 Plot of the comparative measurements (half-hour averages) performed with the OPSIS AR 502Z system No. 461 and the Syntec Spectrax BTX analyzer GC 855 in the six-month summer period

Fig. 7 shows a typical daily profile. The statistical analysis of the measurement data obtained over one month is given in Fig. 8.

Further to the comparative measurements with the gas chromatograph, a series of comparative measurements is being conducted with passive collecting devices. These were arranged at three measuring points distributed over the measuring path (first third, middle, last third). The typical collecting period varied between 2 and 3 weeks.

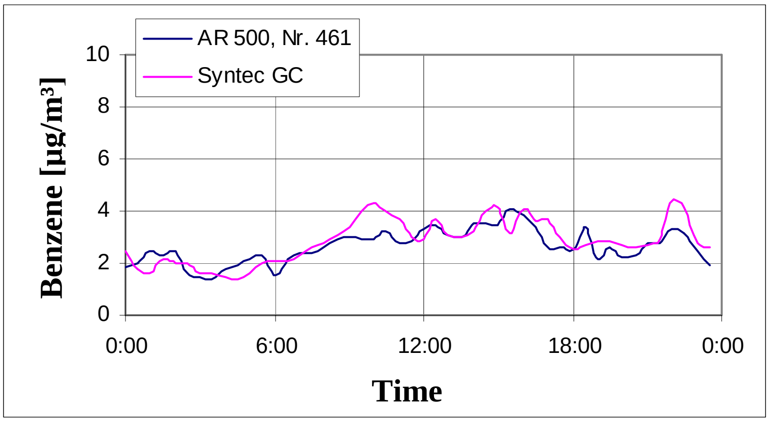

Fig. 7 Plot of the comparative measurements (half-hour averages) performed with the OPSIS AR 502Z system No. 461 and the Syntec Spectrax BTX analyzer GC 855.

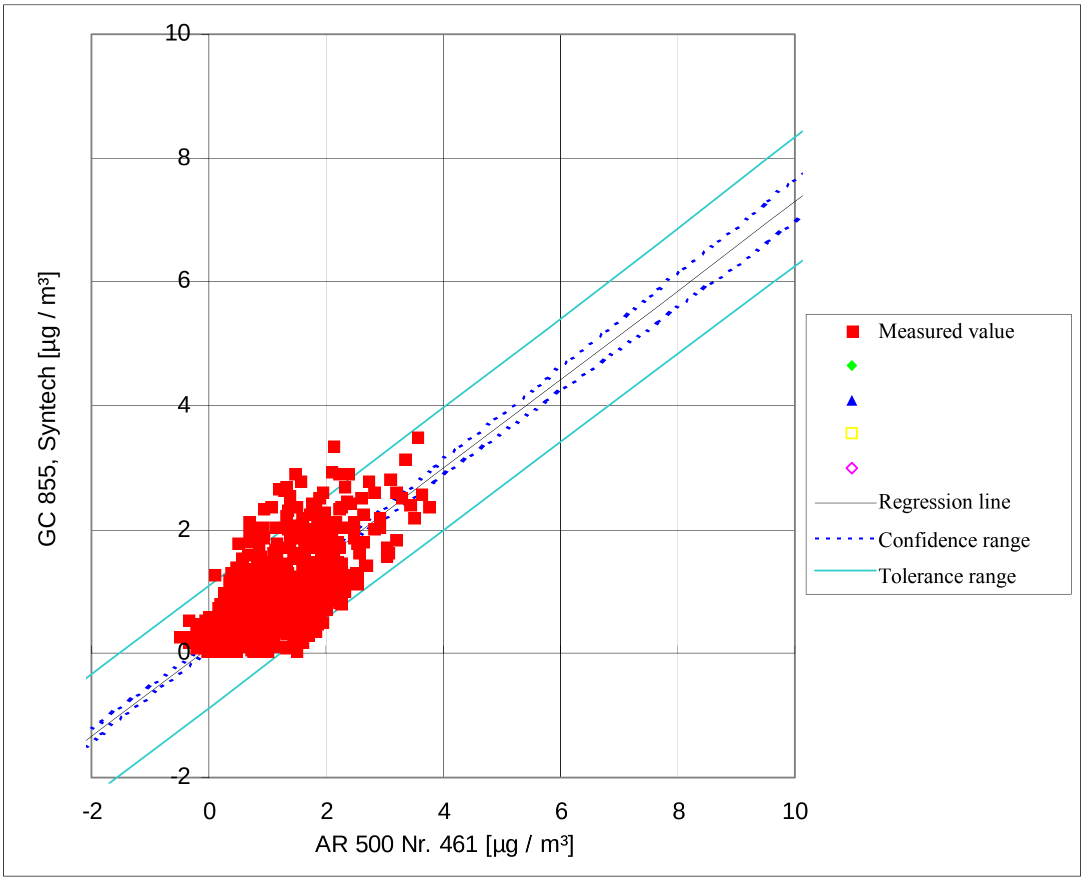

Fig. 8 Plot of the comparative measurements (half-hour averages) performed with the OPSIS AR 502Z system No. 461 versus a Syntec Spectrax BTX analyzer GC 855

Table 1 Results of the comparative measurements obtained with the long-path gas chromatograph and three passive long-term collecting devices distributed over 3 points of the measuring path

Collecting period		Mean value				Individual measurements at passive collecting points		
		460	461	GC	Passive collector	Point 1	Point 2	Point 3
		µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m3	µg/m³
15-05-00	22-05-00	1.8	1.8	1.9	2.8	3.2	2.4	--
22-05-00	05-06-00	1.7	1.6	2.0	2.6	1.4	3.5	3.0
05-06-00	26-06-00	1.2	0.9	0.8	1.9	2.1	1.9	1.8
26-06-00	10-07-00	2.5	1.8	2.4	1.7	1.5	2.0	1.7
10-07-00	24-07-00	1.9	1.5	2.3	1.8	2.2	2.2	2.1

The measuring devices were also operated throughout the six-month winter period. The values measured during this half of the year tended to be higher, although the levels determined with the GC system were less markedly increased than those measured with the OPSIS long-path analyzer. Fig. 9 plots a comparison between one single point measurement and a linear measurement taken in winter. It is clearly evident that the concentration curves of the two measuring devices exhibit the same trend, with the long-path analyzer returning consistently higher levels than the single-point measurement.

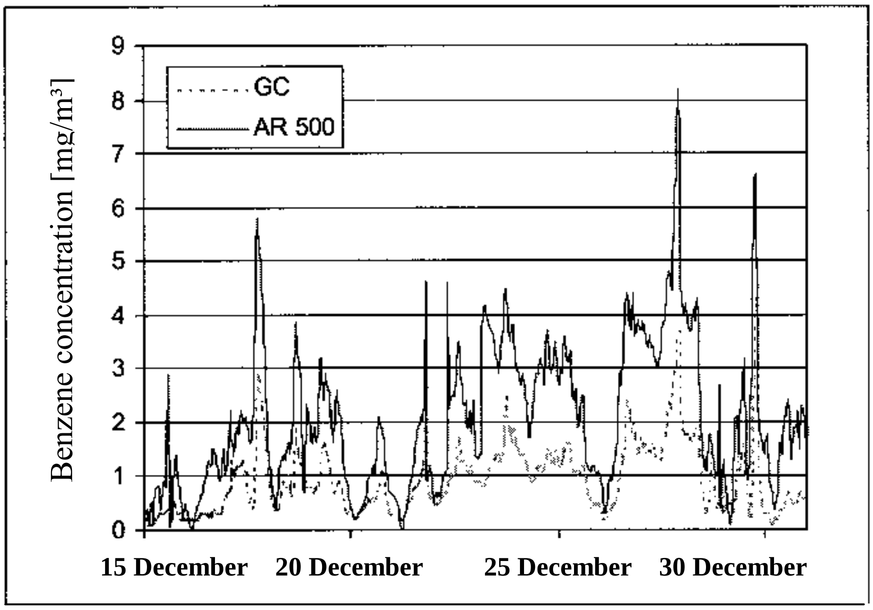

Fig. 9 Plot of the comparative measurements performed in the winter season (half-hour averages) with the OPSIS AR 502Z analyzer (No. 460) and the Syntec Spectras BTX Analyzer GC 855

A statistical evaluation of the measurements yields a correlation coefficient of r = 0.909 between the two measuring systems (refer to Fig. 10).

Concurrently with the benzene concentration, the other constituents for which the OPSIS AR 502Z measuring device had been previously suitability-tested were likewise determined. The following graphs and statistical analyses summarize the results of these parallel measurements. However, these can merely reflect a period of approx. 15 days since the gas chromatograph had broken down in the meantime.

Equipment			OPSIS AR 502Z		
Process handled by					
Processing file			Benzene Rep 2001		
Measuring period			Dec. 00 – Jan 01		
System			Parking lot		
Constituent	Gas		Benzene		
Data range			15 days		
Results					
Sample size		n	=	776	
Upper limit for benzene		MBE		300	µg/m³
t-value for selected confidence level		t95	=	1.966	
Standard deviation from double measurements		sd	=	0.951	
Repeatability		R(d)	=	160	
Standard deviation		s	=	0.275	
Correlation coefficient		r	=	0.9039	
Y = b *c + c Gradient		b	=	0.446	
Rise (ordinate difference)		c	=	0.026	µg/m³
Mean		System 1	=	2.004	µg/m³
Mean		System 2	=	0.919	µg/m³

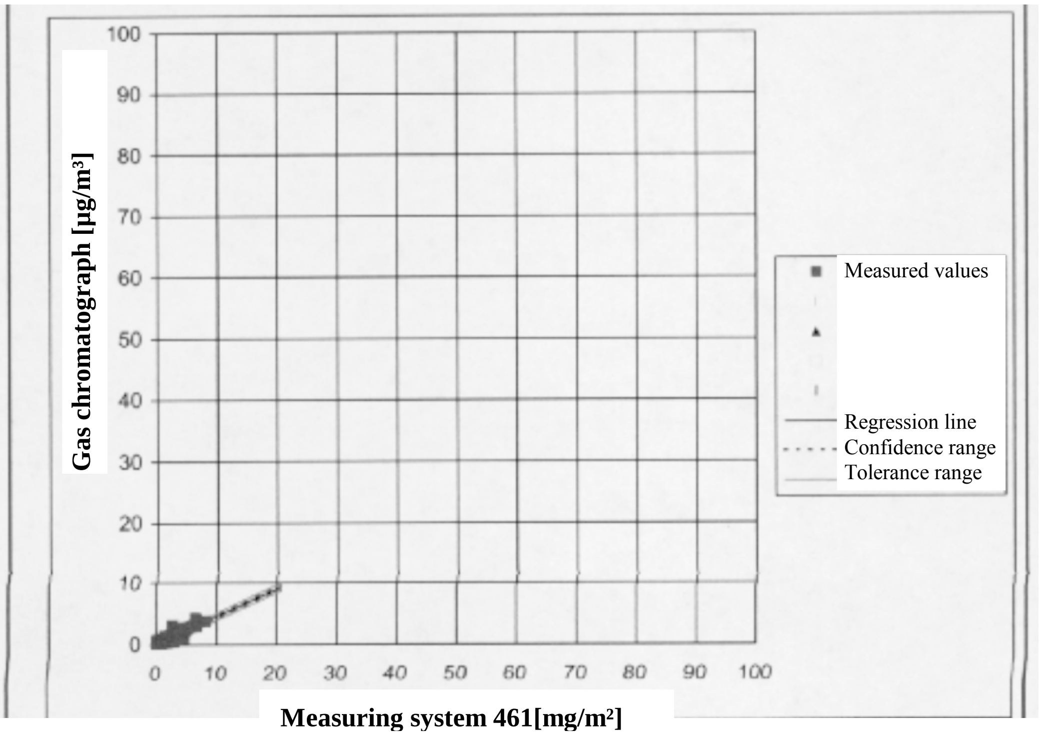

Fig. 10   Evaluation of the comparative benzene concentration measurements obtained by the long-path and single-point methods

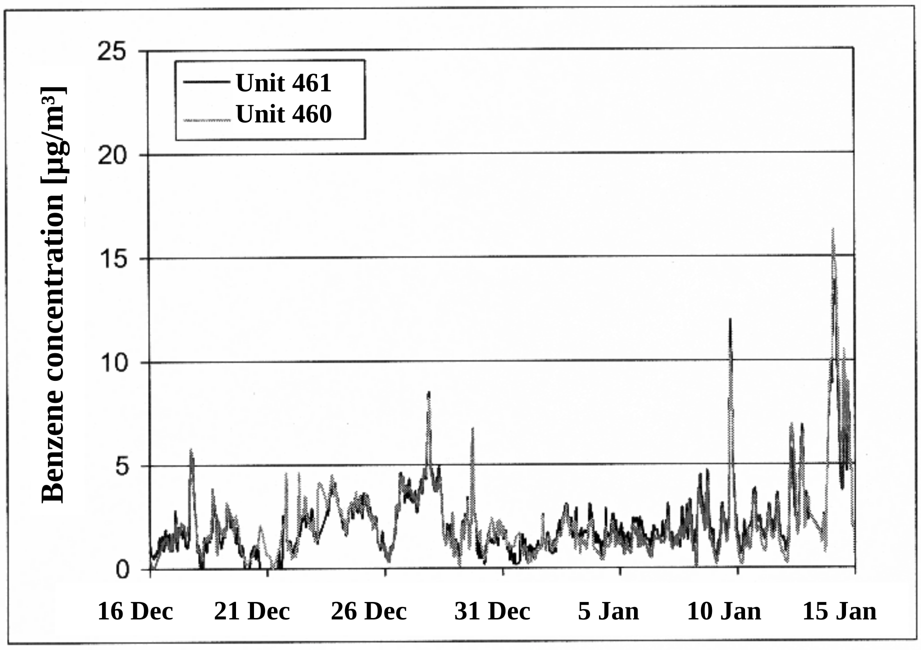

Fig. 11 Benzene concentration graphs plotted by the two OPSIS measuring systems between 15 December 2000 and 15 January 2000

The correlation coefficient between the single-point measurement and the long-path measurement was r = 0.773 in the summer and r = 0.909 in the winter. Considering that this is a comparison between a single-point measuring set-up and a linear measurement over a distance of 300 m, the two values exhibit a good degree of coincidence. The OPSIS systems thus ensures a plausible measurement. It should also be noted when comparing these values that the gas chromatograph generates its half-hour averages from only 10 instantaneous samples, compressing 5 instantaneous measuring results from a 15-minute interval into one 15-minute value. Two of these 15-minute values are then combined into a half-hour average. The coefficient of correlation between the results displayed by the two long-path systems was in excess of r = 0.99 over the period evaluated.

Evaluation: The minimum requirement is met.

IV.1.1.5 Unauthorized change of settings

> A feature must be provided which allows the settings of the measuring systems to be locked against unauthorized or inadvertent manipulation while the system is in operation.

The measuring system can be protected by activating various password levels, providing security against unauthorized or inadvertent manipulation. Operating access can also be restricted to individual levels for the different groups of personnel.

Evaluation: The minimum requirement is met.

IV.1.1.6 Live zero / zero position

> The position of the measuring system's zero point must be sufficiently spaced from the electric zero level to allow sensing of the permissible zero drift (live zero).

The analog output of the measuring system is a current signal with 4 ... 20 mA live zero point. Moreover, all data are durably stored on the hard disk integrated into the system and will thus remain available for further digital processing.

Evaluation: The minimum requirement is met.

IV.1.1.7 Detection limit

> The detection limit of each measuring system should not exceed 10% of the defined long-term ambient air concentration level (IW 1). If the ambient air concentration level is unknown, a suitable reference value shall be determined and stated by the test institute in coordination with the other test institutes. The detection limit shall be determined under near-field conditions.

To determine the detection limit, the systems were subjected to 15 cycles in which zero gas was introduced alternately with 5 other test gas concentrations for a duration of 15 minutes in each case. No adjustment whatsoever was performed over the test interval. The test results are summarized in Table 2.

Benzene detection limit	System No. 460 [µg / m³]	System No. 461 [µg / m³]	
	0.11	-0.05	
	0.35	-0.01	
	0.44	-0.38	
	0.44	-0.25	
	0.49	-0.30	
	0.50	-0.23	
	0.51	-0.08	
	0.52	-0.21	
	0.52	-0.20	
	0.55	-0.21	
	0.55	-0.11	
	0.58	-0.17	
	0.60	-0.18	
	0.62	-0.10	
	0.62	-0.16	
s_{xO} =	0.13	0.10	µg/m³
$x = 3 * s_{xO}$	0.39	0.29	µg/m³

Table 2: Detection limits as determined by laboratory tests

These tests showed a detection limit of 0.39 µg/m³ for System 1 and 0.29 µg/m³ for System 2. The detection limit is thus below 10% of the 10 µg/m³ reference value for both systems.

Evaluation: The minimum requirement is met.

IV.1.1.8 Upper limit of effective measuring range

> The upper limit of the effective measuring range of each system should be equal to at least 2.0 times the short-term ambient air concentration level (IW 2); peak load measurements should likewise be possible.

The measuring range is freely selectable via the software. During the tests we applied concentrations of up to 300 µg/m³ as recommended in the DIN 33963-1 standard. These produced no limitations in equipment functionality whatsoever. The associated analog output can be freely selected. Irrespective of the measuring range adopted, all recorded values remain available for further analysis on the analyzer's hard disk.

Evaluation: The minimum requirement is met.

IV.1.1.9 Repeatability

> The repeatability of the measuring method
>
> $$R = \frac{IW\ 2}{U}$$
>
> is to be determined via double measurements with two identical measuring systems and should not be less than 10.

Repeatability is defined as the maximum difference between to randomly selected individual values obtained under reference conditions. It was determined in the laboratory using two identical systems operating in parallel. The repeatability value was calculated by means of the formula

$$R = \frac{IW2}{U} \geq 10, \text{ where } U = \pm S_D \cdot t_{(n;0.95)} \text{ and } S_D = \sqrt{\frac{1}{2n} \cdot \sum_{i=1}^{n} (x_{1i} - x_{2i})^2}$$

R = repeatability at IW 2

U = uncertainty

IW 2 = in this case, the reference value (= 10 µg/m³)

S_D = standard deviation derived from double measurements

n = number of double measurements (n = 15)

$t_{(n;0.95)}$ = student factor for 95% certainty

x_{1i} = measuring signal of System 1 at ith concentration

x_{2i} = measuring signal of System 2 at ith concentration

The results of these investigations are summarized in Table 3.

The repeatability was determined by applying 6 sample gas concentrations 15 times to each of the measuring systems. The resulting measurement pairs were used to compute the measurement uncertainty for each concentration class. The repeatability was found to be larger than 10 for each concentration class

Table 3: Standard deviation, uncertainty range and repeatability in the laboratory tests

Test gas concentration	Average System 1	Average System 2	S_D	U	R_N	R
µg/m²	µg/m³	µg/m³				
0	0.00	0.13	0.11	0.240	--	56.6
1.15	1.28	0.94	0.26	0.544	2.1	
5.45	5.41	5.19	0.18	0.386	14.1	
11.18	10.38	10.32	0.08	0.177	63.3	
55.20	49.58	49.72	0.31	0.652	84.7	
161.50	149.52	148.86	1.12	2.394	67.4	
330.90	317.47	317.01	0.66	1.416	233.6	

In order to determine the field repeatability, two measuring systems of identical design were installed in the field with a measuring path of 300 m. The distance between the two measuring paths was approx. 10 m. The measurements taken were integrated into half-hour averages and then analyzed. The measured values essentially varied between 0 and 2 µg/m³. Fig. 12 shows a graph of the measurements. Table 4 summarizes the result of the repeatability tests. Related to the reference value of 10 µg/m³, the repeatability was R = 13 (six-month summer period) and R = 11 (six-month winter period, Fig. 10) respectively, and R' = 2 when related to the mean value of all measurements.

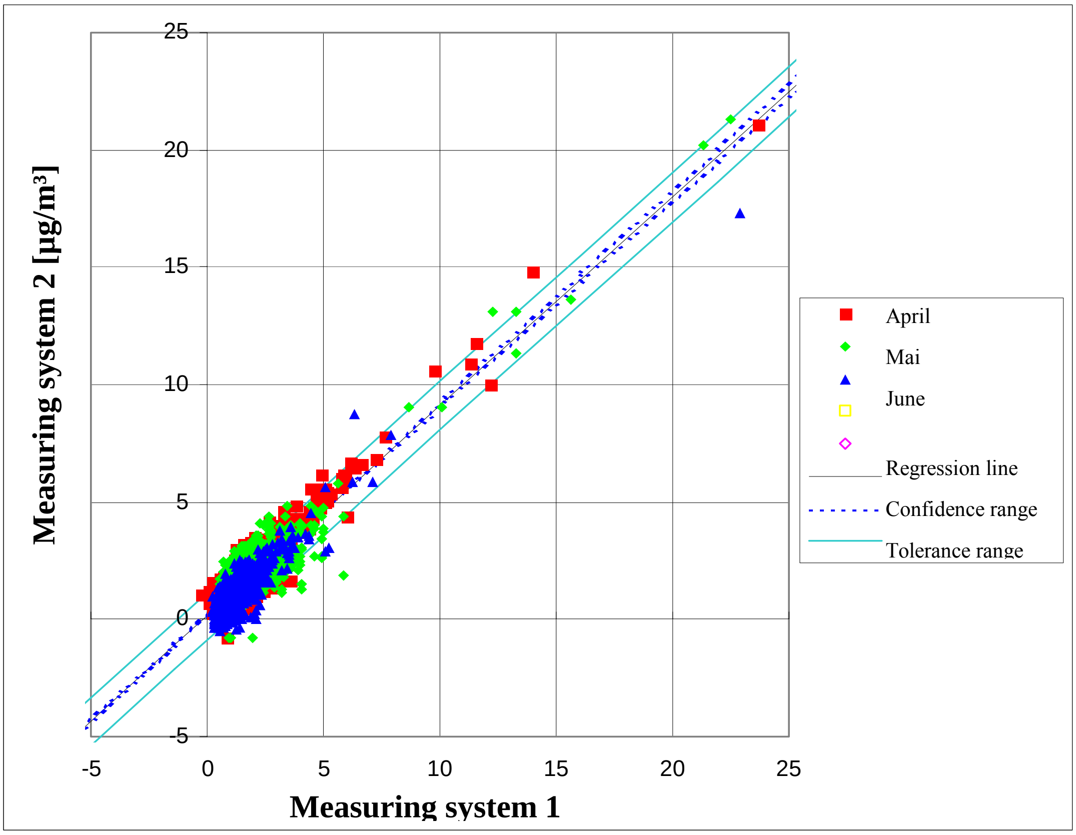

Fig. 9: Repeatability as determined by double field measurements with two OPSIS AR 502Z measuring systems in the months of April, May and June 2000

Sample size	n	=	4038	
Upper limit for benzene	MBE		10	µg/m³
t-value for selected confidence level	t95	=	1.961	
Standard deviation from double measurements	sd	=	0.381	
Repeatability	R(d)	=	13	
Standard deviation	s	=	0.522	
Correlation coefficient	r	=	0.9039	
Y = b *c + c Gradient	b	=	0.894	
Rise (ordinate difference)	c	=	0.131	µg/m³
Mean	System 1	=	1.518	µg/m³
Mean	System 2	=	1.489	µg/m³

Table 4: Repeatability as determined by double field measurements with two OPSIS AR 502Z measuring systems in the months of April, May and

In December 2000 and January 2001 both measuring systems were set to take continuous SO_2, NO_2 and O_3 measurements concurrently with the benzene concentration levels. The results are summarized in the following graphs and tables.

Evaluation: The minimum requirement is met.

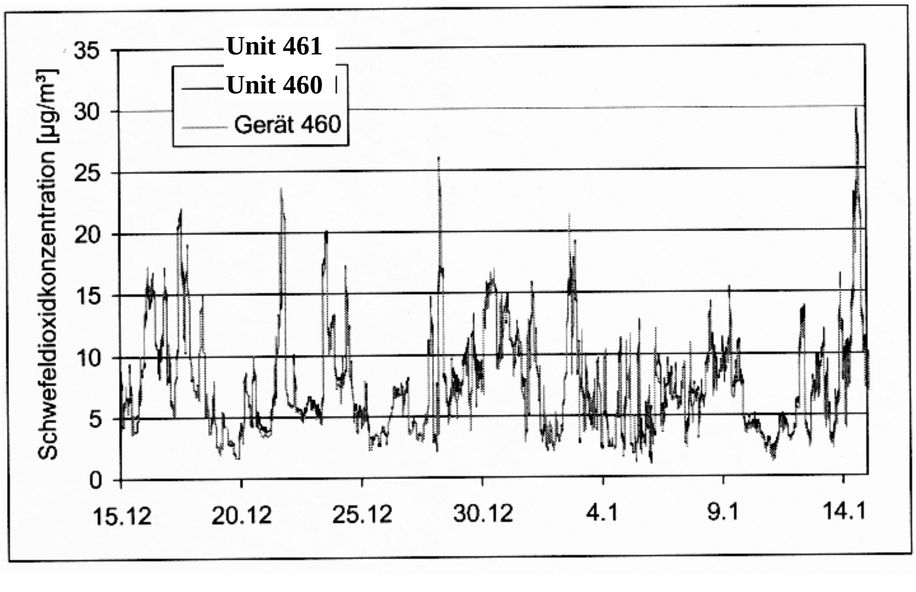

Fig. 13: Time-based graph of the measurements taken by the two OPSIS AR 502Z long-path analyzing systems for the SO_2 constituent

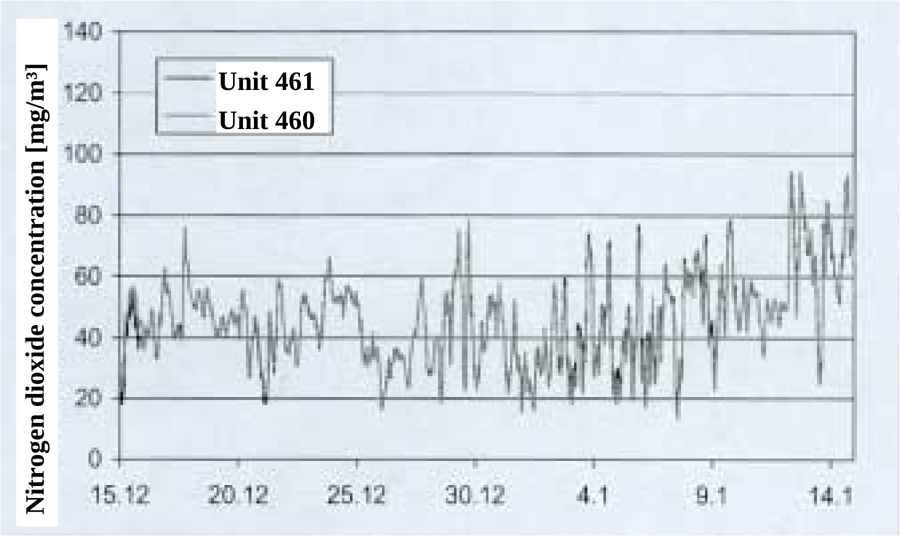

Fig. 14: Time-based graph of the measurements taken by the two OPSIS AR 502Z long-path analyzing systems for the NO_2 constituent

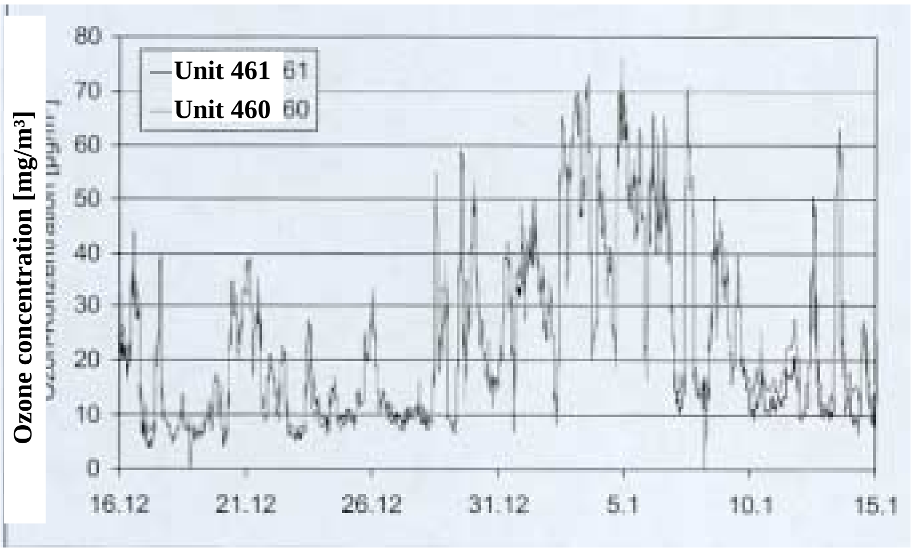

Fig. 15: Time-based graph of the measurements taken by the two OPSIS AR 502Z long path analyzing systems for the ozone constituent

Equipment			OPSIS AR 502Z		
Process handled by					
Processing file			SO_2 for Benzene Rep 2001		
Measuring period			Dec. 00 – Jan 01		
System			Parking lot		
Constituent	Gas		Sulphur dioxide		
Data range			32 days		
Results					
Sample size		n	=	1536	
Upper limit for benzene		MBE		400	µg/m³
t-value for selected confidence level		t95	=	1.963	
Standard deviation from double measurements		sd	=	0.507	
Repeatability		R(d)	=	402	
Standard deviation		s	=	0.656	
Correlation coefficient		r	=	0.9887	
Y = b *c + c Gradient		b	=	0.969	
Rise (ordinate difference)		c	=	0.013	µg/m³
Mean		System 1	=	7.745	µg/m³
Mean		System 2	=	7.489	µg/m³

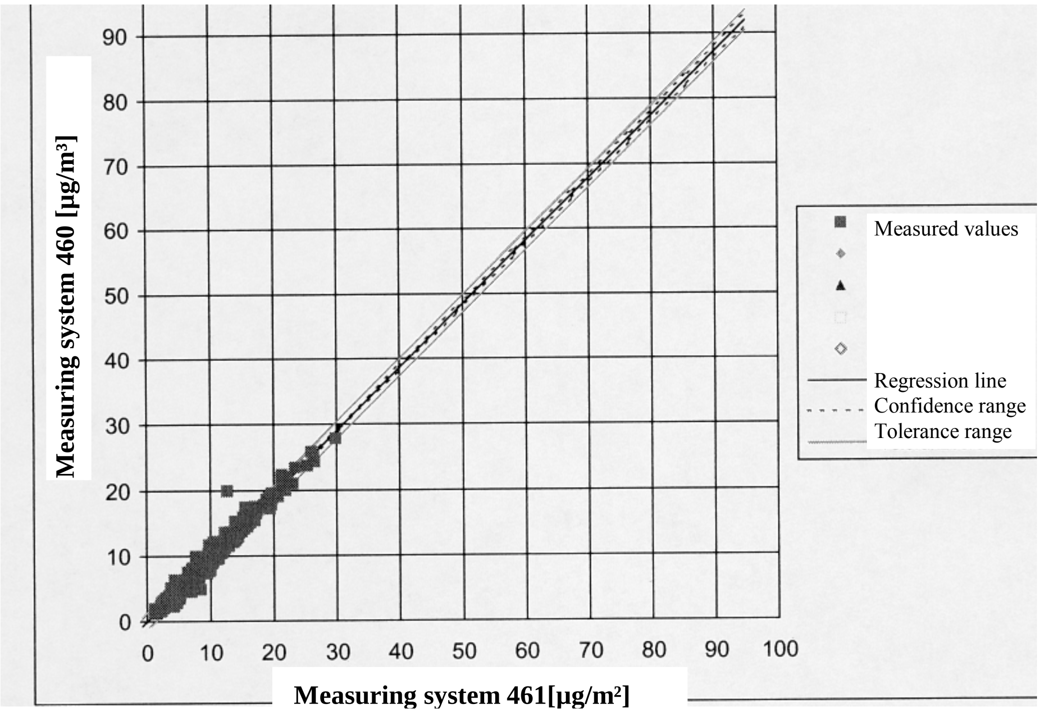

Fig. 16: Plot of the concurrent sulphur dioxide and benzene measurements

Equipment			OPSIS AR 502Z		
Process handled by					
Processing file			NO_2 for Benzene Rep 2001		
Measuring period			Dec. 00 – Jan 01		
System			Parking lot		
Constituent	Gas		Nitrogen dioxide		
Data range			32 days		
Results					
Sample size		n	=	1536	
Upper limit for benzene		MBE		400	µg/m^3
t-value for selected confidence level		t95	=	1.963	
Standard deviation from double measurements		sd	=	1.232	
Repeatability		R(d)	=	165	
Standard deviation		s	=	1.709	
Correlation coefficient		r	=	0.9937	
Y = b *c + c Gradient		b	=	1.000	
Rise (ordinate difference)		c	=	0.368	µg/m^3
Mean		System 1	=	46.181	µg/m^3
Mean		System 2	=	45.832	µg/m^3

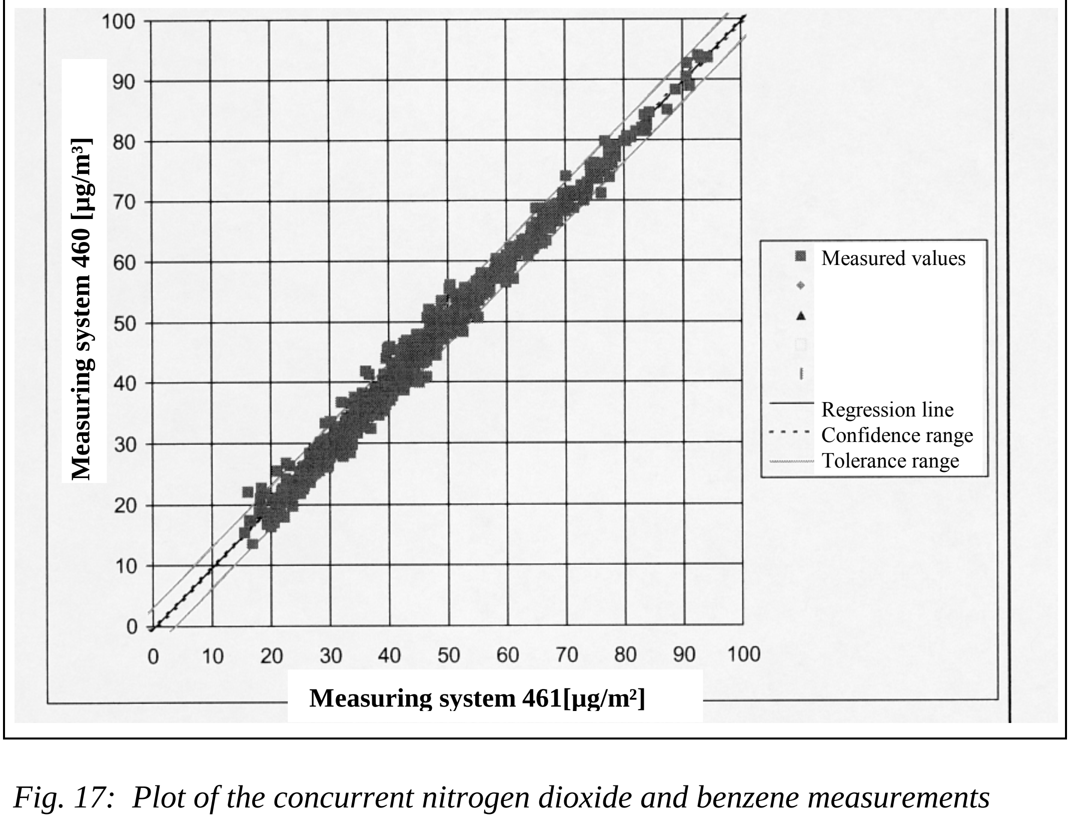

Fig. 17: Plot of the concurrent nitrogen dioxide and benzene measurements

Equipment			OPSIS AR 502Z		
Process handled by					
Processing file			Ozone for Benzene Rep 2001		
Measuring period			Dec. 00 – Jan 01		
System			Parking lot		
Constituent	Gas		Ozone		
Data range			32 days		
Results					
Sample size		n	=	1536	
Upper limit for benzene		MBE		360	µg/m³
t-value for selected confidence level		t95	=	1.963	
Standard deviation from double measurements		sd	=	2.068	
Repeatability		R(d)	=	89	
Standard deviation		s	=	2.771	
Correlation coefficient		r	=	0.9858	
Y = b *c + c Gradient		b	=	0.999	
Rise (ordinate difference)		c	=	0.979	µg/m³
Mean		System 1	=	23.751	µg/m³
Mean		System 2	=	24.695	µg/m³

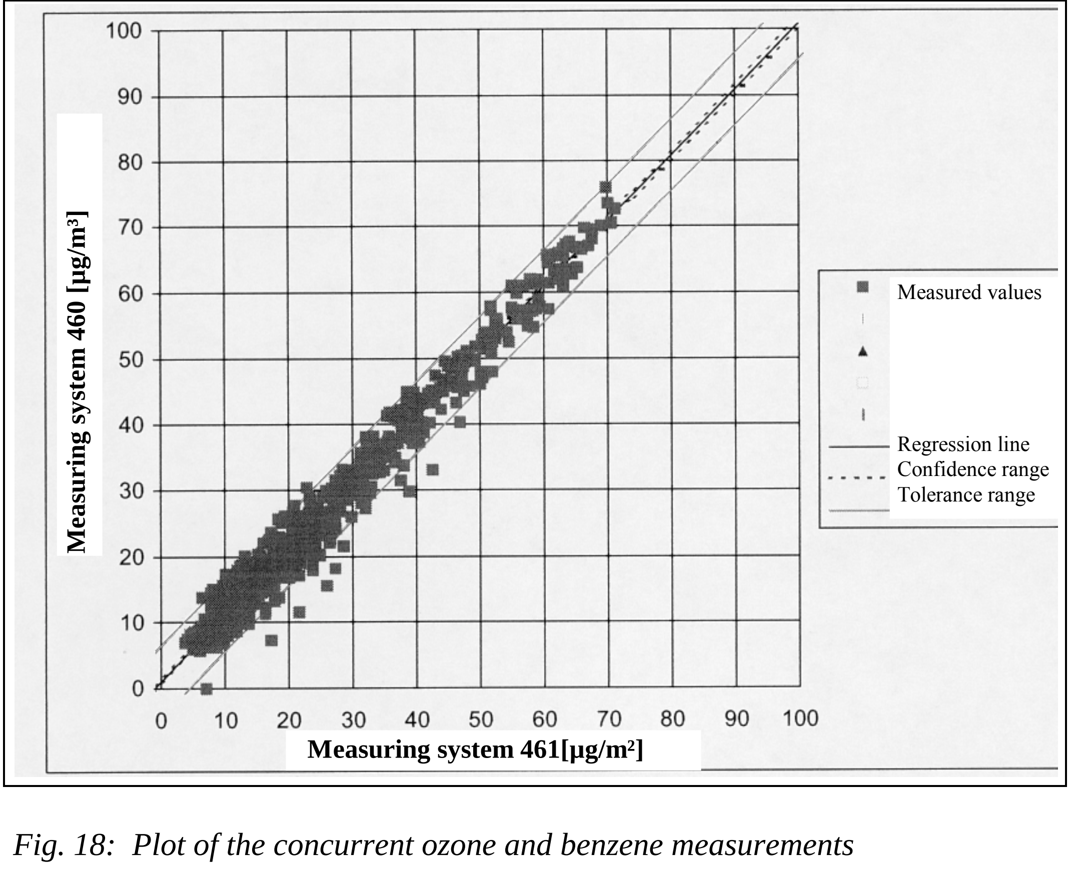

Fig. 18: Plot of the concurrent ozone and benzene measurements

Equipment			OPSIS AR 502Z		
Process handled by					
Processing file			Benzene Rep 2001		
Measuring period			Dec. 00 – Jan 01		
System			Parking lot		
Constituent	Gas		Benzene		
Data range			32 days		
Results					
Sample size		n	=	1452	
Upper limit for benzene		MBE		10	µg/m³
t-value for selected confidence level		t95	=	1.963	
Standard deviation from double measurements		sd	=	0.479	
Repeatability		R(d)	=	11	
Standard deviation		s	=	0.676	
Correlation coefficient		r	=	0.9442	
Y = b *c + c Gradient		b	=	1.003	
Rise (ordinate difference)		c	=	0.053	µg/m³
Mean		System 1	=	2.204	µg/m³
Mean		System 2	=	2.159	µg/m³

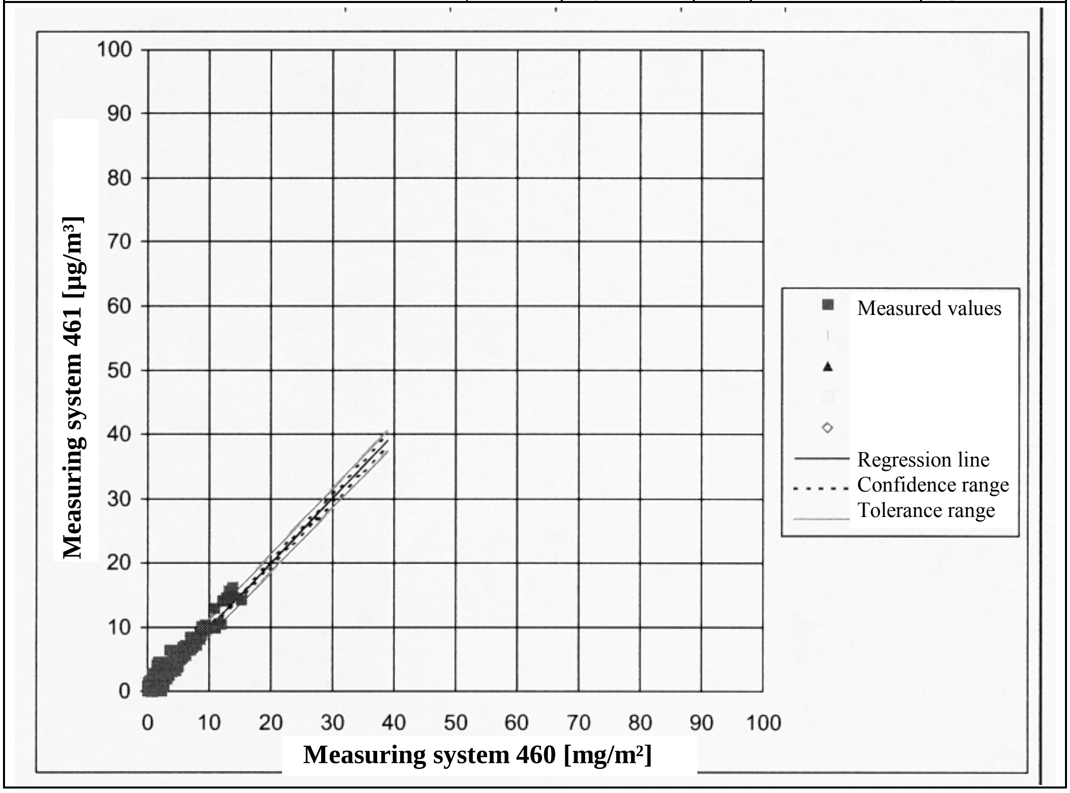

Fig. 19: Plot of the benzene measurements

IV.1.1.10 Ambient temperature impact on zero point measuring signal

> The temperature dependence of the zero point measuring signal should not exceed ± 2% of the measuring signal corresponding to the short-term ambient air concentration level (IW 2) when the ambient temperature varies by 10 K in the +5°C to +40°C range.

The measuring systems were tested with zero gas (SL) in the acceptable +5°C to +35°C temperature range. The ambient temperature was varied inside a climatic chamber in 15 K steps, starting from 20°C. The relative humidity was kept at a constant 60%. The dwell time at each step was 8 hours. A summary is given in table 5.

Table 5: Influence of ambient temperature on the analyzer output signal at the zero point.
Deviation in percent of reference value (average of three measurements)

Temperature		Deviation	
Starting temperature °C	Final temperature °C	System 1 (#460) %	System 2 (#461) %
20	5	0.8	0.4
5	35	0.3	0.8
20	20	0.9	1.1
35	20	0.4	0.4

In the preliminary investigations of the temperature influence, the impact on the measuring signal was never found to exceed ± 1.1% within the specified acceptable temperature range.

Evaluation: The minimum requirement is met.

IV.1.1.11 Ambient temperature impact on sensitivity

> The temperature dependence of the system's sensitivity should not exceed ± 2% of the value determined in section 1.4.1 or 1.5.1 (Analytical function), respectively, when the ambient temperature varies by 10 K in the +5°C to +40°C range.

The measuring systems were tested with test gas in the specified acceptable temperature range (5°C to +35°C). The ambient temperature was varied inside a climatic chamber in 15 K steps, starting from 20°C. The relative humidity was kept at a constant 60%. The dwell time at each step was 8 hours. A summary is given in table 6.

Table 6: Influence of the ambient temperature on analyzer sensitivity at the reference value (10 µg/m³)
Deviation in percent of reference value (average of three measurements)

Temperature		Deviation	
Starting temperature °C	Final temperature °C	System 1 (#460) %	System 2 (#461) %
20	5	-2.5	-2.6
5	20	0.9	0.7
20	35	1.8	2.2
35	20	-1.2	1.1

Table 7: Influence of the ambient temperature on analyzer sensitivity at five times the reference value
Deviation in percent of reference value x 5 (average of 3 measurements)

Temperature		Deviation	
Starting temperature °C	Final temperature °C	System 1 (#460) %	System 2 (#461) %
20	5	-1.3	-0.3
5	20	1.6	-2.7
20	35	2.1	2.2
35	20	1.3	1.8

The temperature impact tests showed no unacceptably high influence of temperature on the measurement signal within the permitted temperature range.

Evaluation: The minimum requirement is met.

IV.1.1.12 Impact of measured gas temperature on zero point measuring signal

> The temperature dependence of the zero point measuring signal should not exceed ± 2% of the measuring signal corresponding to the short-term ambient air concentration level (IW 2) when the sample temperature at sampling time varies by 10 K in the -20°C to +40°C range.

As a long-distance measuring system, the OPSIS measuring device operates in situ. The measured gas is not conditioned in any way whatsoever. For this reason it suffices to log the sample temperature into the OPSIS system itself or into a downstream evaluating system. No separate testing of this measuring parameter was conducted therefore.

Evaluation: Minimum requirement not applicable.

IV.1.1.13 Impact of measured gas temperature on sensitivity

> The temperature dependence of the system's sensitivity should not exceed ± 2% of the value determined in section 1.4.1 or 1.5.1 (Analytical function), respectively, when the sample temperature at sampling time varies by 10 K in the -20°C to +40°C range.

As a long-distance measuring system, the OPSIS measuring device operates in situ. The measured gas is not conditioned in any way whatsoever. For this reason it suffices to log the sample temperature in the OPSIS system itself or in a downstream evaluating system. No separate testing of this measuring parameter was conducted therefore.

Evaluation: Minimum requirement not applicable.

IV.1.1.14 Zero drift

> The variation of the zero point measuring signal over time should not exceed ± 2% of the measuring signal corresponding to the short-term ambient air concentration value (IW 2) within 24 hours, nor ± 10% of that measuring signal within the maintenance interval.

In earlier suitability tests the zero and reference points had been validated on a calibration rig installed in the measuring container. For this purpose the measuring path was disconnected from the analyzer and the calibration path was activated via a multiplexer. Zero and sample gas could then be introduced into the calibration path. Any deviations determined were automatically corrected by the measuring system and taken into account in the subsequent measurements. This control function is fully automatic and was software-programmable.

However, the method outlined above is not feasible for the measurement of benzene. This is mainly because the insertion of the multiplexer into the light path would result in a severe attenuation of the light intensity available for the measurement. The remaining light level was found to be no longer sufficient for a proper field measurement. On the other hand, the multiplexer is indispensable for a fully automatic control system.

In the course of the first part of the field tests (April through July), no changes were made to the OPSIS system settings. The zero point of both systems was periodically controlled by applying test gas manually. As will be appreciated *inter alia* from Fig. 12, there was no significant drift in the course of the test interval.

Zero point and test gas checks were performed manually at 2 to 3-week intervals over the course of the tests. The deviation from the preceding result was never larger than 0.5 mg/m^3.

The newly developed FC 150 system described above makes it possible to carry out an automatic zero and sample gas check without the use of a multiplexer. Both measuring systems were equipped with this technology and were thus operated for a period of 6 weeks. The results are summarized in the following charts and tables.

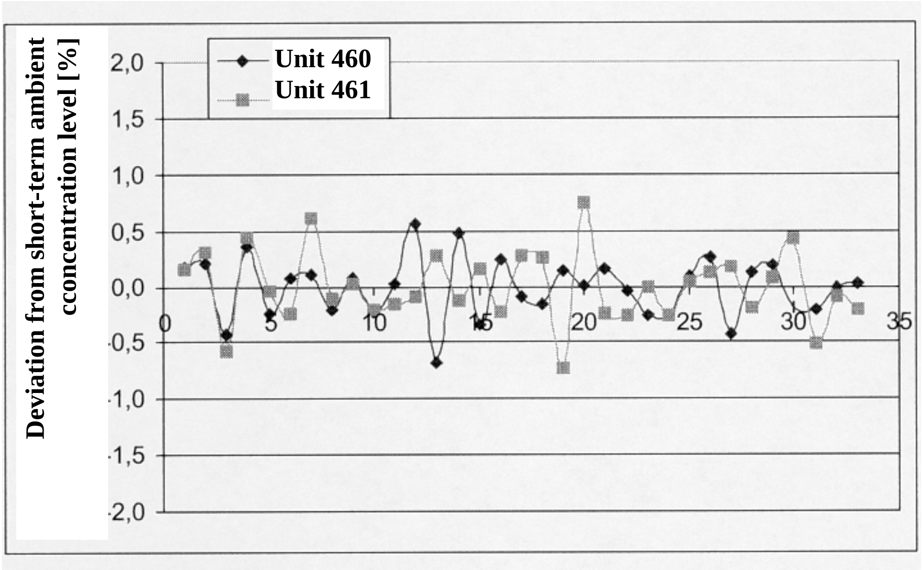

Fig. 20 Zero point variation over time during the field tests

The time-related drift over the maintenance interval is defined by

$$\Delta x_0\,[\%] = \frac{x_{02} - x_{01}}{IW\ 2} \cdot 100\% \leq \pm 10\%$$

where

Δx_0 = average zero drift [%] over time, related to IW 2
x_{01} = zero point at time t_1 (from regression analysis)
x_{02} = zero point at time $t_2 = t_1 + 24$ h (from regression analysis)
IW 2 = 300 $\mu g/m^3$

The average zero point variation within 24 hours observed during the field tests was as follows for the respective systems:

System 1 : - 0.01 % System 2: 0.01 %

The average drift of the zero point measuring signal over the maintenance interval never exceeded the following values:

System 1 : -0.01 % System 2 : 0.01%

Evaluation: The minimum requirement is met

IV.1.1.15 Sensitivity drift

The variation of the system's sensitivity over time should not exceed ± 2% of the value determined in section 1.4.1 or 1.5.1 (Analytical function), respectively, within 24 hours, nor ± 10% of that value throughout the maintenance interval.

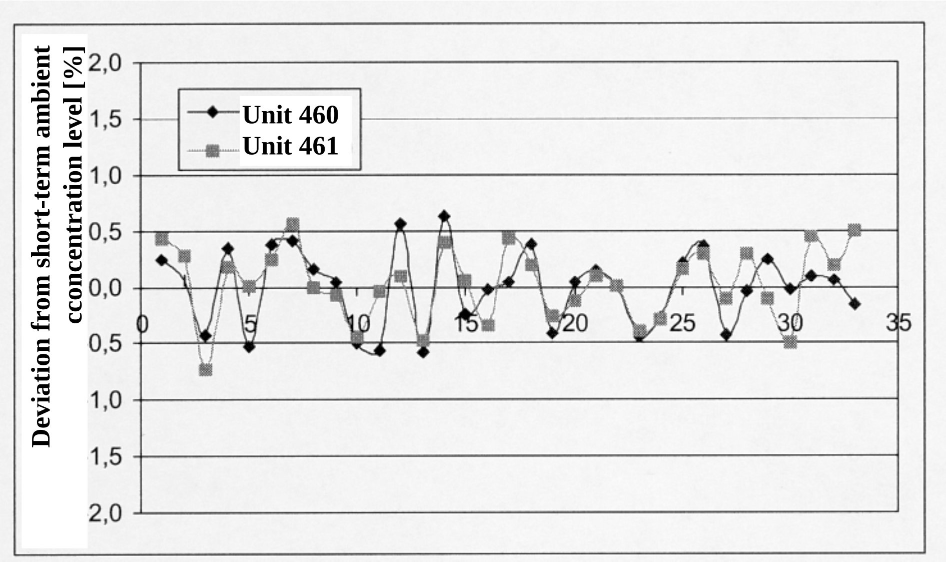

Fig. 21 Reference point variation over time during the field tests

To calculate the variation of the zero point measuring signal over time in percentage terms, the following equation was used:

$$\Delta k\,[\%] = \frac{k_1 - k_2}{k_1} \cdot 100\% \leq \pm 2\%$$

where

Δ_k = average sensitivity drift [%] over time
k_1 = sensitivity at time t_1 (from regression analysis)
k_2 = sensitivity at time t_1 + 24 h (from regression analysis)

The average sensitivity variation within 24 hours observed during the field tests was as follows for the respective systems:

System 1 : - 0.01 % System 2: 0.03 %

The average sensitivity drift over the maintenance interval never exceeded the following values:

System 1 : -0.01 % System 2 : 0.03%

Evaluation: The minimum requirement is met

IV.1.1.16 Maintenance interval

> The maintenance interval of the measuring systems must be determined and specified. The maintenance interval shall be at least 14 days.

The theoretical maintenance interval is determined by

- a change in sensitivity by ± 10%, or
- a change in the zero signal by ± 10% of the IW 2 value

On both systems the sensitivity drift was larger than their zero drift. The theoretical maintenance interval must hence be determined from these characteristics. This is done as follows:

$$W = t_{x01} + t_{x02}$$

where:

W = maintenance interval in days
t_{x01} = start of maintenance interval at sensitivity x_{01}
t_{x02} = end of maintenance interval at sensitivity $x_{02} = x_{01} + 10\%$

The values of x_{01} and x_{02} were determined by regression analysis of the deviations over time observed during the field tests. Due to the low amounts of drift involved, one would obtain the following maintenance intervals:

System 1 (No. 460) : W = 350 days and
System 2 (No. 461) : W = 490 days

In view of these low drift levels we recommend a maintenance interval of three months.

Evaluation: The minimum requirement is met.

IV.1.1.17 Mains voltage

> The influence on the measuring signal of voltage fluctuations in the 220 +15/-20 V range, as habitually encountered in electric mains systems, shall be specified. The measuring system should be protected against short-time electrical power failures by means of a buffer device.

The mains voltage fed to both measuring systems (i.e., the entire system consisting of the analyzer and light source) was reduced from 230 to 190 volts, then raised to 253 volts. At each measuring point the analyzer was fed with zero gas and with a reference point gas in the IW 2 range. The time intervals between mains voltage changes were 15 to 20 minutes. This test was repeated three times.

Neither the zero point nor the sensitivity of the systems were found to be mains voltage related. The analyzer is not buffered against electrical mains failures. A restart software causes the analyzer to revert to measuring operation upon recovery of the mains supply. All previous measuring data and settings are stored in memory and not affected by power failures.

Evaluation: The minimum requirement is met.

IV.1.1.18 Measured value output

> The measuring signals should be provided in the form of a load-independent current output (0 ... 20 mA). The measuring system must have an output for connection to an analog display in its front panel.

The measuring system possesses a number of analog outputs. Among these is a standard analog 0 ... 20 mA measuring signal output. The evaluation and control of the entire measuring system is based on a PC with monitor, where all data supplied by the system can be visualized. This naturally comprises the measured values, which are indicated on this monitor on a default basis.

Evaluation: The minimum requirement is met.

IV.1.2 Measuring systems for stationary use in a monitoring system

IV.1.2.1 System functions

> Key system functions must be supervisable via status signals which can be transmitted telemetrically.

The measuring system can be controlled and monitored by modem in the same way as if the user were standing directly next to the equipment.

Evaluation: The minimum requirement is met.

IV.1.2.2 Mode changeover

> The changeover between measuring and calibration mode should be achievable telemetrically via computer-actuated normally open contacts, as well as by manual release.

The FC 150 testing device can be operated fully telemetrically.

Evaluation: The minimum requirement is met.

IV.1.1.9 Availability

> The availability rate of the measuring systems must be at least 80% but should preferably reach 90%. The availability rate is defined as the ratio between measuring time and time of use. Time of use is the sum total of all measuring times, down times, and maintenance times. The measuring time is the period during which the measuring system supplies signals useful for the measuring purpose.

The availability rate is determined from the ratio between measuring time and time of use.

Table 8: Determination of the availability rate

		System 1 (460)	System 2 (461)
Total operating time	h	2184	2184
System down time	h	55	--
Maintenance, adjustment	h	110	110
Actual operating time	h	2019	2074
Availability	%	92.4	95.0

The downtime of the #460 system can be explained largely by malfunctions in the automatic light path optimization. These were caused by a sub-optimal grid adjustment inside the analyzer. Since this cause was not immediately identified during the tests, the error occurred repeatedly throughout the test program. The #461 system showed no comparable problems.

In the second field test part carried out between 15 December 2000 and 15 January 2001, no down times were observed. Moreover, no intervention was required on the equipment with the exception of the automatic quality assurance steps performed by each system. As a result, the availability rate during this period was close to 100%.

The availability rate was found to be 92.4% and 95%, respectively.

Evaluation: The minimum requirement is met.

IV.1.2.4 Calibration time

> The time required for system calibration should not exceed 5% of the measuring time. The calibration time is deemed to constitute measuring time.

Manual validations conducted with the FC 150 in use show that a total of 30 minutes is necessary per calibration process, including all flushing times. It was found with the automatic calibration unit that at least three measuring cycles at the zero and reference point are required for each constituent. Depending on the analyzer equipment configuration, this process may take between 30 and 45 minutes (4 constituents, each calibrated for zero and reference level).

Evaluation: The minimum requirement is met.

IV.1.3 Measuring systems for mobile use

IV.1.3.1 Setup/run-in times

> The setup and run-in times of the measuring system shall be determined. Functional impairments sustained in transit as a result of the site change shall be described.

The system was not tested in mobile use during these tests.

Evaluation: The minimum requirement is not applicable.

IV.1.4 Measuring systems for gaseous air pollutants

IV.1.4.1 Analytical function

> The suitability test shall comprise a determination by regression computing of the correlation between the measuring signal and the mass concentration of the target substance in the outdoor air, as determined by a means of a reference method, or the mass concentration of the test gases (analytical function).

The analytical function expresses the correlation between the measured value and preset quantities of the target substance. Since the OPSIS system performs an in-situ measurement over long measuring paths, a calibration rig belonging to the system had to be used for these tests. An open-type rig was employed to accommodate flow cells of various lengths, which permitted the use of different concentrations over the measuring range.

The characteristic parameters of the calibrating function

$$y = m * x + b$$

were determined by linear regression. The analytical function is the inverse of the calibrating function, viz.

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

In this expression the gradient *m* of the regression line characterizes the sensitivity of the measuring system while the ordinate segment *b* describes its zero point.

The pre-defined test gas concentrations (x-axis) were assigned to the appropriate analyzer measuring signals (y-axis). The measured values described below were acquired with the test set-up including the FC 150 calibration system. Since only one such system was available, the functions were recorded successively. For this purpose the lightguide of the second system was connected to the receiver of the other measuring system. The resulting characteristics of the two instruments tested are shown in Table 9.

Table 8: Results of the calibrating and analytical function tests

	Calibrating function y = m * x + b		Analytical function x = 1/m * y - b/m	
System No.	m µg/m^3 / µg/m^3	b µg / m^3	1/m µg/m^3 / µg/m	b/m µg / m^3
System 1 (460)	0.983	0.362	1.017	0.368
System 2 (461)	0.982	0.228	1.018	0.232

Linearity

Linearity is deemed to be ensured when the group averages of the measuring signals deviate from the calibrating function by no more than 2% in the range of IW 1 and IW 2.

To validate this linearity, the deviations of the group averages of the individual concentrations from the test gas target values were calculated as follows:

$$\frac{x_1 - x_{target}}{x_{target}} \cdot 100\% \leq \pm 2\%$$

where

x_1 = average concentration of ith concentration group

x_{target} = test gas target concentration

Tables 10 and 11 summarize the linearity deviations in percentage and absolute terms for all test gas concentrations used.

Table 10: Results of the linearity tests – System 1 (No. 460)

System 1 (No. 460)			
Test gas target concentration µg/m^3	Measured concentration µg/m^3	Deviation µg/m^3	 %
0	0.48	0.48	
5.24	5.13	-0.11	-2.1
9.76	9.55	-0.21	-2.2
16.11	15.85	-0.26	-1.6
19.24	18.97	-0.27	-1.4
40.32	40.1	-0.22	-0.5
70.78	70.5	-0.73	-1.0
100.77	99.09	-1.68	-1.7

Table 11: Results of the linearity tests – System 2 (No. 461)

System 2 (No. 461)			
Test gas target concentration	Measured concentration	Deviation	
µg/m³	µg/m³	µg/m³	%
0	-0.60	-0.60	
5.24	5.20	-0.04	-0.8
9.76	9.69	-0.07	-0.7
16.11	15.87	-0.24	-1.5
19.24	19.10	-0.14	-0.7
40.32	40.26	-0.06	-0.2
70.78	69.74	-1.04	-1.5
100.77	99.94	-0.83	-0.8

Linearity evaluation

In both systems the group averages of the measuring signals deviate only by a small margin from the calibrating function at the test gas levels employed. The calibrating functions are therefore of sufficient linearity.

Evaluation: The minimum requirement is met.

IV.1.4.2 Cross-sensitivity

> The interference caused by cross-sensitivity to accompanying substances in the measured gas, in typical atmospheric concentrations, should not exceed ± 6% of the short-time ambient air concentration value (IW 2) in the range of the ambient air concentration levels (IW 1 and IW 2). Compounds to be taken specifically into account in this context are CO_2, H_2O, SO_2, NO, NO_2, H_2S, NH_3, and selected carbohydrates.

The interference due to accompanying substances in the measured gas shall not exceed ± 6% of the IW 2 value.

$$QE = \frac{x_s}{IW\ 2} \cdot 100\% \leq 6\%$$

where

x_s = $x_m - x_0$

x_m = measured value including interference

x_0 = measured value without interference

IW2 = 300 µg/m³ in this case

Interfering constituents should be introduced in the concentrations in which they may actually occur in the atmosphere under unfavourable conditions. Cross-sensitivity tests were conducted for the following substances:

Interfering constituent	Abbreviation	Concentration
Methane	CH_4	0.3 % by volume
Ethane	C_2H_4	500 µg/m³
Toluene	$C_6H_6CH_3$	123 µg/m³
Xylene	C_8H_{10}	184 µg/m³
Phenol	C_6H_5OH	75 µg/m³
Sulphur dioxide	SO_2	805 µg/m³
Carbon monoxide	CO	4100 µg/m³
Carbon dioxide	CO_2	0.3 % by volume
Hydrogen sulphide	H_2S	506 µg/m³
Ozone	O_3	406 µg/m³
Nitrogen monoxide	NO	446 µg/m³
Acetone	C_3H_6O	approx. 1000 µg/m³
Dinitrogen monoxide	N_2O	655 µg/m³
Ammonia	NH_3	253 µg/m³
Formaldehyde	CHO	approx. 2000 µg/m³

The tests were conducted with test gas concentrations of 0 µg/m³ and approx. 10 µg/m³, repeating each measurement three times. For results refer to Tables 12 and 13.

Table 12: Results of the cross-sensitivity tests, OPSIS AR 502Z #460

								Mean		Deviation	
		NP	RP	NP	RP	NP	RP	NP	RP	NP	RP
CO_2	without CS	-0.4	12.1	-0.4	12.3	0.1	11.8	-0.2	12.1		
	with CS	-0.6	12.2	-0.6	11.9	-0.1	11.9	-0.4	12.0	-2.0	-0.6
Methane	without CS	-0.4	12.1	-0.4	12.3	0.1	11.8	-0.2	12.1		
	with CS	-0.6	12.2	-0.6	11.9	-0.1	11.9	-0.4	12.0	-2.0	-0.6
N_2O	without CS	-0.4	11.3	-0.7	11.3	-0.5	12.2	-0.5	11.6		
	with CS	-0.4	12.1	-0.5	11.5	-0.2	12.0	-0.4	11.9	1.7	2.3
Ethane	without CS	-0.4	11.3	-0.7	11.3	-0.5	12.2	-0.5	11.6		
	with CS	-0.4	12.1	-0.5	11.5	-0.2	12.0	-0.4	11.9	1.7	2.3
H_2S	without CS	-0.4	11.6	-0.4	11.8	-0.5	11.9	-0.4	11.8		
	with CS	-0.5	11.4	-0.4	11.9	-0.5	12.0	-0.5	11.8	-0.3	0.0
Toluene	without CS	0.2	9.5	0.1	9.3	0.2	9.3	0.2	9.4		
	with CS	0.2	9.5	0.0	9.5	0.1	9.4	0.1	9.5	-0.7	1.1
Xylene	without CS	0.1	9.4	0.2	9.5	0.2	9.5	0.2	9.5		
	with CS	0.2	9.5	0.1	9.5	0.3	9.3	0.2	9.4	0.3	-0.4
Phenol	without CS	-0.3	11.2	-0.4	11.5	-0.6	12.1	-0.4	11.6		
	with CS	-0.4	11.3	0.4	11.6	-0.6	12.3	-0.2	11.7	2.3	1.1
Ozone	without CS	-0.3	11.6	-0.3	11.2	-0.4	12.1	-0.3	11.6		
	with CS	-0.4	11.4	-0.3	11.2	-0.6	11.8	-0.4	11.5	-1.0	-1.4
NO_2	without CS	-0.4	11.3	-0.4	11.4	-0.8	11.6	-0.5	11.4		
	with CS	-0.4	11.2	-0.3	11.6	-0.6	11.5	-0.5	11.4	1.0	1.0
NO	without CS	-0.3	12.4	-0.3	12.1	-0.6	12.0	-0.4	12.2		
	with CS	-0.3	12.1	-0.2	11.8	-0.4	12.0	-0.3	12.0	1.0	-1.6
CO	without CS	-0.7	11.8	-0.7	12.0	-0.7	11.6	-0.7	11.8		
	with CS	-0.5	11.8	-0.7	11.8	-0.9	11.7	-0.7	11.8	0.0	-0.3
NH_3	without CS	-0.7	11.8	-0.7	12.0	-0.7	11.6	-0.7	11.8		
	with CS	-0.5	11.8	-0.7	11.8	-0.9	11.7	-0.7	11.8	0.0	-0.3
Acetone	without CS	-0.3	12.4	-0.6	12.2	-0.8	12.2	-0.6	12.3		
	with CS	-0.4	11.8	-0.7	11.8	-0.8	12.3	-0.6	12.0	-0.7	-2.4
Formaldehyde	without CS	-0.2	11.9	-0.2	11.7	-0.4	12.2	-0.3	11.9		
	with CS	-0.3	11.7	-0.4	11.7	0.3	12.2	-0.1	11.9	1.3	-0.6
SO_2	without CS	-0.2	11.8	-0.5	11.8	-0.8	11.7	-0.5	11.8		
	with CS	-0.2	11.8	-0.5	11.8	-0.8	11.9	-0.5	11.8	0.0	0.6

Table 13: Results of the cross-sensitivity tests, OPSIS AR 502Z #461

								Mean		Deviation	
		NP	RP	NP	RP	NP	RP	NP	RP	NP	RP
CO_2	without CS	0.1	11.7	-0.1	11.9	0.0	11.9	0.0	11.8		
	with CS	-0.1	11.9	-0.1	12.1	0.1	12.1	0.0	12.0	-0.3	1.7
Methane	without CS	0.1	1.7	-0.1	11.9	0.0	11.9	0.0	11.8		
	with CS	-0.1	11.9	-0.1	12.1	0.1	12.1	0.0	12.0	-0.3	1.7
N_2O	without CS	-0.1	11.7	-0.2	11.7	-0.3	12.0	-0.2	11.8		
	with CS	0.1	11.7	0.4	11.3	-0.2	12.1	0.1	11.7	3.0	-0.8
Ethane	without CS	-0.1	11.7	0.4	11.3	-0.2	12.1	0.1	11.7		
	with CS	0.1	11.7	0.4	11.3	-0.2	12.1	0.1	11.7	3.0	-0.8
H_2S	without CS	0.1	11.8	-0.1	11.8	-0.1	11.8	0.0	11.8		
	with CS	-0.1	11.7	-0.1	11.8	0.0	11.8	-0.1	11.8	-0.3	-0.3
Toluene	without CS	0.2	9.8	0.2	0.6	0.1	9.6	0.2	9.7		
	with CS	0.3	9.6	0.0	9.5	0.2	9.5	0.2	9.5	0.0	-1.4
Xylene	without CS	0.0	9.5	0.1	9.6	0.0	9.5	0.0	9.5		
	with CS	0.1	9.8	0.2	9.5	0.1	9.5	0.1	0.6	1.0	0.7
Phenol	without CS	-0.1	11.2	0.0	11.2	-0.1	11.2	-0.1	11.2		
	with CS	0.1	11.8	0.2	11.3	0.1	11.2	0.1	11.4	2.0	2.1
Ozone	without CS	0.2	11.7	0.0	11.1	0.2	11.3	0.1	11.4		
	with CS	0.2	11.7	0.0	11.2	0.3	11.3	0.2	11.4	0.3	0.3
NO_2	without CS	0.1	11.6	0.0	11.3	0.1	11.2	0.1	11.4		
	with CS	0.2	11.7	0.2	11.6	0.1	11.5	0.2	11.6	1.0	2.1
NO	without CS	0.1	11.8	0.2	11.7	0.2	11.6	0.1	11.7		
	with CS	0.1	11.8	0.1	11.6	0.2	11.6	0.1	11.7	-0.3	-0.3
CO	without CS	0.1	11.6	0.2	11.6	0.1	11.6	0.1	11.6		
	with CS	-0.1	11.6	0.1	11.4	0.1	11.5	0.0	11.5	-1.0	-0.9
NH_3	without CS	0.2	11.7	-0.1	11.8	-0.1	11.4	0.0	11.6		
	with CS	0.3	11.5	-0.1	11.8	0.1	11.2	0.1	11.5	1.0	-1.1
Acetone	without CS	-0.1	11.3	-0.2	11.1	-0.1	11.8	-0.1	11.4		
	with CS	-0.2	11.4	-0.2	11.2	-0.2	11.8	-0.2	11.5	-0.7	0.6
Formaldehyde	without CS	0.2	11.6	-0.4	11.3	-0.1	11.3	-0.1	11.4		
	with CS	0.1	11.5	-0.3	11.4	-0.1	11.3	-0.1	11.4	0.0	0.0
SO_2	without CS	0.1	11.3	0.2	11.5	0.1	11.2	0.1	11.3		
	with CS	0.1	11.2	0.1	11.1	0.2	11.1	0.1	11.1	0.0	-1.8

On the whole, no significant cross-sensitivity of the measuring signal to the relevant accompanying substances could be identified. The influence of water vapour could not be tested in the laboratory. A simulation of moisture was not feasible in the measuring range of interest since no heatable measuring path was available. In the field tests, varying relative air humidities up to 100% (see Fig. 22) had no appreciable effect on the measuring accuracy.

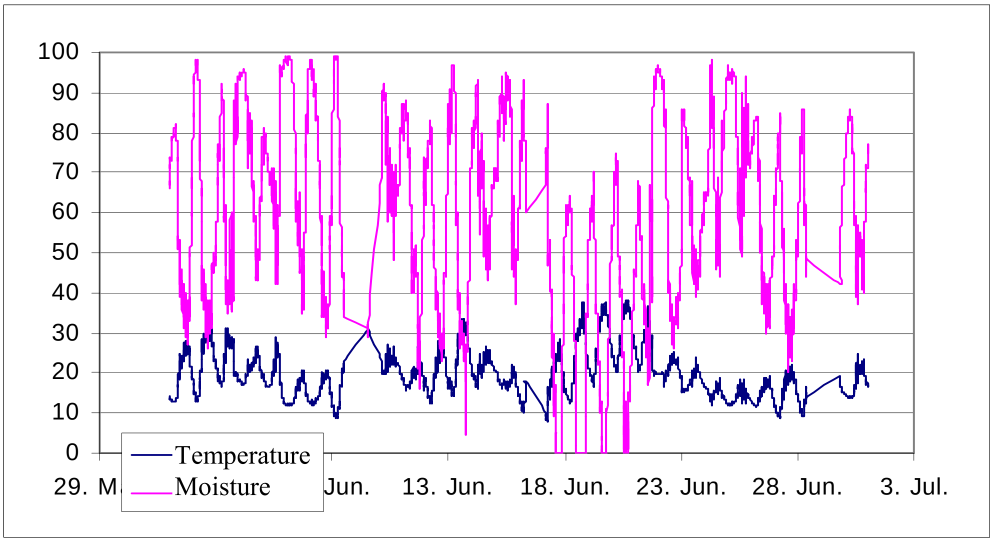

Fig. 22 Weather data (relative air humidity and temperature) at the field test site

Evaluation: The minimum requirement is met.

IV.1.4.3 Half-hour values

The measuring method should permit the formation of half-hour values.

The measuring system is of the multi-constituent type. Where it is used for several constituents, these are determined sequentially. In the present suitability test a total of 4 constituents was activated. Each individual measurement took 30 seconds, i.e., approx. 15 individual measurements lasting 30 seconds each were carried out per half hour under these conditions. A statistically significant half-hour average can thus be determined.

Evaluation: The minimum requirement is met.

IV.1.4.4 Response time

The response time (90% time) of the measuring system shall not exceed 180 seconds.

The measuring system is of the multi-constituent type. Where it is used for several constituents, these are determined sequentially. In the present suitability test a total of 4 constituents was activated. Each individual measurement took 30 seconds, i.e., the cycle time amounted to 120 s. Since the individual constituents are measured in situ, the maximum response time will therefore be 150 s.

Evaluation: The minimum requirement is met.

IV.1.4.5 Electrical power failure

> In the case of a system breakdown or electrical power failure, an uncontrolled release of operating gas and calibration gas must be prevented.

With this measuring system, operating and calibrating cases are released solely from the appropriate gas cylinders during the calibrating cycle. In the case of an electrical power failure the solenoid control valves will close automatically so that any further release of gas will be prevented.

Evaluation: The minimum requirement is met.

V. Recommendations for practical use

The OPSIS system requires the following maintenance steps:

- Visual inspection of the entire system
- System check
- Check of the light level, possibly with cleaning of optical boundary surfaces or re-adjustment of the light path
- Verification of the standard deviations (a reference calibration is necessary if frequent negative standard deviations are observed)
- Reference calibration
- Backup of hard-drive data
- Examination/maintenance of the overall system with re-certification of the test gases employed.

The attached Manual gives detailed instructions on how there steps are to be performed.

VI. Overview of test results

Page*)	Abbreviated title	Test result	Evaluation
12	IV.1 Minimum requirements on continuously operating ambient air concentration measuring systems during suitability testing		
12	IV.1.1 General		
12	IV.1.1.1 Normative conditions	The suitability tests were conducted in compliance with specified requirements. The equipment version / system features were documented.	fulfilled
12	VI.1.1.2 Equipment modifications	The manufacturer was advised in writing that any modification of the system must be indicated to the test institute.	fulfilled
12	IV.1.1.3 Test location	To the required extent, individual portions of the test were conducted both in the laboratory and in the field. For details refer to the appropriate subsections.	fulfilled
13	IV.1.1.4 Field test duration	The endurance test was carried out at a single test location starting 1 April 2000. From this date the measuring systems were operated for a period of approx. 4 months. The systems were again operated for field testing in the months of December 2000 and January 2001.	fulfilled
17	IV.1.1.5 Unauthorized change of settings	The measuring system can be protected by activating various password levels, providing security against unauthorized or inadvertent manipulation. Operating access can be restricted to the necessary levels can be restricted to the different groups of personnel.	fulfilled
18	IV.1.1.6 Live zero point	The analog output of the measuring system is a current signal with 4 .. 20 mA live zero point. Moreover, all data are durably stored on the hard disk integrated into the system and will thus remain available for further digital processing.	fulfilled
18	IV.1.1.7 Detection limit	The tests showed a detection limit of 0.39 $\mu g/m^3$ for System 1 and 0.29 $\mu g/m^3$ for System 2.	fulfilled

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*) refers to the pagination of the original (German-language) document

Page	Abbreviated title	Test result	Evaluation
19	IV 1.1.8 Upper limit of effective measuring range	The measuring range is freely selectable via the software. During the tests we applied concentrations up to 300 µg, as recommended in DIN 33963-1. These produced no limitations in equipment functionality whatsoever. The associated analog output can be freely selected. Irrespective of the measuring range adopted, all recorded values remain available for further analysis on the analyzer's hard disk.	fulfilled
19	IV.1.1.9 Repeatability	For the repeatability test, test gas was applied to both systems in 6 concentrations. This was repeated 15 times. From the double measurements thus obtained, the uncertainty for each concentration class was computed. The repeatability at IW 2 is larger than 10 for each concentration class, except for the class of about 1 µg/m³.	fulfilled
26	IV.1.1.10 Ambient temperature impact on zero point measuring signal	The impact of temperature on the measuring signal was never found to be in excess of ± 1.1% within the specified acceptable temperature range (0 ... 35°C).	fulfilled
27	IV.1.1.11 Ambient temperature impact on sensitivity	The impact of temperature on the measuring signal was never found to be in excess of ± 2.7% within the specified acceptable temperature range (0 ... 35°C).	fulfilled
28	IV.1.1.12 Impact of measured gas temperature on zero point measuring signal	As a long-distance measuring system, the OPSIS instrument performs its measurements in situ. The measured gas is not conditioned in any way whatsoever. It suffices, therefore, to log the measured gas temperature in the OPSIS system itself or in a downstream evaluation unit. This measuring criterion was therefore not separately tested.	not applicable
28	IV.1.1.13 Impact of measured gas temperature on sensitivity	As a long-distance measuring system, the OPSIS instrument performs its measurements in situ. The measured gas is not conditioned in any way whatsoever. It suffices, therefore, to log the measured gas temperature in the OPSIS system itself or in a downstream evaluation unit. This measuring criterion was therefore not separately tested.	not applicable
28	IV.1.1.14 Zero drift	During the field test, the average drift of the zero point over 24 hours amounted to -0.01% for System 1 and 0.01% for System 2. The average time-related drift of the zero point measuring signal over the maintenance interval amounted to a maximum of -0.01% for System 1 and 0.01% for System 2.	fulfilled

Page	Abbreviated title	Test result	Evaluation
29	IV.1.1.15 Sensitivity drift	During the field test, the average time-related change in sensitivity over 24 hours amounted to -0.01% for System 1 and -0.03% for System 2. The average time-related change in sensitivity over the maintenance interval amounted to a maximum of -0.01% for System 1 and 0.03% for System 2.	fulfilled
31	IV.1.1.16 Maintenance interval	The low amounts of drift would give the following theoretical maintenance intervals: System 1 (460): W = 350 days and System 2 (461): W = 490 days In view of these low drift levels we recommend a maintenance interval of three months.	fulfilled
32	IV.1.1.17 Mains voltage	Neither the zero point nor the sensitivity of the systems were found to be mains voltage related. The analyzer is not buffered against electrical mains failures. A restart software causes the analyzer to revert to measuring operation upon recovery of the mains supply. All previous measuring data and settings are stored in memory and not affected by power failures.	fulfilled
25	IV.1.1.18 Measured value output	The measuring system possesses a number of analog outputs. Available among these is a standard analog 0 ... 20 mA measuring signal output. The evaluation and control of the entire measuring system is based on a PC with monitor, where all data supplied by the system can be visualized. This naturally comprises the measured values, which are indicated on this monitor on a default basis.	fulfilled
32	IV.1.2 Measuring systems for stationary use in a monitoring system		
32	IV.1.2.1 System functions	The measuring system can be controlled and monitored by modem in the same way as if the user were standing directly next to the equipment.	fulfilled
33	IV.1.1.2 Mode changeover	The FC 150 testing system can be operated fully telemetrically.	fulfilled
33	IV.1.2.3 Availability	The availability rate was 92.4% and 95%, respectively.	fulfilled

Page	Abbreviated title	Test result	Evaluation
33	IV.1.2.4 Calibration time	Manual validations conducted with the FC 150 in use show that a total of 30 minutes is necessary per calibration process, including all flushing times. It was found with the automatic calibration unit that at least three measuring cycles at the zero and reference point are required for each constituent. Depending on the analyzer equipment configuration, this process may take between 30 and 45 minutes (4 constituents, each calibrated for zero and reference level).	fulfilled
34	IV.1.3 Measuring systems for mobile use		
34	IV.1.3.1 Setup / run-in times	The system was not tested in mobile use during these tests.	not applicable
34	IV.1.4 Measuring systems for gaseous air pollutants		
34	IV.1.4.1 Analytical function	In both systems the group averages of the measuring signals deviate but slightly from the calibrating function. The calibrating functions are therefore of sufficient linearity.	fulfilled
36	IV.1.4.2 Cross-sensitivity	On the whole, no significant cross-sensitivity of the measuring signal to the relevant accompanying substances could be identified. The influence of water vapor could not be tested in the laboratory. A simulation of moisture was not feasible in the measuring range of interest. In the field tests, varying relative air humidities up to 100% had no appreciable effect on the measuring accuracy (refer to Fig. 22).	fulfilled
40	IV.1.4.3 Half-hour values	The measuring system is of the multi-constituent type. Where it is used for several constituents, these are determined sequentially. In the present suitability test a total of 4 constituents was activated. Each individual measurement took 30 seconds, i.e., approx. 15 individual measurements lasting 30 seconds each were carried out per half hour under these conditions. A statistically significant half-hour average can thus be determined.	fulfilled

Page	Abbreviated title	Test result	Evaluation
40	IV.1.4.4 Response time	The measuring system is of the multi-constituent type. Where it is used for several constituents, these are determined sequentially. In the present suitability test a total of 4 constituents was activated. Each individual measurement took 30 seconds, i.e., the cycle time amounted to 120 s. Since the individual constituents are measured in situ, the maximum response time will be 150 s.	fulfilled
41	IV.1.4.5 Electrical power failure	With this measuring system, operating and calibrating cases are released solely from the appropriate gas cylinders during the calibrating cycle. In the case of an electrical power failure the solenoid control valves will close automatically so that any further release of gas will be prevented.	fulfilled

VII. Announcement proposal

In view of the favorable results achieved, the following recommendation for announcement as a suitability-tested measuring device is herewith issued:

Multi-constituent Measuring System AR 502Z with FC 150 Calibration Unit
Benzene

Manufacturer : OPSIS AB, 244 02 Furulund, Sweden

Suitability : path-integrating measurement of benzene in outdoor air in stationary use

Measuring ranges considered in the suitability tests:

0 ... 300 µg/m³

Notes:
- The suitability tests were conducted over a 300m measuring path
- The measuring system was not tested in foggy weather.

Restrictions: The analyzer environment should be air-conditioned where temperatures are expected to exceed 35°C.

Ambient Concentration Control / Air Quality Management Dept.

Bernard Gerchel Dr. Peter Wilbring

Cologne, 26 January 2001
936-wil-hä

VIII. Bibliography

[1] Nationwide Uniform Practices for Ambient Air Concentration Monitoring:

Guidelines for the design and suitability testing of measuring systems for continuous ambient air concentration monitoring, Circular Letter of the Ministry of the Interior of 19 August 1981 - U II 8 - 556, 134/4

[2] Nationwide Uniform Practices for Ambient Air Concentration Monitoring:

Guidelines for the definition of reference methods, the selection of equivalent measuring methods, and the use of calibration methods. Circular letter of the Ministry of the Environment of 9 February 1988 - G I 2 - 556 134/4, page 377 through 378.

[3] Federal States' Committee for Ambient Quality Control - Air / Monitoring Subcommittee

Testing plan for suitability tests of measuring systems for continuous ambient air concentration monitoring (October 1980 edition).

[4] Measurement of organic compounds in outdoor air, DIN 33963-1, of February 1997

IX Appendices

Appendix 1: Detection limit

Appendix 2: Repeatability

Appendix 3: Calibrating function

MANUALS

DATA SHEETS