

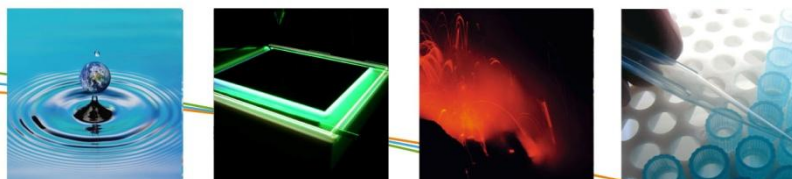
Final report

VALIDATION OF GRADKO DIFFUSIVE SAMPLERS FOR VOLATILE ORGANIC COMPOUNDS

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2012/MRG/R/026

January 2012



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SUMMARY

Within this project the performance of the Gradko modular diffusive sampler for Volatile Organic Compounds has been evaluated under prescribed laboratory and field conditions.

The uptake rate of the Gradko sampler was calculated from a series of laboratory validation experiments designed as prescribed in the European Standard EN 13528-2:2002: 21 ml/min for Benzene, 18 ml/min for Toluene and 16 ml/min for m-Xylene.

This European standard also specifies performance requirements for desorption efficiency, two weeks' storage stability, sampler integrity and blank value. These criteria were met for the Gradko diffusive sampler, with Benzene, Toluene and m-Xylene as target analytes.

On the same occasion, the possible effects of environmental factors on the sampler performance were assessed: air velocity (in the range of 0.15 to 0.80 m/s), sampler orientation, analyte concentration, exposure time and the presence of interferents. From the laboratory results, these factor effects were observed to be negligible.

The shelf life of the Gradko sampler is minimum three months.

In earlier experiments (2002 - 2003), no back diffusion was observed for the Gradko diffusive sampler.

The relative expanded measurement uncertainty, calculated from the field comparison of the Gradko diffusive samplers to the pumped activated charcoal tubes (as a reference method), is 15% for Benzene, 9.7% for Toluene and 17% for m,p-Xylene.

These uncertainties apply to a measurement for exposures from 2 to 4 weeks and fulfil the data quality objectives of EU directive 2008/50/EC for fixed and indicative measurements of respectively 25% and 30%.

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CHAPTER 1 INTRODUCTION

Within this project the performance of the Gradko modular diffusive sampler for Volatile Organic Compounds is studied.

In a first stage laboratory validation tests at controlled conditions are performed.

In a second stage samplers are compared to the reference method in field conditions.

The laboratory validation results are reported in CHAPTER 2, the field validation results in CHAPTER 3.

CHAPTER 2 LABORATORY VALIDATION

Dynamic gas phase calibration mixtures of Volatile Organic compounds in air are generated using the capillary dosage technique.

The true concentration of a pollutant in the test atmosphere is calculated from:

- The amount of pollutant emitted into the carrier gas (in $\mu\text{g}/\text{min}$, obtained through continuous gravimetric measurements),
- The volumetric carrier gas flow (in l/min).

A humidified air flow is added. Both flows are mass flow controlled and determined using a primary volume flow meter.

The atmosphere is fed into a glass exposure chamber with controlled conditions of temperature, relative humidity and wind speed.

The calculated atmosphere concentration - traceable to national standards - is verified by a reference method, the pumped activated charcoal tube method.

This experimentally determined value is within $\pm 10\%$ of the calculated value.

The VOC concentrations at the inlet and outlet of the chamber are determined using Radiello type diffusive samplers (with solvent desorbable activated charcoal) exposed together with the test samplers, as an independent sampling method.

The difference between the outlet and inlet concentration is less than 5%.

Temperature and relative humidity are recorded continuously.

Wind speed is calculated from the internal diameter of the exposure chamber and the flow through the chamber.

The analysis of test samplers, as well as activated charcoal tubes and Radiello samplers is accomplished by solvent desorption with Carbon Disulphide and quantification of VOCs via gas chromatography with mass spectrometer detector. At each occasion, the ISO-17025 accredited analytical method MIM-GA-012 is used.

Laboratory validation of the Gradko diffusive sampler for the determination of VOCs in ambient air is performed according to EN 13528-2 (2002) "Diffusive samplers for the determination of concentrations of gases and vapours- Requirements and test methods - Part 2: Specific requirements and test methods" (cf. Table 1).

An overview of the experiments performed within this validation study is given in Table 2.

Table 1: Summary of the EN 13528-2 evaluation protocol

| Characteristic | Experimental Design | Interpretation of Results |
|--------------------------|--|---|
| 1. Desorption efficiency | Conduct the determination at loadings corresponding to exposure concentrations at e.g. 0.6 , 1 and 1.5 x the limit value (LV) and exposure times appropriate for the practical application of the sampler e.g. 1, 2 and 4 weeks. | The desorption efficiency shall be ≥ 0.75 with repeatability standard deviation ≤ 0.1 |
| 2. Back diffusion | Expose 2 sets of test samplers (at least six replicates) to a calibration gas mixture (20 °C, 50 % RH): <ul style="list-style-type: none"> One set: intermediate concentration and exposure time (1 LV, 2 weeks) Second set: exposure regime should cycle every 24 hours, i.e. 12 hours at 2 times the intermediate concentration and 12 hours in clean air, and this for the total exposure time. | - |
| 3. Nominal uptake rate | Expose samplers in a test atmosphere at intermediate concentration and exposure time (1 LV, 2 weeks), 20 °C, 50 % RH, wind speed see 4. | - |
| 4. Factor effects | <p><u>Factor</u></p> <p>Air velocity: 0.1 - 2.0 m/s</p> <p>Sampler orientation: parallel and perpendicular to air flow</p> <p>Analyte concentration: 0.6 and 2 LV</p> <p>Exposure time: typically 1 and 4 weeks</p> <p>Relative humidity: 20 and 80 %</p> <p>Temperature: 10 and 30 °C</p> <p>Interferent: presence, absence</p> | |
| 5. Storage stability | Expose 2 sets of samplers (6 per set) at 80 % RH, 20 °C, and 1 LV for the appropriate time. Analyze first set within one day, second set after 2 weeks storage at room temperature, or as otherwise directed by the manufacturer. | The difference between means of stored sampler sets and set analyzed within one week shall be $\leq 10\%$ |
| 6. Shelf life | Observe the test sampler throughout evaluation at the maximum storage temperature specified by the manufacturer. | Note shelf storage time at which changes (e.g. in blank values) begin to occur. |

-
- | | | |
|--|---|--|
| 7. Sampler integrity (cf. Sampler leak test) | Expose sealed (at least 6 replicates) in an atmosphere of test analyte corresponding to 10 LV for an intermediate averaging time. | Mass above the blank value shall be $\leq 1/3$ of the calculated mass uptake rate by the sampler for an exposure at the lowest concentration and for a typical exposure time (e.g. 0.6 LV - 1 week). |
| 8. Blank value | Analyse 6 unexposed samplers to determine the mean blank value of analyte and the standard deviation of the blank value. | The blank value shall be $\leq 1/3$ of the calculated mass uptake rate by the sampler for an exposure at the lowest concentration and for a typical exposure time (e.g. 0.6 LV - 1 week). |
| 9. Accuracy and precision: behaviour in the field | Consider problems not predictable from laboratory experiments. Expose samplers and independent method samplers to the same environment. | Calculate bias and precision. Compare with laboratory results. |

Table 2: Exposure test scheme for selected Volatile Organic compounds following EN 13528-2

| Benzene concentration ($\mu\text{g}/\text{m}^3$, at 20 °C) | Exposure time (days) | Benzene ($\mu\text{g}/\text{m}^3 \cdot \text{min}$) | Number of exposed samplers | Temperature (°C) | Relative humidity (%) | Wind speed (m/s) | Additional analytes |
|--|----------------------|---|---|------------------|-----------------------|------------------|-----------------------------------|
| Blank value | | | | | | | |
| n/a | n/a | n/a | 6 | n/a | n/a | n/a | n/a |
| Sampler integrity | | | | | | | |
| 700 | 1 | 1008000 | 6 | ± 20 | ± 50 | ± 0.3 | T, m-X |
| Nominal uptake rate | | | | | | | |
| 5 | 14 | 100800 | 12 | ± 20 | ± 50 | ± 0.3 | T, m-X |
| Factor effects: Sampler orientation, analyte concentration, exposure time | | | | | | | |
| 5 | 7 | 50400 | 3 / 3 | ± 20 | ± 50 | ± 0.3 | T, m-X |
| | 14 | 100800 | 3 | | | | |
| | 28 | 201600 | 6 | | | | |
| 10 | 7 | 100800 | 6 3 + 3 (orientation) | ± 20 | ± 50 | ± 0.3 | T, m-X |
| 10 | 1 | 14400 | 6 | ± 20 | ± 50 | ± 0.3 | T, m-X |
| Shelf life | | | | | | | |
| 10 | 7 | 100800 | 6 | ± 20 | ± 50 | ± 0.3 | T, m-X |
| Factor effects: Presence of interfering VOCs | | | | | | | |
| 7.5 | 4 | 43200 | 12 | ± 20 | ± 50 | ± 0.3 | T, m-X and 10 additional VOCs (*) |
| Desorption efficiency | | | | | | | |
| 2.5 – 10 | 7 – 28 | 75500 - 600000 | 12 + 6 (amount of extraction solution) | n/a | n/a | n/a | T, m-X and 10 additional VOCs (*) |

(*) Toluene (T), m-Xylene (m-X), o-Xylene, Ethylbenzene, Styrene, 1,2,4-Trimethylbenzene, 1,4-Dichlorobenzene, Trichloroethylene, Tetrachloroethylene, Methyl t-butyl ether, Ethyl acetate and n-Butyl acetate

2.1. DESORPTION EFFICIENCY

Experimental design:

Analytical recoveries are determined by the phase equilibrium method.

Millilitre amounts (2 and 3 ml) of two analytical standards (containing 13 analytes in carbon disulphide) are added to unused blank samplers.

Spiked samplers are shaken for 30 minutes.

Both analytical standards (with analyte concentration 0.4 and 8 µg /g CS₂) and the sample solutions are analyzed by GC-MS.

Number of samplers: 12 spiked samplers (6 at each loading);
(1) by adding 3 ml aliquots of an analytical standard

6 spiked samplers (3 at each loading)
(2) by adding 2 ml aliquots of an analytical standard

Results:

Analytical recovery for benzene

Table 3: Analytical recovery of benzene from the passive sampler with Carbon disulphide

| Spike (µg) | Benzene (µg/m ³ . min) | Recovery (%) | Mean | RSD |
|---------------|--------------------------------------|--|------|-------|
| 1.6 (2) | ± 75000 | 0.99 1.00 0.99 | 0.99 | 0.3 % |
| 2.6 (1) | ± 130000 | 1.00 0.99 1.00 0.99 0.99 | 1.00 | 0.6 % |
| 7.1 (2) | ± 350000 | 1.02 1.01 1.01 | 1.01 | 1.0 % |
| 12 (1) | ± 600000 | 1.00 1.00 1.02 1.01 1.03 1.01 | 1.01 | 1.0 % |

The overall desorption efficiency for benzene from the diffusive sampler is 100 % (1.2 % RSD).

Results (continued):

Analytical recovery for additional analytes

The extraction efficiency results for the additional analytes from dry passive samplers are provided in Table 4.

Table 4: Analytical recovery of selected Volatile Organic Compounds from the passive sampler with Carbon disulphide

| Analyte | Spike (μg) | Mean recovery | RSD |
|------------------------|----------------------------|------------------|------|
| Methyl t-butyl ether | 1.6 - 13 | 0.98 | 2.5% |
| Trichloroethylene | 1.6 - 12 | 1.01 | 1.8% |
| Toluene | 1.6 - 12 | 1.00 | 1.6% |
| Tetrachloroethylene | 1.6 - 12 | 1.01 | 1.8% |
| n-Butyl acetate | 1.7 - 14 | 1.02 | 1.5% |
| Ethylbenzene | 1.5 - 11 | 1.02 | 2.3% |
| m-, p-Xylene | 1.5 - 11 | 1.01 | 2.1% |
| o-Xylene | 1.5 - 11 | 0.96 | 2.7% |
| Styrene | 1.6 - 12 | 0.39 | 39 % |
| 1,2,4-Trimethylbenzene | 1.6 - 11 | 1.02 | 1.8% |
| 1,4-Dichlorobenzene | 1.6 - 11 | 0.92 | 2.6% |
| Ethyl acetate | 1.8 - 15 | 0.91 | 9.1% |

The desorption efficiency values of styrene are less than 75 % and are concentration dependent:

- 20 % (21 % RSD) if 1.6 μg ,
- 28 % (7.8 % RSD) if 2.6 μg ,
- 41 % (2.9 % RSD) if 7.0 μg ,
- 57 % (1.3% RSD) if 12 μg spiked.

Also for Ethyl acetate, a small loading dependency is observed:

- 82 % (0.3 % RSD) if 1.8 μg ,
- 84 % (2.4 % RSD) if 3.0 μg ,
- 98 % (1.6 % RSD) if 8.6 μg ,
- 100 % (1.3 % RSD) if 15 μg applied.

Conclusion:

Desorption efficiencies are close to 100 % for the majority of volatile organic compounds studied.

The desorption efficiency values for Ethyl acetate (> the 75 % EN 13528-2 acceptance criterion) are concentration dependent, but still practicable (< 3 % RSD).

It is advisable to determine a Styrene desorption efficiency curve for each batch of samplers.

No dependency of desorption efficiency on the desorption volume (2 ml versus 3 ml) is observed, offering a way of achieving higher method sensitivity.

2.2. BACK DIFFUSION

Experimental design:

This experiment was part of the validation of the prototype basic model diffusive sampler (experimented in 2002-2003, cf. VITO-report with reference 2004/MIM/R/024, experiment 11).

The effect of a period of exposure of test samplers to zero concentration following a period of exposure to Benzene (in presence of Toluene, Ethylbenzene and m-Xylene) is examined.

Two sets of samplers are exposed to the test atmosphere for four hours. Hereupon, one set is removed from the chamber; the remaining set is exposed to nitrogen for a further four hours.

Both sets of test samplers are analyzed via GC-MS.

Results:

Sampler analysis: % Difference between means of both sampler sets is - 3% for benzene, -2% for toluene, 0.5% for Ethyl benzene and 2% for m-Xylene

Table 5: Results back diffusion test with basic model

| Exposure to a standard atmosphere | Exposure to zero concentration | Benzene | Toluene | Ethyl benzene | m-Xylene |
|--|--------------------------------|---------|---------|---------------|----------|
| Adsorbed quantity ($\mu\text{g}/\text{sampler}$) | | | | | |
| 240 min | - | 8.64 | 86.7 | 177 | 249 |
| 240 min | 240 min | 8.39 | 84.6 | 178 | 255 |

Conclusion:

No significant effect of exposure to zero concentration on the sampler performance is observed.

2.3. BLANK VALUE

Experimental design:

According to EN 13528-2 guidelines, the blank value shall be less than one-third of the calculated mass uptake by the sampler for an exposure at the lowest concentration and for a typical averaging time.

If test samplers are exposed to 0.6LV for 1 week, the maximum permitted blank value is 0.22 µg for benzene, 0.58 µg for Toluene and 0.12 µg for m-Xylene.

Fictive limit values are established for Toluene and m-Xylene based on ratios in relation to benzene, as observed in field experiments.

As a part of the experiments performed within this validation study, blank samplers are often analyzed via GC-MS.

Results:

Table 6 shows typical blank values for each of the experimented compounds.

Table 6: Typical blank values for the Gradko sampler within laboratory and preliminary field validation experiments

| µg/sampler | Benzene | Toluene | m-Xylene |
|----------------------|-----------------------|-----------------------|-----------------------|
| EN 13528-2 criterion | 0.22 | 0.58 | 0.12 |
| Blank 1 | 0.069 | 0.168 | 0.091 |
| Blank 2 | <u>(0.303)</u> | 0.252 | <u>(0.143)</u> |
| Blank 3 | 0.029 | 0.050 | 0.038 |
| Blank 4 | 0.038 | 0.092 | 0.069 |
| Blank 5 | 0.040 | 0.124 | 0.071 |
| Blank 6 | 0.037 | 0.116 | 0.059 |
| Blank 7 | 0.039 | <u>(0.623)</u> | <u>(0.122)</u> |
| Blank 8 | 0.037 | 0.116 | 0.059 |
| Blank 9 | 0.034 | 0.125 | 0.054 |
| Blank 10 | 0.038 | 0.073 | 0.073 |
| Blank 11 | 0.051 | <u>(1.248)</u> | 0.115 |
| Blank 12 | 0.055 | <u>(1.126)</u> | <u>(0.127)</u> |
| Blank 13 | 0.041 | 0.384 | 0.072 |
| Mean | 0.042 | 0.150 | 0.070 |
| SD | 0.011 | 0.099 | 0.021 |

The calculated blank value for benzene, 0.042 µg/sampler, represents only 4 % of the minimum sampler load experimented during the laboratory validation.

For toluene this value is 5 %, for m-Xylene 14 %.

All sampler results are corrected for these calculated blank values.

Conclusion:

In the context of this laboratory validation, the blank value of the sampler for benzene, toluene and m-Xylene is acceptable (< the EN 13528-2 criterion).

The reproducibility of the blank results can be improved, especially for toluene where some outlying results were observed.

In situations where rural background sites are sampled with the Gradko basic model sampler, and thus the sampler load is low, the blank value of the sampler is recommended to be maximum 0.1 µg and reproducible for each of the analytes. It is advised to establish this value as the QA/QC criterion for the sampler blank, in these cases.

2.4. SAMPLER INTEGRITY

Experimental design:

Unopened samplers are exposed to a standard atmosphere of Benzene (in presence of Toluene and m-Xylene), corresponding to ten times the limit value for two weeks.

To determine the sampler integrity, the set of exposed (unopened) samplers is analyzed via GC-MS.

| | |
|--------------------------------------|---|
| Number of samplers: | 6 sealed (unopened) samplers |
| Calculated atmosphere concentration: | 244 $\mu\text{g}/\text{m}^3$ Benzene (cf. 10 LV for 2 weeks exposure time) |
| Exposure time: | 4485 min (\pm 3 days) |
| Factor effects: | \pm 20 °C and \pm 50 % RH, \pm 0.3 m/s, 729 $\mu\text{g}/\text{m}^3$ Toluene, 158 $\mu\text{g}/\text{m}^3$ m-Xylene |

Results:

| | |
|--|---|
| Independent sampling method: Active samplers: | 237 $\mu\text{g}/\text{m}^3$ Benzene, 723 $\mu\text{g}/\text{m}^3$ Toluene, 155 $\mu\text{g}/\text{m}^3$ m-Xylene |
| Sampler analysis: | No additional Benzene, Toluene and m-Xylene (above its blank value) is detected in any sampler. (estimated LOQ is 0.1 $\mu\text{g}/\text{sampler}$) |

Conclusion:

The leak tightness of the passive sampler fulfils the EN 13528-2 criterion.

The sampler design ensures adequate leak tightness, critical to maintaining sample integrity and preventing contamination of a clean sampling device.

2.5. FACTORIAL RESULTS: AIR VELOCITY

Experimental design:

This experiment was part of the validation of the prototype basic model diffusive sampler (experimented in 2002-2003, cf. VITO-report with reference 2004/MIM/R/024, experiment 19).

Results:

Table 7: Effect of air velocity on the performance of the prototype basic model diffusive sampler

| | Air velocity (m/s) | | | | Effect of increased air velocity |
|---------------|-----------------------|------------|----------------------|------------|--|
| | 0.22 | | 0.42 | | |
| | Average peak area | RSD (%) | Average peak area | RSD (%) | |
| Benzene | 1 291 607 | 3.1 | 1 400 278 | 2.3 | + 8% |
| Toluene | 12 030 629 | 3.6 | 13 049 653 | 2.7 | + 8% |
| Ethyl benzene | 25 471 870 | 4.0 | 27 752 249 | 3.4 | + 9% |
| m-Xylene | 24 093 364 | 4.3 | 26 317 231 | 3.6 | + 9% |

Conclusion:

Based on these tests, no substantial effect (above $\pm 10\%$) of air velocity on the sampler performance is expected in the range of 0.15 to 0.80 m/s.

The influence of air velocity on the sampler performance will be further investigated in field trials.

2.6. FACTORIAL RESULTS: SAMPLER ORIENTATION

Experimental design:

Test samplers are exposed to a standard atmosphere of Benzene (in presence of Toluene and m-Xylene), corresponding to two times the limit value for one week.

For one set of samplers the orientation shall be the position that offers the minimum resistance to the air flow; for the other set the orientation shall be the position that offers the maximum resistance to the air flow.

Both sets of test samplers are analyzed via GC-MS.

| | |
|--------------------------------------|---|
| Number of samplers: | 9 samplers parallel to the air flow, 3 samplers perpendicular to the air flow |
| Calculated atmosphere concentration: | 10.9 $\mu\text{g}/\text{m}^3$ Benzene (cf. 2 LV for 1 week exposure time) |
| Exposure time: | 8348 min (\pm 6 days) |
| Factor effects: | 21.5 °C and 46.8 % RH, \pm 0.3 m/s, 32.6 $\mu\text{g}/\text{m}^3$ Toluene, 7.16 $\mu\text{g}/\text{m}^3$ m-Xylene |

Results:

| | |
|-----------------------------------|---|
| Independent sampling method: | |
| Active samplers: | 11.1 $\mu\text{g}/\text{m}^3$ Benzene, 32.8 $\mu\text{g}/\text{m}^3$ Toluene, 6.84 $\mu\text{g}/\text{m}^3$ m-Xylene |
| Radiello type diffusive samplers: | 11.7 $\mu\text{g}/\text{m}^3$ Benzene, 33.1 $\mu\text{g}/\text{m}^3$ Toluene, 6.60 $\mu\text{g}/\text{m}^3$ m-Xylene |
| Sampler analysis: | % Difference between means of both sampler sets is 1.7 % for Benzene, 2.1 % for Toluene and 4.0 % for m-Xylene |

Table 8: Effect of sampler orientation on sampler performance

| $\mu\text{g}/\text{sampler}$ | Parallel to the air flow | | | Perpendicular to the air flow | | |
|------------------------------|--------------------------|------|-------|-------------------------------|------|-------|
| | Mean | SD | RSD | Mean | SD | RSD |
| Benzene | 1.94 | 0.09 | 4.5 % | 1.98 | 0.12 | 6.2 % |
| Toluene | 4.95 | 0.21 | 4.2 % | 5.05 | 0.31 | 6.1 % |
| m-Xylene | 0.99 | 0.04 | 3.7 % | 1.03 | 0.06 | 5.9 % |

Conclusion:

The orientation of the sampler with respect to the direction of air flow is not critical.

2.7. FACTORIAL RESULTS: EXPOSURE TIME

Experimental design:

Test samplers are exposed for four consecutive weeks to a standard atmosphere of Benzene (in presence of Toluene and m-Xylene), corresponding to the limit value.

Sampling periods range from 1 to 4 weeks.

Passive samplers are collected (and replaced with new ones) during each sampling period: four sets of one week-samplers, two sets of two weeks-samplers and one set of four weeks-samplers.

Each set of samplers are analyzed via GC-MS.

| | |
|--------------------------------------|---|
| Number of samplers: | Samplers in a set of three replicates per time period |
| Calculated atmosphere concentration: | 4.66 $\mu\text{g}/\text{m}^3$ Benzene (cf. 1 LV for 1 - 4 weeks exposure time) |
| Exposure time: | 1, 2 and 4 weeks |
| Factor effects: | 22.2 °C and 47.1 % RH, ± 0.3 m/s, 14.0 $\mu\text{g}/\text{m}^3$ Toluene, 3.06 $\mu\text{g}/\text{m}^3$ m-Xylene |

Results:

| | |
|--|---|
| Independent sampling method: Active samplers: | 4.63 $\mu\text{g}/\text{m}^3$ Benzene, 12.7 $\mu\text{g}/\text{m}^3$ Toluene, 2.80 $\mu\text{g}/\text{m}^3$ m-Xylene |
| Radiello type diffusive samplers: | 4.75 $\mu\text{g}/\text{m}^3$ Benzene, 12.9 $\mu\text{g}/\text{m}^3$ Toluene, 2.89 $\mu\text{g}/\text{m}^3$ m-Xylene |

Sampler analysis:

Figure 1 shows the results of the linear regression analysis for the determination of the benzene uptake rate. The regression line is forced through the origin and is calculated for each sampling period (1 week, 2 and 4 weeks).

The uptake rate found is 21.9 ml/min.

The determination coefficient of $R^2 = 0.9995$ underlines that there is no dependence of the Benzene uptake rate on the exposure time.

Similar results are obtained for Toluene and m-Xylene.

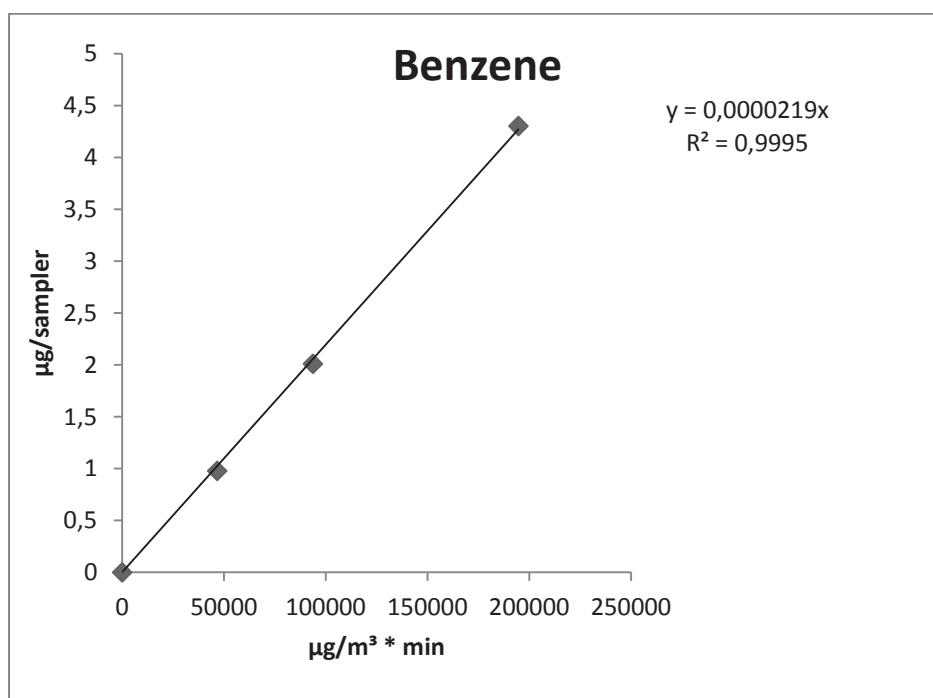


Figure 1: Effect of exposure time on sampler performance

Conclusion:

There is no effect of exposure time on the uptake rate of the passive sampler.

2.8. FACTORIAL RESULTS: EXPOSURE TIME AND CONCENTRATION (AND SHELF LIFE)

Experimental design:

A series of experiments are conducted:

- To determine the nominal uptake rate for Benzene, Toluene and m-Xylene and
- Its relationship with exposure time and concentration;
- To check the shelf life of the sampler 3 months upon manufacturing.

Factor effects:

± 20 °C (with t_{\min} 21,4 °C and t_{\max} 23,1 °C),
 ± 50 % RH (with RH_{\min} 38.5% and RH_{\max} 47.1%),
 ± 0.3 m/s.

Results:

From the laboratory experiments, overall uptake rates (at 20 °C) are calculated as slopes of the observed mass of analytes on the sampler ($\mu\text{g}/\text{sampler}$) versus the load of exposed samplers in $\mu\text{g}/\text{m}^3 \cdot 10^{-6} \cdot \text{min}$, using linear regression:

- 21 ml/min for Benzene,
- 18 ml/min for Toluene and
- 16 ml/min for m-Xylene.

No clear effect of concentration level/exposure time on the uptake rate for Benzene, Toluene and m-Xylene is observed ($R^2 > 0.97$).

As an example the linear regression curve for Benzene (involving 81 samplers) is shown in figure 2.

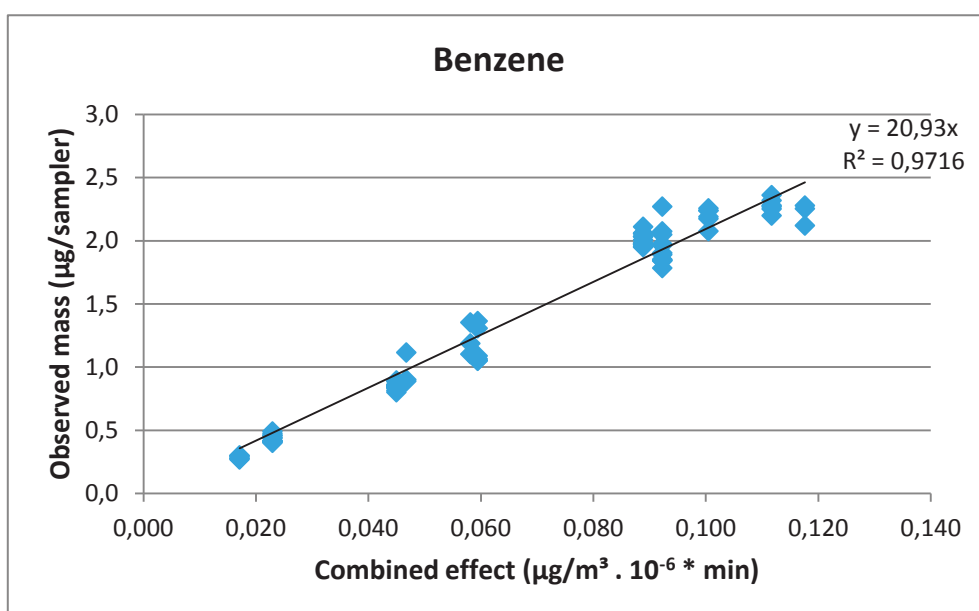


Figure 2: Determination of the Benzene uptake rate for the Gradko sampler under laboratory conditions

The nominal uptake is 20 ml/min for Benzene, 17 ml/min for Toluene and 16 ml/min for m-Xylene (at 20 °C).

Conclusion:

No dependency of the uptake rate on the exposure time and concentration is observed.

The validity of the overall uptake rate for Benzene, Toluene and m-Xylene - **21**, **18** and **16** ml/min respectively, at 20 °C - will be checked under field conditions.

The shelf life of the sampler is minimum 3 months. Over this period of time, no increased blank values were observed.

2.9. FACTORIAL RESULTS: INTERFERENTS

Experimental design:

Test samplers are exposed simultaneously to the pollutants of interest and co-pollutants that are likely to be encountered in the practical use of the passive sampler:

- Benzene, Toluene and m-Xylene,
- o-Xylene, Ethylbenzene, Styrene, 1,2,4-Trimethylbenzene, 1,4-Dichlorobenzene, Trichloroethylene, Tetrachloroethylene, Methyl t-butyl ether, Ethyl acetate and n-Butyl acetate.

Test samplers are analyzed via GC-MS.

| | |
|--------------------------------------|---|
| Number of samplers: | 12 samplers |
| Calculated atmosphere concentration: | 7.81 $\mu\text{g}/\text{m}^3$ Benzene (cf. 0.5 LV for 2 weeks exposure time) |
| Exposure time: | 5760 min (4 days) |
| Factor effects: | 23.1 °C and 49.9 % RH, ± 0.3 m/s, 7.18 $\mu\text{g}/\text{m}^3$ Toluene, 5.35 $\mu\text{g}/\text{m}^3$ m-Xylene, 5 - 8 $\mu\text{g}/\text{m}^3$ of each co-pollutant |

Results:

| | |
|-------------------|--|
| Sampler analysis: | No significant loss in recovery is observed, 9.4 % for Benzene and 3.3 % for m-Xylene; for Toluene a positive bias of 0.8 % is observed. |
|-------------------|--|

Conclusion:

The ability of the Gradko diffusive sampler to collect Benzene, Toluene and m-Xylene when other potential interferences are present is confirmed.

U_{ref} values (at 20 °C) for the co-pollutants are:

- 14 ml/min for Tetrachloroethylene, n-Butyl acetate and 1,4-Dichlorobenzene;
- 15 ml/min for Methyl t-butyl ether, Trichloroethylene, Ethylbenzene and o-Xylene;
- 19 ml/min for 1,2,4-Trimethylbenzene.

These results should be confirmed in additional laboratory and/or field experiments.

CHAPTER 3 FIELD VALIDATION

Preliminary field experiments are designed to assess the storage stability of target analytes in different matrices if adsorbed on Gradko samplers.

The appropriateness of the dedicated Gradko protective shelter for outdoor VOC measurements is also appraised.

This study evaluates the performance of the Gradko sampler in the field by comparing integrated diffusive sampling concentrations from Gradko samplers with measurement results from the following methods:

- A diffusive sampling method involving the Radiello type sampler (RAD);
- The pumped activated charcoal tube method (AC);
- Continuous monitoring by a BTEX-analyzer at a monitoring site nearby (VMM).

The comparison is made at two monitoring stations of the telemetric network of the Flemish Environment Agency (VMM), Laakdal (a rural background monitoring station) and Zelzate (an industrial monitoring station).

Both passive (Gradko and RAD) and active (AC) samplers are collected and replaced at the same time during five sampling periods from October 28 to November 29, 2011.

In Laakdal, the field campaign includes two measuring periods of 2 weeks (week 1 - 2, week 3 - 4) and one of 4 weeks (week 1 - 4) for evaluation of the sampling duration.

In Zelzate, solely two-weekly measurements are conducted (week 1 - 2 and week 3 - 4).

Data from the VMM analyzers are averaged over these exact sampling periods.

3.1. STORAGE STABILITY OF EXPOSED SAMPLERS

Experimental design:

Storage samples for Volatile Organic Compounds are prepared by collecting samples from ambient air during a field trial in a cycle shed at Vito, Mol.

Eighteen storage samples are prepared. Six of the samples are analyzed immediately.

The remaining twelve samples are divided in two sets:

- One set is stored at reduced temperature (4 °C);
- the other set is stored at room temperature.

Three samples from each set are analyzed via GC-MS weekly for two weeks.

| | |
|--------------------------------------|--|
| Number of samplers: | Samplers in a set of three replicates per storage condition |
| Calculated atmosphere concentration: | 0.41 µg/m ³ Benzene (at 20 °C) (cf. 0.1 LV for 2 weeks exposure time) |
| Exposure time: | 19855 min (± 2 weeks) |
| Factor effects: | 16.4 °C (with t_{\min} 5.4 °C and t_{\max} 29.4 °C) 55.4 % RH, 0.1 m/s, 1.20 µg/m ³ Toluene, 0.53 µg/m ³ m-Xylene |

Results:

Independent sampling method:

Active samplers: 0.41 µg/m³ Benzene ,
1.20 µg/m³ Toluene, 0.53 µg/m³ m-Xylene

Sampler analysis:

The storage stability results show that the difference between means of stored sampler sets (cf. day 7 and 14) and the set analyzed at day 0 is less than 10 %, both at room temperature and 4 °C.

Table 9: Storage test for Benzene, Toluene and m-Xylene on passive samplers from preliminary field experiments

| $\mu\text{g}/\text{sampler}$ (Mean) | Ambient storage | | | Refrigerated storage | | |
|--|-----------------|---------|----------|----------------------|---------|----------|
| | Benzene | Toluene | m-Xylene | Benzene | Toluene | m-Xylene |
| Day 0 | 0.17 | 0.42 | 0.20 | 0.17 | 0.42 | 0.20 |
| Day 7 | 0.17 | 0.43 | 0.19 | 0.16 | 0.39 | 0.18 |
| Day 14 | 0.17 | 0.42 | 0.20 | 0.18 | 0.41 | 0.18 |

Conclusion:

The passive sampler can easily be stored for 14 days both at room temperature and at 4 °C in a refrigerator.

Once desorbed, storage up to one month in well capped vials will not affect the sampler results.

3.2. EFFECT OF THE SHELTER DESIGN ON THE SAMPLER PERFORMANCE

A preliminary field experiment is elaborated at a rural background site in Geel (with Benzene concentration $0.4 \mu\text{g}/\text{m}^3$ at 20 °C) to evaluate the possible influence of the dedicated Gradko shelter (illustrated in Figure 3) on the sampler performance.



Figure 3: Dedicated shelter for the Gradko sampler

Six samplers are placed under a canopy roof (without a shelter); at both pillars of the roof a Gradko shelter is attached, each containing three samplers.

The exposure time of Gradko samplers is 2 weeks.

There is no significant effect of the dedicated Gradko shelter on the sampler performance, as can be concluded from the benzene data:

- $0.14 \pm 0.01 \mu\text{g}/\text{sampler}$ for the canopy roof,
- $0.13 \pm 0.01 \mu\text{g}/\text{sampler}$ for both Gradko shelters.

In this experiment, the contribution of the sampler blank value to the observed sampler load is 24% for benzene, 36% for Toluene and 64% for m-Xylene.

The measurement results for Toluene and m-Xylene shall not be considered as the blank value for both compounds does not meet the EN 13528-2 criterion.

3.3. SAMPLER BLANK

In cases where passive samplers are used for short term sampling of ambient VOC concentrations, high sampler blanks can impede the measurement accuracy for the analytes involved (cf. data from preliminary field experiments).

In this context, particular attention has been given to improving the Gradko sampler pre-treatment and conditioning process.

Before conducting the actual field trial, typically involving low ambient concentrations, a set of Gradko samplers is produced to meet the most stringent QA/QC criteria.

From this dedicated sampler set, 9 blank samplers are analyzed via GC-MS in accordance with the ISO-17025 accredited analytical method MIM-GA-012.

The limit of quantification for MIM-GA-012 compounds adsorbed on Gradko samplers is 0.04 µg.

Sampler blanks are below the limit of quantification (LOQ) for Benzene, Methyl-t-butyl ether, Trichloroethylene, Tetrachloroethylene, Ethylbenzene, o-Xylene, Styrene and 1,4-Dichlorobenzene.

Analytes detected above LOQ in sampler blanks are Toluene and m-,p-Xylene, likewise 1,2,4-Trimethylbenzene.

Table 10 shows typical blank values for a dedicated set of Gradko samplers.

Table 10: Typical blank values for Gradko samplers used within the actual field trial

| µg/sampler | Toluene | p-, m-Xylene | 1,2,4-TMB |
|-------------|--------------|--------------|--------------|
| Blank 1 | 0.198 | 0.042 | 0.043 |
| Blank 2 | 0.195 | 0.043 | 0.047 |
| Blank 3 | 0.219 | 0.048 | 0.049 |
| Blank 4 | 0.198 | 0.045 | 0.047 |
| Blank 5 | 0.223 | 0.047 | 0.047 |
| Blank 6 | 0.217 | 0.046 | 0.050 |
| Blank 7 | 0.201 | 0.041 | 0.045 |
| Blank 8 | 0.200 | 0.042 | 0.046 |
| Blank 9 | 0.193 | 0.045 | 0.049 |
| Mean | 0.205 | 0.044 | 0.047 |
| SD | 0.011 | 0.002 | 0.002 |

Still, Toluene blank mass loadings exceed the certification criterion of 0.1 µg/sampler (cf. laboratory validation, paragraph 2.3).

Whereas in the laboratory experiments often outlying blank (and thus sample) results were observed for Toluene, the reproducibility of actual blank results is acceptable (RSD 5%).

When applying the actual set of Gradko samplers , two weeks exposure will lead to accurate passive measurements provided that Toluene concentrations exceed $2 \mu\text{g}/\text{m}^3$; lower Toluene concentrations should be sampled during 4 weeks.

VOC detection limits for a one-week sampling period are found to be dependent on the sampler conditioning procedure.

In this context, solely two and four weeks exposures of Gradko samplers will be experimented within the field trial.

3.4. FIELD VALIDATION OF THE GRADKO SAMPLER

The measurement results for both monitoring stations (in Laakdal and Zelzate) are given in Table 11 and 12.

For each of the experimented measurement methods, the observed VOC concentrations have been standardized to 20 °C.

The overall uptake rate for Benzene, Toluene and m-Xylene derived from laboratory validation experiments (21, 18 and 16 ml/min respectively, at 20 °C), is used to calculate the Gradko measurement results.

Precision is found to be satisfactory with coefficients of variation for batches of 3 to 9 Gradko samplers between 1 % and 6 % for analyte concentrations ranging from 0.8 to 4 µg/m³, which appears to be independent of concentration level and sampling duration (2 to 4 weeks).

By studying the ratios of the mean results obtained by the Gradko sampler and the Radiello sampler (cf. Table 13), their comparability is confirmed.

Table 13: VOC measurements by Radiello and Gradko samplers at two monitoring sites

| Ratio (C _{Gradko} /C _{RAD}) | Benzene | Toluene | m,p-Xylene |
|---|---------|---------|------------|
| <i>Laakdal</i> | | | |
| 2 weeks exposure | 1.05 | 1.01 | 1.19 |
| 2 weeks exposure | 0.96 | 1.01 | 0.99 |
| 4 weeks exposure | 1.07 | 0.95 | 1.03 |
| Overall ratio | 1.03 | 0.99 | 1.07 |
| <i>Zelzate</i> | | | |
| 2 weeks exposure | 1.06 | 1.02 | 1.11 |
| 2 weeks exposure | 0.95 | 0.98 | 1.04 |
| Overall ratio | 1.01 | 1.00 | 1.08 |

Table 11: Laakdal - Comparison of VOC concentrations measured with diffusive samplers and the reference method

| Concentration ($\mu\text{g}/\text{m}^3$) | Benzene | Toluene | m,p-Xylene |
|--|-----------------------------------|-----------------------------------|-----------------------------------|
| 2-weekly sampling period (week 1-2) | | | |
| Pumped charcoal tubes (ref. value) | 1.39 \pm 0.03 (n = 3) (1.9%) | 2.16 \pm 0.10 (n = 3) (4.7%) | 2.68 \pm 0.07 (n = 3) (2.8%) |
| Gradko type diffusive sampler | 1.19 \pm 0.03 (n = 6) (2.6%) | 1.73 \pm 0.04 (n = 6) (2.3%) | 2.61 \pm 0.08 (n = 6) (3.1%) |
| Radiello type diffusive sampler | 1.13 \pm 0.06 (n = 3) (5.3%) | 1.71 \pm 0.09 (n = 3) (5.3%) | 2.20 \pm 0.10 (n = 3) (4.7%) |
| 2-weekly sampling period (week 3-4) | | | |
| Pumped charcoal tubes (ref. value) | 2.44 \pm 0.06 (n = 3) (2.6%) | 4.51 \pm 0.15 (n = 3) (3.3%) | 3.86 \pm 0.36 (n = 3) (9.3%) |
| Gradko type diffusive sampler | 1.94 \pm 0.04 (n = 6) (2.0%) | 3.74 \pm 0.07 (n = 6) (2.0%) | 3.31 \pm 0.03 (n = 6) (1.0%) |
| Radiello type diffusive sampler | 2.03 \pm 0.04 (n = 3) (1.8%) | 3.71 \pm 0.12 (n = 3) (3.4%) | 3.33 \pm 0.11 (n = 3) (3.2%) |
| 4-weekly sampling period (week 1-4) | | | |
| Gradko type diffusive sampler | 1.63 \pm 0.04 (n = 3) (2.7%) | 2.47 \pm 0.05 (n = 3) (2.1%) | 2.70 \pm 0.03 (n = 3) (0.9%) |
| Radiello type diffusive sampler | 1.53 \pm 0.07 (n = 3) (4.4%) | 2.59 \pm 0.09 (n = 3) (3.7%) | 2.62 \pm 0.11 (n = 3) (4.1%) |

Table 12: Zelzate - Comparison of VOC concentrations measured with diffusive samplers and the reference method

| Concentration ($\mu\text{g}/\text{m}^3$) | Benzene | Toluene | m,p-Xylene |
|--|-----------------------------------|-----------------------------------|-----------------------------------|
| 2-weekly sampling period (week 1-2) | | | |
| Pumped charcoal tubes (ref. value) | 1.36 \pm 0.03 (n = 3) (1.8%) | 2.70 \pm 0.11 (n = 3) (4.2%) | 0.94 \pm 0.07 (n = 3) (7.2%) |
| Gradko type diffusive sampler | 1.14 \pm 0.05 (n = 9) (4.0%) | 2.13 \pm 0.13 (n = 9) (5.9%) | 0.81 \pm 0.02 (n = 9) (2.5%) |
| Radiello type diffusive sampler | 1.08 \pm 0.06 (n = 3) (5.9%) | 2.08 \pm 0.13 (n = 3) (6.1%) | 0.73 \pm 0.04 (n = 3) (5.8%) |
| 2-weekly sampling period (week 3-4) | | | |
| Pumped charcoal tubes (ref. value) | 2.49 \pm 0.09 (n = 3) (3.8%) | 4.27 \pm 0.19 (n = 3) (4.4%) | 1.33 \pm 0.11 (n = 3) (8.2%) |
| Gradko type diffusive sampler | 2.05 \pm 0.05 (n = 9) (2.4%) | 3.53 \pm 0.07 (n = 9) (2.0%) | 1.17 \pm 0.02 (n = 9) (1.8%) |
| Radiello type diffusive sampler | 2.15 \pm 0.07 (n = 3) (3.3%) | 3.61 \pm 0.12 (n = 3) (3.3%) | 1.12 \pm 0.04 (n = 3) (3.3%) |

For Benzene, 48 pairs of data (Gradko passive samplers versus the AC reference method) are collected over a range of concentrations from 0.3 to 2.1 $\mu\text{g}/\text{m}^3$.

For Toluene, Gradko measurement results range from 0.8 to 3.7 $\mu\text{g}/\text{m}^3$.

For m-, p-Xylene these values are 0.3 to 3.1 $\mu\text{g}/\text{m}^3$.

By applying a linear regression forced through the origin, the results given in figure 4 are obtained, including both individual results from preliminary field experiments (cf. Mol and Geel) and results from the actual field trial (cf. Laakdal en Zelzate).

Significant correlations (with $R^2 > 0.99$) are found between the Gradko samplers and the co-located activated charcoal tubes.

The measured results for both diffusive samplers (Gradko, Radiello) obtained in this field campaign result in a slightly lower VOC concentration (cf. Table 11, 12) than obtained with the reference method (pumped sampling). This effect is small as illustrated by the expanded uncertainty calculations (below).

Based on these field comparison data (and thus involving these uptake rates) and using the ISO 20988 approach (cf. evaluation method A5, case 2, in Annex B.7), the expanded uncertainty of the Gradko sampler under field conditions is evaluated.

The expanded uncertainty (expressed at a 95% confidence level) is calculated to be 15% for Benzene, 9.7% for Toluene and 17% for m,p-Xylene, if 2-weeks exposure to the annual average limit value (5 $\mu\text{g}/\text{m}^3$ for Benzene). Fictive limit values are established for Toluene and m, p-Xylene based on ratios in relation to benzene, as observed in field experiments: 13 $\mu\text{g}/\text{m}^3$ for Toluene and 2.3 $\mu\text{g}/\text{m}^3$ for m, p-Xylene.

Resulting uncertainties fulfil the 25% uncertainty requirement of EU directive 2008/50/EC for fixed ambient air measurements of Benzene. For indicative measurements this data quality objective is 30%.

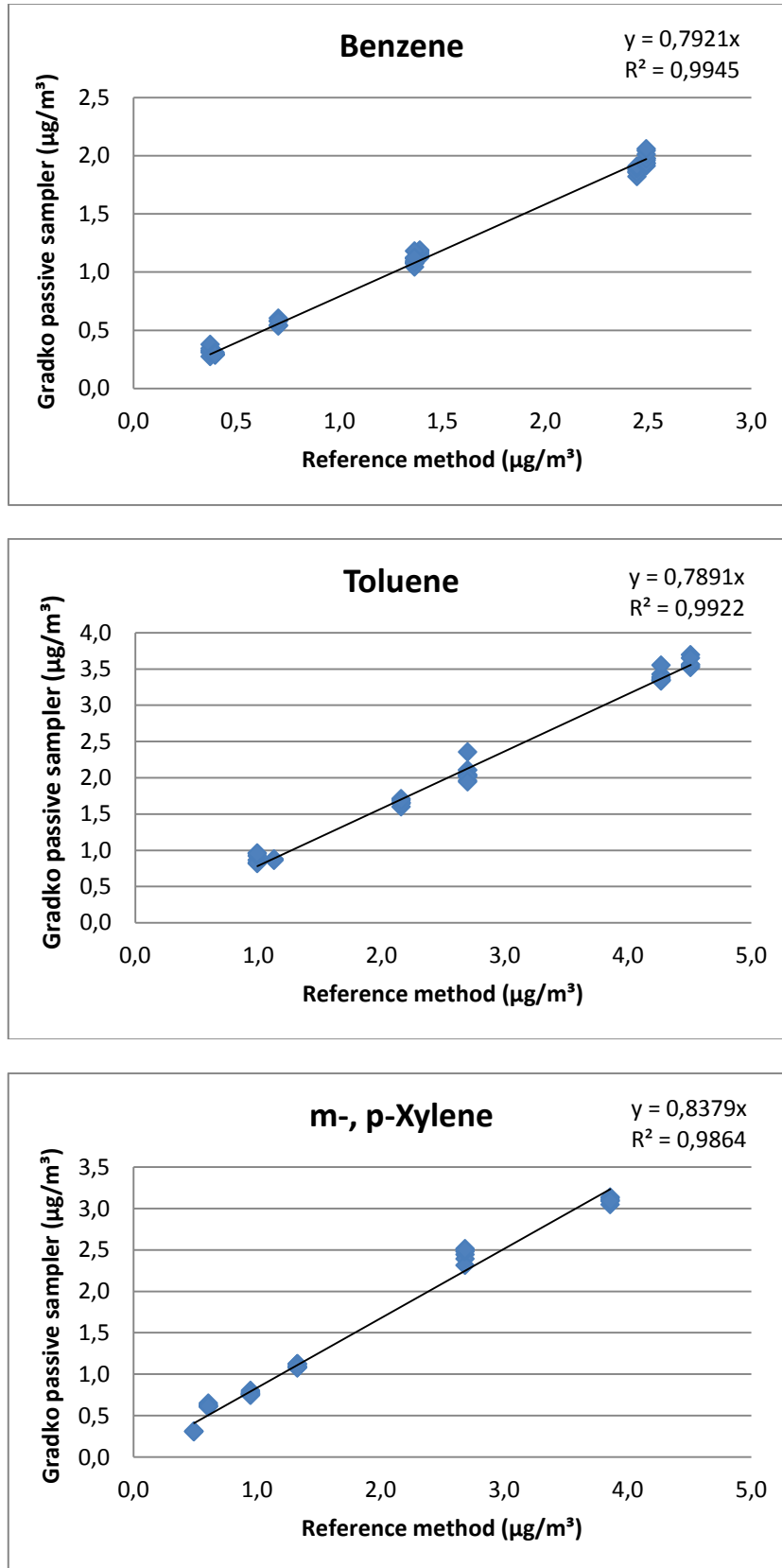


Figure 4: Comparison between results of the Gradko passive sampler with the reference method in the field

The validity of the measurement results from the AC reference method is confirmed through comparison with the results from the VMM BTEX analyzer at both monitoring stations.

Continuous BTEX measurements are performed in accordance with method EN 14662-3:2005 “Standard method for measurement of benzene concentrations, automated pumped sampling with in situ gas chromatography” (also labelled as a reference method for Benzene measurements within EU directive 2008/50/EC).

As an example, the results for both reference methods at the industrial monitoring station Zelzate are given in table 14.

Table 14: *Example of relationships between results of the activated charcoal method and a BTEX analyzer*

| Zelzate | AC ($\mu\text{g}/\text{m}^3$) | VMM ($\mu\text{g}/\text{m}^3$) | Ratio |
|--------------|------------------------------------|-------------------------------------|-------|
| Benzene | | | |
| week 1-2 | 1.4 | 1.5 | 1.13 |
| week 3-4 | 2.5 | 2.6 | 1.04 |
| Toluene | | | |
| week 1-2 | 2.7 | 2.8 | 1.04 |
| week 3-4 | 4.3 | 4.5 | 1.04 |
| m-,p- Xylene | | | |
| week 1-2 | 0.9 | 1.0 | 1.08 |
| week 3-4 | 1.3 | 1.4 | 1.04 |

CHAPTER 4 CONCLUSION

Laboratory validation of the Gradko diffusive sampler for the determination of VOCs in ambient air is performed according to the EN 13528-2.

This European standard specifies performance requirements for desorption efficiency, two weeks' storage stability, sampler integrity and blank value. These criteria were met for the Gradko diffusive sampler, with Benzene, Toluene and m-Xylene as target analytes.

In earlier experiments (2002 - 2003), no back diffusion was observed for the Gradko diffusive sampler.

The shelf life of the sampler is minimum 3 months.

The overall uptake rate of the Gradko sampler at 20 °C, calculated from the laboratory validation experiments, is 21 ml/min for Benzene, 18 ml/min for Toluene and 16 ml/min for m-Xylene.

No clear effect of the following parameters on Gradko sampler performance is observed: air velocity (in the range of 0.15 to 0.80 m/s), sampler orientation (parallel and perpendicular), analyte concentration, exposure time (1, 2 and 4 weeks) and presence of interferents.

During field validation experiments at a rural background monitoring station (cf. Laakdal), the Gradko sampler was exposed for 2 to 4 weeks sampling periods.

The precision of replica field measurements (involving 3 to 9 Gradko samplers) range from 1 % to 6%, for analyte concentrations from 0.8 to 4 µg/m³.

When exposed for 14 to 30 days in the field, the comparability of Gradko sampler results to those obtained with co-located Radiello type diffusive samplers, is good, with ratios of average results ranging from 0.95 (for Toluene) to 1.19 (for m-, p-Xylene).

When assessing measurement uncertainty from the field comparison data set (Gradko samplers and activated charcoal tubes) using the ISO 20988 approach, a relative expanded uncertainty (expressed at a 95% confidence level) of 15% for Benzene, 9.7% for Toluene and 17% for m,p-Xylene is found.

These uncertainties qualify the Gradko diffusive sampler for ambient air quality assessment through fixed (and indicative) VOC measurements (EU Directive 2008/50/EC).