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Sorbisense GWS40 Passive Sampler

Joint verification report

Volatile organic compounds in groundwater

March 2010   **Joint verification report**

Sorbisense GWS40 Passive Sampler

Joint verification report

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2 INTRODUCTION

Environmental technology verification (ETV) is an independent (third party) assessment of the performance of a technology or a product for a specified application, under defined conditions and Quality Assurance (QA).

This verification was a joint verification between NOWATECH Water Monitoring ETV Center (NOWATECH WMC), operated by DHI, and the Advanced Monitoring Systems Center (AMS) operated by Battelle under a cooperative agreement with the US Environmental Protection Agency (US EPA). The plan used during testing and verification consisted of a joint verification protocol /1/ and test plan /2/. The compliance with both scheme's requirements was ensured through a process document /3/.This report is a summary of the verification done and the performance data obtained.

2.1 Name of product

The product verified was the Sorbisense GWS40 passive sampling system (106-012-11) with samplers (cartridges) for analysis of volatile organic compounds (VOCs) (no., 043-091-12, 043-101-12, 043-102-12). Analysis of the samplers was performed by ALcontrol under ISO 17025 accreditation. The passive samplers and the subsequent analysis of the cartridges constitute the product.

2.2 Name and contact of vendor

Sorbisense A/S, Niels Pedersens Allé 2, DK-8830 Tjele, Denmark, phone +45 8999 2505. Contact: Hubert de Jonge, e-mail hubert@sorbisense.com

Laboratory responsible for the analysis of samples (subcontractor to the vendor): ALcontrol Laboratories, Steenhouwerstraat 15, 3194 AG Hoogvliet, Netherlands, phone +31 (0)10 231 47 00. Contact: Jaap Willem Hutter, e-mail j.hutter@alcontrol.nl

2.3 Name of center/verification responsible

NOWATECH Water Monitoring ETV Center (NOWATEC WMC), DHI, Agern Allé 5, DK-2970 Hørsholm, Denmark.

Verification responsible: Christian Grøn, e-mail chg@dhigroup.com, phone +45 4516 9570

US EPA Advanced Monitoring System Center, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201-2693, US

Verification responsible: Anne M. Gregg (AMG), e-mail gregga@battelle.org, phone +1 614-424-7419

2.4 Verification Test Organization

The verification was conducted as a joint verification between NOWATECH ETV project and the US ETV Program. The verification was planned and conducted to satisfy the requirements of the ETV scheme currently being established by the European Union (EU ETV) and the US ETV Program. Verification and tests were performed by DHI as NOWATECH Water Monitoring ETV Center (NOWATECH WMC) under contract with Nordic Innovation Centre, Nordic Council of Ministers. Battelle was participating as the manager of the ETV AMS Center through a cooperative agreement with the US EPA.

The day to day operations of the verification and tests were coordinated and supervised by DHI personnel, with the participation of the vendor, Sorbisense. The testing was conducted in the DHI laboratories, Hørsholm, Denmark and in the field in the Copenhagen area, Denmark. DHI operated the samplers during the verification. Sorbisense provided the sampling systems, the samplers and the analysis of samplers for the test. Furthermore, Sorbisense provided user manuals and operation instructions, and participated in development of protocol and plans with DHI. Battelle ensured that the verification and tests were planned and conducted to satisfy the requirements of the US ETV program, including input and concurrence from its stakeholder group, as described in a process document /3/ produced to ensure the compliance of the verification with the US ETV requirements by Battelle AMS. Battelle also participated in the development of the joint verification protocol, joint test plan, and process document, for the verification and tests and performed quality assurance of the verification and tests. US EPA participated through reviewing and approving the test planning documents and verification reports. The EPA AMS project officer and quality assurance staff reviewed and approved the plan and report documents.

Three technical experts provided independent expert review during the planning, conducting and reporting of the verification and tests.

The organization chart in Figure 1 identifies the relationships of the organization associated with this verification and tests.

Figure 1   Organization of the verification and tests.

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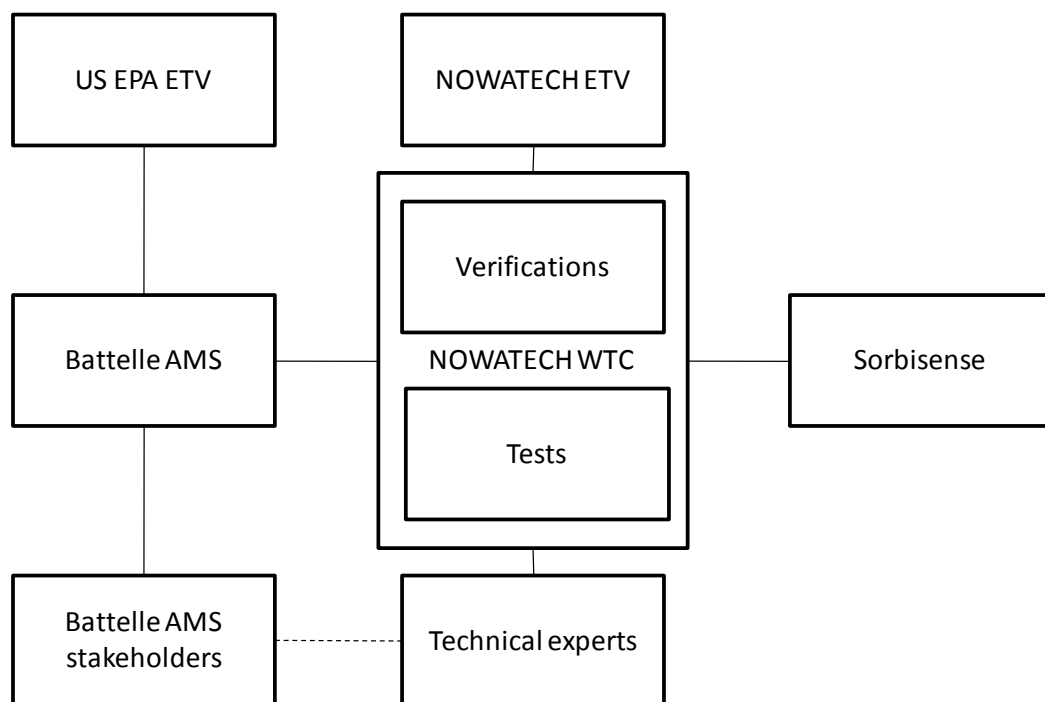
2.5   Technical experts

The technical experts assigned to this verification and responsible for review of the verification protocol, test plan, process document and report documents were:

Dietmar Müller (DM), e-mail dietmar.mueller@umweltbundesamt.at, Contaminated Sites, Umweltbundesamt, Spittelauer Lände 5, 1090 Wien, Austria, phone +43-(0)1-313 04/5913,

Mike Sherrier (MS), e-mail michael.p.sherrier@usa.dupont.com, DuPont, Chestnut Run Plaza, Bldg 715-230, 4417 Lancaster Pike, Wilmington, DE 19805, US, phone +1 302-999-2533,

Cynthia Paul (CP), e-mail paul.cindy@epa.gov, U.S. Environmental Protection Agency, 919 Kerr Research Drive, P.O. Box 1198. Ada, OK 74820, US, phone: +1 580-436-8556.
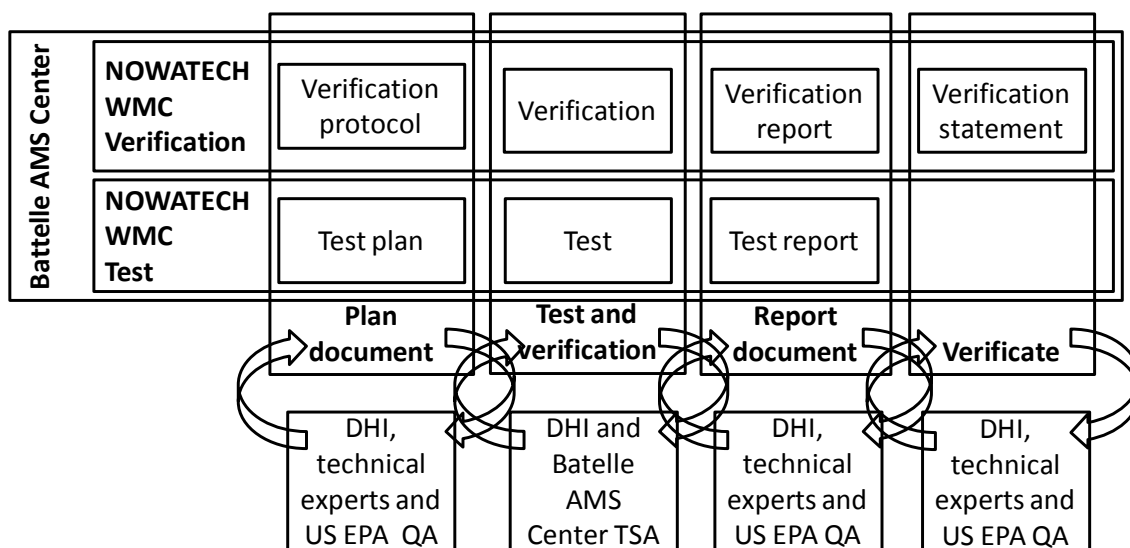
2.6   Verification process

Verification and tests were conducted in two separate steps, as required by the EU ETV. The steps in the verification are shown in

Figure 2. In addition to the plan document (verification protocol and test plan), a process document was prepared that describes the cooperation between the European and US organizations /3/.

Figure 2   Verification steps.

Battelle AMS Center	NOWATECH WMC Verification	Verification protocol	Verification	Verification report	Verification statement
	NOWATECH WMC Test	Test plan	Test	Test report	
		Plan document	**Test and verification**	**Report document**	**Verificate**
		DHI, technical experts and US EPA QA	DHI and Batelle AMS Center TSA	DHI, technical experts and US EPA QA	DHI, technical experts and US EPA QA

The Plan Document above includes the Process Document as well. The US EPA reviewed the verification report and statement. The EPA did not review or approve the test report.

References for the verification process are the Quality Management Plan for the Battelle AMS /4/ and the Quality Manual for the ETV operations at DHI following the NOWATECH Quality Manual Template /5/.

A joint US EPA ETV and NOWATECH ETV verification statement has been issued after completion of the verification.

This verification report, and verification statement is viewed by the US ETV program as one consolidated verification description. The US EPA does not intend to post the test report on the ETV website.

3   DESCRIPTION OF THE TECHNOLOGY

The technology product verified is a passive sampling system. Passive sampling is based upon distribution of solutes between the sampled medium, *e.g.* a water body, and a collecting medium, the sampler or sampling medium. Flow of solute from one medium to the other continues until equilibrium is established in the system, or until the sampling session is terminated by the user. The amount of solute in the sampling medium is then determined analytically and can be used to calculate the concentration in the sampled medium. With exposure until equilibrium, the sampled medium concentration can be calculated based on the solute distribution factor between the two media involved. With exposure until the sampling session is terminated by the user (before achieving equilibrium), the time-weighted average solute concentration in the sampled medium can be determined from the exposure time and the sampling rate for the solute in question. A wide range of products is available for passive sampling (equilibrium based and rate controlled) of solutes (inorganic and organic) from waters.

4 DESCRIPTION OF THE PRODUCT

The Sorbisense passive sampler is rate controlled with advective flow combined with a patented tracer based calculation of the volume of water of water that the sampler has been exposed to. The sampler consists of a polypropylene cartridge containing, see Figure 3:

- A sorbent that absorbs solutes from water passing through the sampler.
- Tracer salt that dissolves proportionally with the volume of water passing through the cartridge.
- Filters between sorbent and tracer salt compartments.

Figure 3   Principle of the Sorbisense sampler.
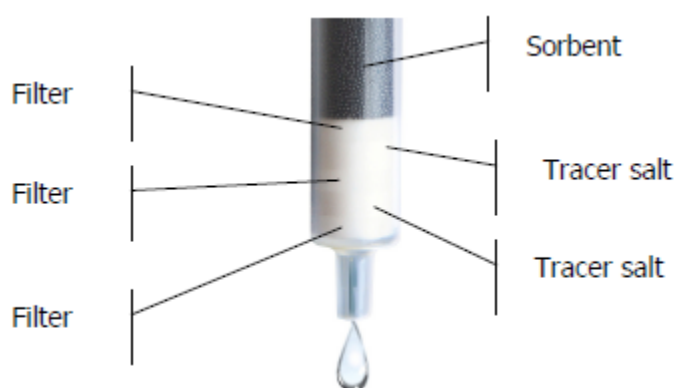
When the sampling period is over, the Sorbisense sampler is sent to a laboratory for extraction and analyses whereupon a time-weighted average solute concentration is reported.

For analysis, the cartridge is cut and the sorbent taken for batch extraction with acetone followed by quantification of sorbed compounds by headspace Gas Chromatography Mass Spectrometry (GC-MS). The tracer salt (calcium citrate) is extracted with 0.2 M HCl and quantification of extracted calcium is determined with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The sampled water volume is calculated from:

$$V = \frac{M_{start,tracersalt} - M_{lab,tracersalt}}{K}$$

The solute water concentration is calculated from:

$$C = M_{solute} / V = \frac{M_{solute} * K}{M_{start,tracersalt} - M_{start,tracersalt}}$$

V= water volume in L; $M_{start, tracersalt}$ = weighed amount of salt in production as mg Ca; $M_{lab, tracersalt}$ = extracted amount of salt in laboratory as mg Ca; C = Volatile Organic Compounds (VOC) concentration in µg/L; M_{solute} = mass of VOC detected in ug; K = solubility of the salt with the standard calibration value as 184 mg Ca/L.

The product verified here is the Sorbisense GWS40 sampling system intended for sampling of shallow groundwater and equipped with samplers for VOC.

Figure 4   Mounting of the GWS40 sampling system.
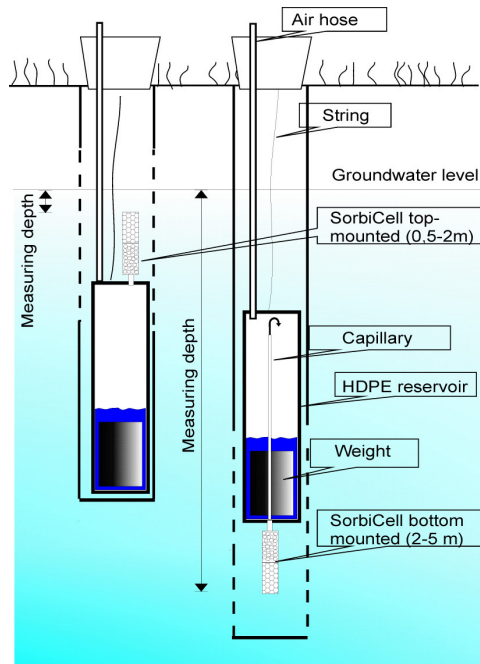
The GWS40 is mounted with an air hose, safety string and Sorbisense samplers (can be mounted in top or bottom of the GWS40) and is subsequently lowered to the desired measuring depth, see Figure 4. The water pressure will push water through the sampler slowly filling the GWS40. The air hose enables the air inside the GWS40 to escape to the atmosphere. When the measuring period is over, the samplers are removed and sent to the laboratory for analysis. The volume of water that passed through the Sorbisense sampler can be calculated manually at this point. See Section 8.4.2 for deployment cost considerations.

5   APPLICATION AND PERFORMANCE PARAMETER DEFINITIONS

The application and the performance parameters were defined as detailed in Appendix 3, in terms of matrix/matrices, targets and effects.

The passive sampler was supplied by the vendor as combined sampling and analysis, and the verification accordingly regards these two steps as one.

Table 1   Application definition for the verification of Sorbisense GWS40 Passive Sampler.

Matrix	Effect	Targets	Technologies
Contaminated groundwater	Measurement of concentrations of volatile organic contaminants **Additional parameters:** • User manual • Product cost • Health and safety	Volatile organic compounds Detection limits (µg/L) Linear range (µg/L) Trueness (%) Robustness (%) Precision (% relative standard deviation, RSD) Discrepancy between sampler result and reference samples[1]	Sorbisense passive sampler with tracer based calculation of the amount of water that the sampler has been exposed to and quantification by extraction of the sampler and head space GC-MS

[1] Positive discrepancy: sampler finds measurable concentration when average of reference samples are below the sampler limit of detection. Negative discrepancy: sampler does not find measurable concentration when average of the reference samples are above sampler limit of detection.

5.1   Matrix/matrices

The matrix of the application is groundwater and the field of application is investigations of (potentially) contaminated groundwater (groundwater investigations).

Investigations at waste disposal sites and groundwater baseline monitoring are excluded from the verifications due to the required high robustness towards high ionic strength and dissolved organic matter concentration, and low detection limits, respectively.

5.2   Target(s)

The target parameters for the application were set in terms of Limit of Detection (LoD), precision, trueness, range of application and robustness, including the frequency of discrepancy between sampler and reference sample results.

5.3   Effects

The compounds verified for measurement with the product were volatile organic compounds, here mono-, di-, tri- and –tetrachloroethenes, benzene, toluene, ethylbenzene and xylenes (BTEX) and methyl-*tert*-butylether (MTBE), see Table 2.

Table 2   Targets compounds of the Sorbisense GWS40 Passive Sampler.

Target compounds	
Chloroethene	Benzene
1,1-Dichloroethene	Toluene
1,2-Dichloroethenes	Ethylbenzene
Trichloroethene	Xylenes
Tetrachloroethene	MTBE

5.4   Performance parameters for verification

The ranges of performance relevant for the application, were derived in Appendix 3, and are presented in Table 3. These ranges were used for planning the verification and testing only. For Sorbisense VOC sampling, concentrations above 2,000 µg/L were not included in the verification (vendor information). The calculations of the performance parameters explaining their principle are given in Table 7.

Table 3   Ranges of performance parameters relevant for groundwater investigations.

Compound	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L	Robust-ness %
Chloroethene	0.02-0.05	<25	75-125	LoD-1*10^6	100±15
1,1-Dichloroethene	0.1-1	<25	75-125	LoD-1*10^6	100±25
1,2-Dichloroethenes	0.1-1	<25	75-125	LoD-1*10^6	100±25
Trichloroethene	0.1-1	<25	75-125	LoD-1*10^6	100±25
Tetrachloroethene	0.1-1	<25	75-125	LoD-1*10^5	100±25
Benzene	0.1-1	<25	75-125	LoD-1*10^6	100±25
Toluene	0.5-5	<25	75-125	LoD-1*10^5	100±25
Ethylbenzene	0.5-5	<25	75-125	LoD-1*10^5	100±25
Xylenes	0.5-5	<25	75-125	LoD-1*10^5	100±25
MTBE	0.2-2	<25	75-125	LoD-1*10^6	100±25

Limit of detection was calculated from the standard deviation of replicate measurements at 5 times the vendor stated detection limit and reflects a less than 5% risk of false positives.

Precision was evaluated under repeatability and reproducibility conditions. Repeatability has been obtained as the standard deviation of measurements done with the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicates measurements on the same or similar objects over a short period of time. Reproducibility has been obtained as the standard deviation of measurements that includes different locations, operators, measuring systems, and replicates measurements on the same or similar objects. In laboratory terminology, repeatability is the within series precision and the reproducibility the between series precision.

Trueness is the correspondence between (mean) concentrations found in measurements and corresponding true concentrations. Besides the quantitative trueness (same number obtained with verified method and reference method), the trueness of detection was assessed as frequency of discrepancy between sampler and reference sample results[1]. In addition to conventional trueness, the trueness of time-weighted averages obtained with the sampler was verified.

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[1] Positive discrepancy: sampler finds measurable concentration when average of reference samples are below the sampler limit of detection. Negative discrepancy: sampler does not find measurable concentration when average of the reference samples are above sampler limit of detection. When calculating the average of the corresponding reference samples, concentrations below the reference sample limit of detection were set to half the reference sample limit of detection.

The range of application is the range from the LoD to the highest concentration with linear response.

The parameters of robustness verified were sampling depth, sampling time, sampling concentration and groundwater ionic strength. Robustness is basically the trueness as found for different values of the robustness parameters, but given here as the ratio between the mean value obtained for the robustness variation and the mean value obtained under reference conditions.

The version of the product verified is designed for sampling shallow aquifers, i.e. with sampling depths from 0.5 to 5 meters below the groundwater table (mbgw). The pressure on samplers will vary with depth to the sampling positions, and pressure variations in the range of 1.05 to 1.5 atmospheres were accordingly verified.

Sampling time variations from three to nine days were verified covering the different sampling times recommended by the vendor for the product tested.

In investigations of contaminated groundwater, both uncontaminated and highly contaminated groundwater was included in the application as defined. The concentrations verified therefore reflect the range from uncontaminated groundwater to highly contaminated groundwater, with at the least 3 concentrations distributed over a relevant range.

In order to reflect the varying ionic strength of groundwaters, groundwater ionic strengths within the electrical conductivity range 10 to 100 mS/m were verified, corresponding to the 5 to 95 percentile of Danish groundwaters /6/.

Impact of other factors such as groundwater flow, well construction or presence of other contaminants than the targets could not be ruled out and was considered in planning the field tests for the verification.

5.5   Additional parameters

Besides the performance parameters obtained by testing, compilation of parameters describing user manual, product costs and occupational health & safety issues of the product were compiled as part of the verification.

6   EXISTING DATA

A test of Sorbisense samplers, similar but earlier product version, for volatile organic contaminants in groundwater wells has been conducted by the laboratory used by the vendor for sampler analysis.

6.1   Summary of existing data

The summarized data as provided by the manufacturer is presented in Figure 5.

The test was set up with polyvinylchloride (PVC) pipes simulating groundwater wells (standpipes), filled with spiked water and equipped with Sorbisense

samplers inserted directly into the water using a pipe adaptor ("pipe"), Sorbi-sense samplers mounted in Groundwater Samplers (GWS) and water samples taken directly from the standpipe ("water samples").

Figure 5   Summarized data on sampler test for selected Volatile Organic Compounds (VOC) as provided by the manufacturer.

Test parameter	Sorbisense	Water samples
VOC Spike level: (average of results)	0, 6, 36, 120, 3000 µg/L	
VOC measuring range:	GWS: 0 – 1980 µg/L Pipe: 0 – 1860 µg/L	0 – 2160 µg/L
VOC recovery: (average of results)	GWS: 85% of spiked level Pipe: 94% of spiked level	75% of spiked level
VOC detection limit:	0.2 µg / V (V = volume sampled)	0.2 µg/L
VOC concentration precision:	GWS: 13.7% of mean Pipe: 8.9% of mean Calculated from 44 duplicates each	30.5% of mean Calculated from 44 triplicates
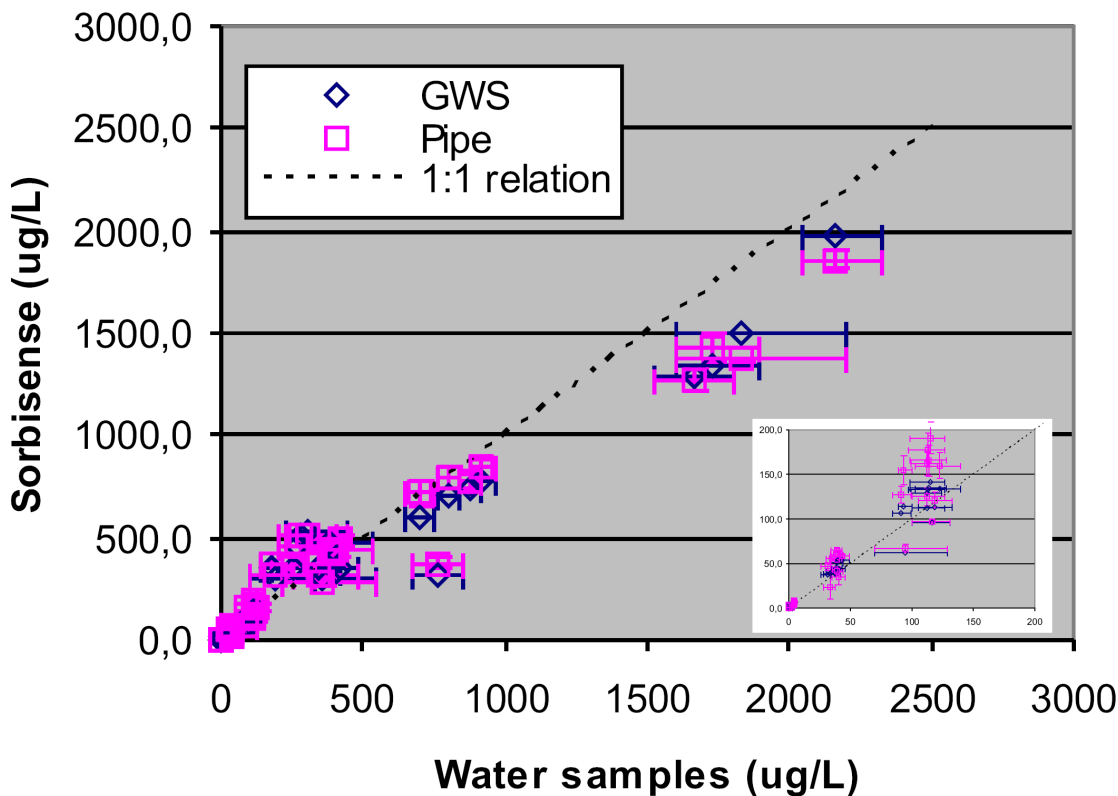
6.2   Quality of existing data

It is not stated whether the testing and analysis were done under the laboratory's ISO 17025 accreditation /7/, therefore the test laboratory cannot be considered independent, and the documentation made available for the verification is not sufficient to allow for an assessment of the data quality.

6.3   Accepted existing data

It was decided that the existing data should not be used as part of the verification due to the data quality issues, see Section 6.2. The data were used as an indication of the performance range to be expected during planning.

7   TEST

Based upon the application and performance parameter identification, Chapter 5, the tests were designed, see below. The detailed test report is a separate document /8/.

7.1   Test design

The test design principle consists of four test scales: laboratory tests with direct application, laboratory test with laboratory dispenser, standpipe tests and field tests. Each scale is further described below and provides information on specified performance parameters. To maintain controlled conditions in the test, each performance parameter was tested at the simplest possible scale. The outline of the tests is shown in Table 4. As an example of the application of the scale principle, consider the test for evaluation of trueness and robustness. Trueness as best possible estimate was evaluated from direct application at the laboratory scale (chloroethene only). Trueness as realistic estimate was evaluated from the standpipe scale simulating a groundwater well (all but chloroethene), and the variation in trueness between groundwater wells (robustness) was evaluated at the field scale. Combining the scales thus provided the best possible estimates of real conditions performance.

The laboratory tests involved direct application of standard solution to the samplers or exposure of samplers to spiked water from a sample dispenser, i.e. without the sampling system. The laboratory tests provided information on the response of the samplers to carefully controlled parameters and best possible information on the performance of the samplers with chloroethene, a compound that could not be included in standpipe tests due to practical and health and safety considerations.

The standpipe tests were intended to simulate groundwater movement through a well established in the laboratory and to enable full control of solute concentrations. The standpipe tests provided more realistic information on the performance of the samplers, while minimizing the variability of the test system as compared to field systems.

The field tests provided information on the robustness of the sampling system under the real conditions of groundwater investigations. In planning the field tests, varying aquifer and well conditions were targeted in order to allow for consideration of any impact of factors such as groundwater flow, well construction, presence of other contaminants than the target solutes, as well as the impact of combined variation of robustness parameters.

Table 4   Test design scales and associated performance parameters.

Laboratory		Standpipe	Field
Direct application	**Dispenser**		
Limit of detection: best possible for chloroethene	None	Limit of detection	None
Precision (repeatability): best possible for chloroethene	None	Precision (repeatability and reproducibility)	Precision (reproducibility)
Trueness: best possible for chloroethene	None	Trueness	None
None	None	Range of application	None
None	Robustness, sampling time and groundwater ionic strength	Robustness, sampling depth	General robustness
None	None	None	Robustness, frequency of discrepancy
None	Robustness, concentration variation and integration	None	None

Expected values calculated from added amounts and volumes of test solutions were used to control the test equipment. For calculating performance parameters, sampler results were compared to reference sample measurements. Especially for field testing, it should be recognized that the concept of a true value is problematic, see Table 5 for the differences between three typical sampling concepts for groundwater.

Table 5   Sampling principles for three types of groundwater sampling.

	Conventional well purge and sampling	**Low flow well purge and sampling**	**Passive sampling**
Sampling period	Point in time, minutes	Point in time, minutes	Period of time, days
Water sampled	Water from large section of aquifer	Water from small section of aquifer	Water flowing through screened interval of well casing

Considering these differences, it is difficult to assign one sampling principle "true". Irrespective of this fact, the field data have been evaluated as if the reference sample measurements could be considered "true", but in assessing the results it should be recalled, that differences may reflect differences in principles rather than differences in "trueness".

7.2　Reference analysis

Reference analysis was done under ISO 17025 accreditation /7/ using a GC-MS-SIM P&T[2] method (EPA 624.2 equivalent /9/) and was documented with analytical performance as shown in Table 6. The required analytical performance for the tests was set as for groundwater investigations in Denmark, see Table 6 and the application and performance parameter definitions, Appendix 3.

Table 6　Required analytical quality for reference analysis and laboratory performance.

	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L
Requirements				
All compounds	0.03	5	90-110	0.03-2000
Laboratory performance		Uncertainty %		
MTBE	0.1	7.0		n.s.[1]
All other compounds	0.02	7.3-14		n.s.

[1] n.s = not specified

It should be noted that the uncertainties stated by the laboratory, Table 6, includes both the random error under reproducibility conditions (requirements set here for the precision under repeatability conditions) and the systematic errors (requirements set here for the trueness).

For MTBE, there was concern whether the analytical laboratory would be able to satisfy the limit of detection of 0.03 µg/L generally required for the quantification of contaminants at trace concentrations in groundwater. Given the limit of detection stated by the vendor, the limit of detection available at the contracted laboratory was considered sufficient.

7.3　Data management

Data storage, transfer and control were done in accordance with the requirements of ISO 9001 /10/ enabling full control and retrieval of documents and records. The filing and archiving requirements of the DHI Quality Manual were followed (10 years archiving).

7.4　Quality assurance

The quality assurance of the tests included control of the reference system, control of the test system and control of the data quality and integrity.

Information on the analytical performance for the sampler analysis was obtained from the responsible laboratory for comparison.

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[2] Gas Chromatography (GC), Mass Spectrometry (MS), Single Ion Monitoring (SIM), Purge and Trap (P&T)

The test and verification reports were subject to review by DHI, the technical experts, and Battelle. The verification report and statement were subject to review by the US EPA. See Figure 2.

As a joint verification with the US EPA ETV, auditing from Battelle AMS Center was included in the quality assurance, in addition to the internal DHI test system audit.

7.5 Test report

The test report /8/ follows the principles of the DHI NOWATECH verification center quality manual (for template see /5/) with data and records from the tests presented. For this joint verification, the requirements of the US EPA ETV format are incorporated as well.

8 EVALUATION

The evaluation included calculation of the performance parameters, see Section 5.4 for definition, evaluation of the data quality based upon the test quality assurance, see Section 7.4 for requirements, and compilation of the additional parameters as specified in Section 5.5.

8.1 Calculation of performance parameters

Calculations are done according to generally accepted statistical principles such as those described in /11/ and as described in Table 7, referring also to the test design shown in Table 4.

Table 7   Calculations used for the test results.

Parameter	Calculation	Explanations
Limit of detection, LoD	$$LoD = 2 \times t_{0.95}(f) \times s_r$$	$t_{0.975}(f)$ is the Student's t factor for f = n-1 degrees of freedom, n being the number of measurements. s_r is the standard deviation of the measurements under repeatability conditions
Precision (repeatability or reproducibility), as relative standard deviation, RSD	$$D_i = \left| x_{i\max} - x_{i\min} \right|$$ $$\bar{x}_i = \frac{\sum x_i}{n}$$ $$d_i = \frac{D_i}{\bar{x}_i}$$ $$\bar{d} = \frac{\Sigma d_i}{m}$$ $$RSD = \frac{\bar{d} * 100}{1.693} \%$$	D_i is the range at level i x_{imin} and x_{imax} are the lowest and highest measurements at level i d_i is the relative range at level i $\bar{d}$ is the mean relative range for all m levels Used with three replicates, i=3 in x_i

Parameter	Calculation	Explanations
Precision (repeatability or reproducibility), as relative standard deviation, RSD	$$\bar{x}_i = \frac{\sum x_i}{n}$$ $$s_i = \sqrt{\frac{\sum(x_i - \bar{x}_i)^2}{n-1}}$$ $$RSD = \frac{s_i}{\bar{x}_i}$$	$\bar{x}_i$ is the mean n is number of measurements s_i is standard deviation Used with more than three replicates, i>3 in x_i
Trueness, T	$$\bar{x}_i = \frac{\sum x_i}{n}$$ $$\bar{y}_i = \frac{\sum y_i}{n}$$ $$T_i = \frac{\bar{x}_i}{\bar{y}_i} \times 100\%$$ $$T = \frac{\sum T_i}{m}$$	$\bar{x}_i$ is the mean of sample measurements at level i, x_i $\bar{y}_i$ is the mean of reference sample measurements at level i, y_i T_i is the trueness at level i T is the mean true value for all levels
Ratio, Ra	$$Ra_i = \frac{x_i}{\bar{y}_{i,j}}$$	x_i is one sample measurement $\bar{y}_{i,j}$ is the mean of the reference sample measurement done before and after the sample measurement Used for field measurements
Test of significance of mean difference	$$t_{0.975(f)} > \frac{|\bar{d}|}{s_d}\sqrt{n}$$	A paired t-test was applied. $t_{0.975}(f)$ is Student's t-factor for two-sided test at 95% confidence level. n is number of measurements $\bar{d}$ is the mean difference between the concentrations of the two methods. s_d standard deviation on the difference between methods
Range of application	Visual identification of linear range, linear regression of results within linear range to yield slope (a), intercept (b) and coefficient of regression (R^2).	None
Robustness	$$R = \frac{T_{ro}}{T_{re}} \times 100\%$$	T_{ro} is the trueness under the conditions of robustness test T_{re} is the trueness under the reference conditions
Trueness, concentration integration	$$y_T = \frac{\sum c_i \times t_i}{\sum t_i}$$ $$T_{ci} = \frac{\bar{x}_i}{y_T} \times 100\%$$	y_T is the true, mean concentration over the exposure period c_i and t_i are the concentrations and exposure times for each concentrations steps T_{ci} is the timeintegrated trueness

Parameter	Calculation	Explanations
Test of mean against true value	$$\frac{|\bar{x} - c| \times \sqrt{n}}{s} > t_{0.975}(f)$$	$t_{0.975}(f)$ is Student's t-factor for two-sided test at 95% confidence level, n is number of measurements and c is the true concentration
Test of mean against mean value	$$\frac{|\bar{x_i} - \bar{y_i}|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} > t_{0.975}(v)$$ $$df = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)}{\frac{\left(s_1^2/n_1\right)^2}{n_1 - 1} + \frac{\left(s_2^2/n_2\right)^2}{n_2 - 1}}$$ $$s_i = \frac{\sum (x_i - \bar{x_i})^2}{n-1}$$	This t-test assumes unequal variances and calculates the degrees of freedom from the datasets. s_i is the standard deviation of dataset i, with n_i replicates

8.2   Performance parameter summary

8.2.1   Limit of detection (LoD)
The limits of detection (LoD) are given in Table 8 as calculated from sample measurements at concentrations of five times the limit of detection stated by the vendor. The determination of LoD from standpipe data included the complete passive sampling system, while the direct application test only included the sorbent. Values given as < are estimated maximum LoD calculated from measurements at 10% of range, while the measurements at 5 times the expected limits of detection were below the real limits of detection (excessive non-detects). The analysis of trichloroethene from the standpipe test resulted in a wide range of positive and negative values, thus the high detection limit calculated. The LoD calculated from the direct application test did not indicate a higher LoD for trichloroethene than for the other compounds (data not shown).

Table 8   Calculated limits of detection.

Compound	Laboratory Direct application µg/L	Standpipe µg/L
Chloroethene	<30	
1,1-Dichloroethene		<90
trans-1,2-Dichloroethene		4
cis-1,2-Dichloroethenes		4
Trichloroethene		70
Tetrachloroethene		2
Benzene		3
Toluene		4
Ethylbenzene		5
o-Xylene		4
m/p-Xylenes		3
MTBE		6

The calculated limits of detection are applied as presented.

8.2.2 Precision

The precision in terms of repeatability and reproducibility is presented as calculated from sample measurements in the laboratory (direct application, chloroethene only, lower limit of repeatability), the standpipe and the field in Table 9. Repeatability and reproducibility were calculated from standpipe sample measurements with triplicate measurements at 5 concentration levels up to the maximum range. Reproducibility was also calculated from triplicate measurements in the field and included variability in groundwater concentrations over the sampling period (18 days). For comparison, the corresponding values are given for the reference samples.

Table 9   Precision as repeatability and reproducibility calculated as relative standard deviation (RSD).

Compound	Laboratory Direct application Repeatability Samples RSD %	Standpipe				Field	
		Repeatability		Reproducibility		Reproducibility	
		Samples	Reference samples	Samples	Reference samples	Samples	Reference samples
		RSD %	RSD %	RSD %	RSD %	RSD %	RSD %
Chloroethene	>10					≤51	≤37
1,1-Dichloroethene		11	19	51	13	n.d.[1]	≤23
trans-1,2-Dichloroethene		11	16	45	12	≤66	≤39
cis-1,2-Dichloroethene		10.2	12	60	14	≤113	≤95
Trichloroethene		9.1	13	42	14	≤88	≤84
Tetrachloroethene		8.5	19	38	9.4	≤88	≤84
Benzene		10.0	15	70	15	≤98	≤82
Toluene		9.5	13	59	13	≤51	≤23
Ethylbenzene		8.6	30	46	20	≤43	≤31
o-Xylene		8.8	18	50	12	≤39	≤74
m/p-Xylenes		8.5	22	42	18	≤82	≤61
MTBE		10.6	16	95	17	≤78	≤39

[1] n.d. = no data

Due to the high variability in groundwater concentrations in the field, as seen from the RSD of the reference sample measurements, the reproducibility of the sampler measurements alone cannot be given. In Table 9, reproducibilities in the field are accordingly presented as ≤ the measured RSD.

For the performance parameter *precision,* the laboratory and standpipe results are applied.

8.2.3 Trueness

The trueness of sample measurements relative to reference sample measurements is given in Table 10 as the mean over five concentration levels up to the maximum level. The average trueness of the standpipe tests was in particular affected by high results from the samplers at the highest of the five concentration levels.

Table 10   Relative trueness (T) of sampler results.

Compound	Laboratory Direct application Mean T %	Standpipe Mean T %
Chloroethene	65	
1,1-Dichloroethene		100
trans-1,2-Dichloroethene		101
cis-1,2-Dichloroethene		129
Trichloroethene		110
Tetrachloroethene		137
Benzene		135
Toluene		131
Ethylbenzene		153
o-Xylene		139
m/p-Xylenes		138
MTBE		147

The calculated trueness is applied as presented.

8.2.4   Range of application

The highest concentrations that not be excluded as non-linear as linear for sampler measurements after visual evaluation are given in Table 11 as linear maximum concentration with the coefficient of regression (R^2), the slope (a) and the intercept (b) of the linear plot of sample measurements versus reference sample measurements.

The samplers were tested in ranges up to approximately 2,000 µg/L, see Section 5.4. Linear range data were not available for chloroethene, as this compound could not be included in the multiple concentration tests in the standpipe.

Table 11   Range of application data .

Compound	Standpipe			
	Linear maximum µg/L	Linear regression parameters		
		Coefficient R^2	Slope a	Intercept b
Chloroethene				
1,1-Dichloroethene	1,900	0.88	1.5	-350
trans-1,2-Dichloroethene	1,900	0.87	1.5	-380
cis-1,2-Dichloroethene	1,500	0.93	1.9	-360
Trichloroethene	1,700	0.97	1.5	-240
Tetrachloroethene	1,200	0.93	2.0	-350
Benzene	1,600	0.87	2.0	-390
Toluene	1,500	0.90	2.0	-430
Ethylbenzene	1,600	0.85	2.0	-270
o-Xylene	1,400	0.94	2.1	-410
m/p-Xylenes	1,300	0.92	2.2	-470
MTBE	1,700	0.82	2.3	-580

The linearity of the sampler measurements is further illustrated in for two typical compounds: trichloroethene and MTBE (best and worst case). Confidence interval error bars (α=0.05) are indicated for sample and reference sample measurements.

Figure 6   Linearity plot of trichloroethene and MTBE.
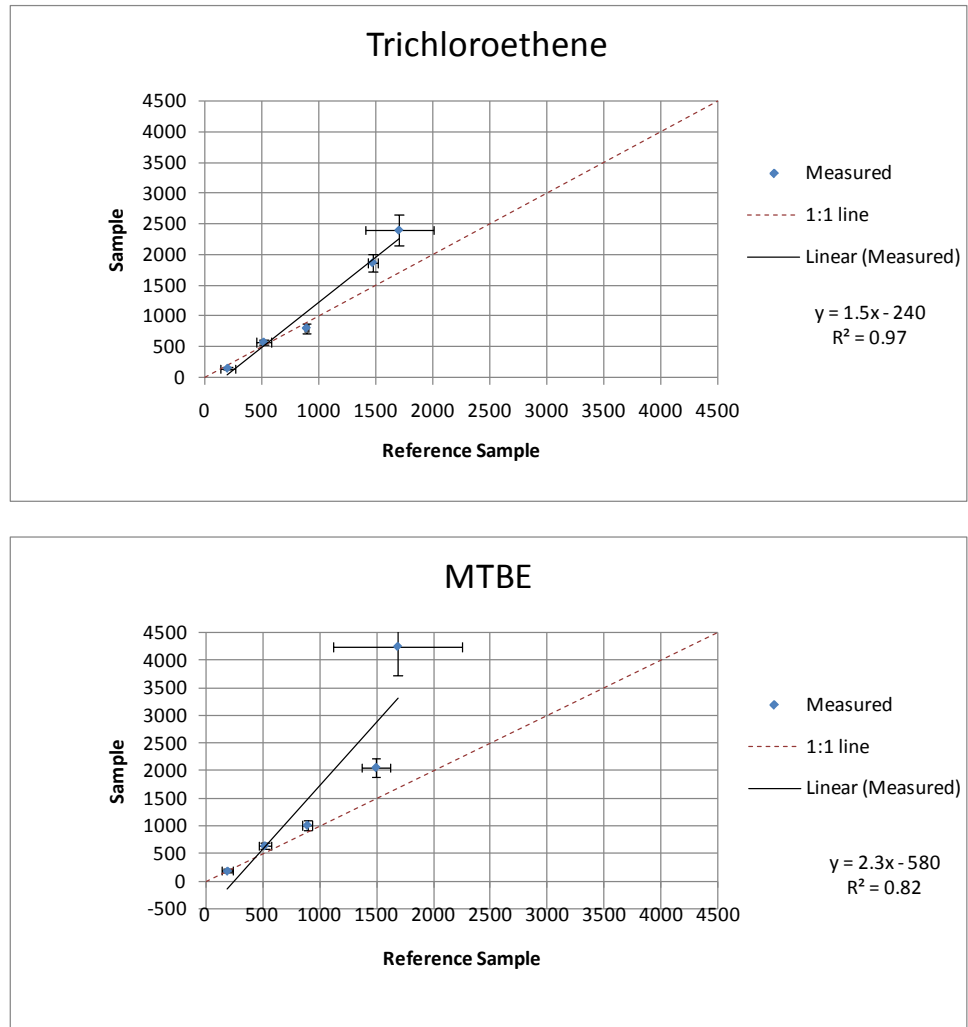
The apparent non-linearity is taken to be due to sampler series to series variation in particular for measurements of the highest concentrations.

As concentrations above the linear range were not tested, the linear maximum values given may not be the highest linear maximum concentrations that could be achieved.

Linear ranges from the limit of detection to the linear maximum is applied.

8.2.5 *Robustness*

The robustness of sample measurements with respect to controlled variations in ionic strength, exposure time, concentrations and sampling depth are given in Table 12, relative to reference conditions. Robustness values significantly different (95% confidence level, two-sided t-test) from 100% are indicated by a number in bold.

Table 12   *Robustness (R) under controlled variations in laboratory dispenser and in stand-pipe. R values significantly different (95% confidence level, two-sided t-test) from 100% indicated in bold.*

Compound	Laboratory					Standpipe
	Dispenser					
	Ionic strength[1]		Exposure time[2]		Concen-tration	Sampling-Depth
	Low R %	High R %	Short R %	Long R %	Variation[3] R %	Deep[4] R %
Chloroethene						
1,1-Dichloroethene	89	86	78	**78**	83	111
trans-1,2-Dichloroethene	94	121	100	102	116	112
cis-1,2-Dichloroethene	85	114	94	93	99	108
Trichloroethene	**83**	102	80	91	102	**120**
Tetrachloroethene	96	100	91	90	90	106
Benzene	**80**	95	**80**	90	108	105
Toluene	**76**	94	**81**	88	95	107
Ethylbenzene	**75**	87	**77**	96	95	101
o-Xylene	**72**	80	**77**	84	91	101
m/p-Xylenes	**78**	84	**82**	88	87	102
MTBE	**67**	96	**68**	87	82	100

[1] Low=10 mS/m, high = 100 mS/m, reference 35 mS/m
[2] Short= 3 days, long = 9 days, reference = 6 days
[3] Successive intervals of 20%, 50% and 80% of measuring range
[4] Deep= 5 m below surface (mbs), reference = 0.5 mbs

The general robustness values of sample measurements relative to reference sample measurements in the field are given in Table 13 as the ratios between sample and reference sample measurements. If sample measurements could not represent the same matrix as reference sample measurements (95% confidence level, paired t-test), the ratio is indicated by a number in bold.

A positive discrepancy was defined as an occasion when the sampler found a measurable concentration, while the average of the two corresponding reference samples was below the sampler's limit of detection. When calculating the average, concentrations below the reference sample limit of detection were set to half the reference sample limit of detection.

A negative discrepancy was defined an occasion when the sampler did not find a measurable concentration, while the average of the two corresponding reference were above the sampler's limit of detection. When calculating the average, concentrations below the reference sample limit of detection were set to half the reference sample limit of detection.

It should be noted that a discrepancy may reflect different principles of sampling rather than error on behalf of one of the methods.

Table 13   General robustness and frequency of discrepancy between sampler result and reference sample result. Field data, n=15.

| Compound	Field		
	Ratio between sample and reference sample measurements -	Positive discrepancy[1] %	Negative discrepancy[1] %
Chloroethene	0.24-2.1	0	0
1,1-Dichloroethene	0.82-1.1	0	0
trans-1,2-Dichloroethene	0.16-24	0	0
cis-1,2-Dichloroethene	0.45-29	0	0
Trichloroethene	0.19-15	0	7
Tetrachloroethene	0.44-4.2	0	0
Benzene	0.71-420	13	0
Toluene	**0.61-170**	13	0
Ethylbenzene	**0.12-13,000**	20	0
o-Xylene	**1.0-50**	0	0
m/p-Xylenes	0.19-500	20	20
MTBE	0.36-5.4	0	0

[1] Positive discrepancy: sampler finds measurable concentration when average of reference samples are below the sampler limit of detection. Negative discrepancy: sampler does not find measurable concentration when average of the reference samples are above sampler limit of detection.

The characteristics of the sample and reference sample measurements, as depicted in Figure 7, illustrates the discussion of the different sampling principles presented in Section 7.1.

MTBE in well B17 exhibited a large variation in concentration obtained both with reference sample measurements, and with sample measurements, expressing time integration and thus concentration integration. Ethylbenzene in well C8 is an example of the sample measurements expressing considerably higher concentrations than reference sample measurements, whereas ethylbenzene in well C11 is an example of the opposite. Combining the information on sampler measurement robustness from the laboratory and standpipe scales with these field scale data, it becomes apparent that selection of true values for well sampling and sample analysis cannot be done unless the reference conditions are adequately decided upon. Considering this, the frequencies of discrepancies only, not field ratio, are included in the performance data. Even for these data, the information conveyed should be carefully considered when interpreting the data.

The robustness is applied as the range of robustness in laboratory and standpipe, whereas the frequency of positive or negative discrepancies from the field tests were applied to illustrate field sample correspondence to reference sample measurements.

Figure 7   Sample and reference sample measurements in the field, selected wells and compounds.
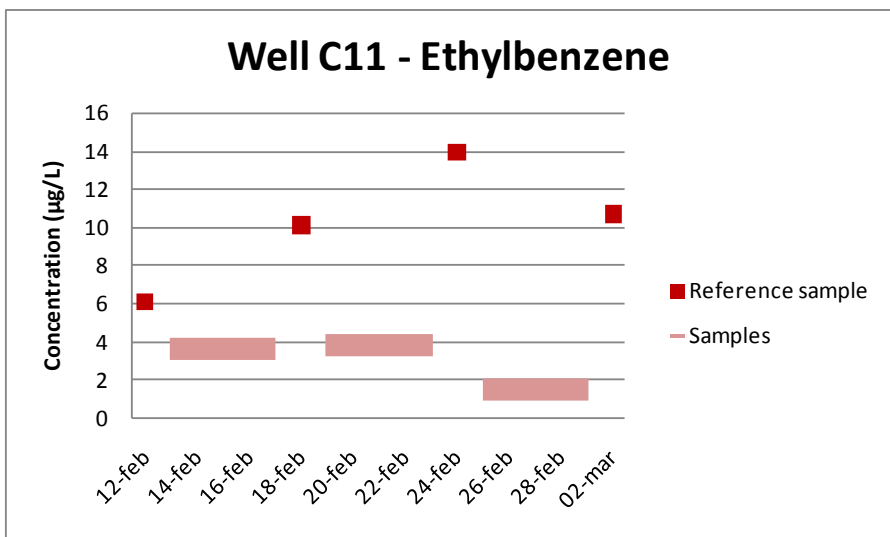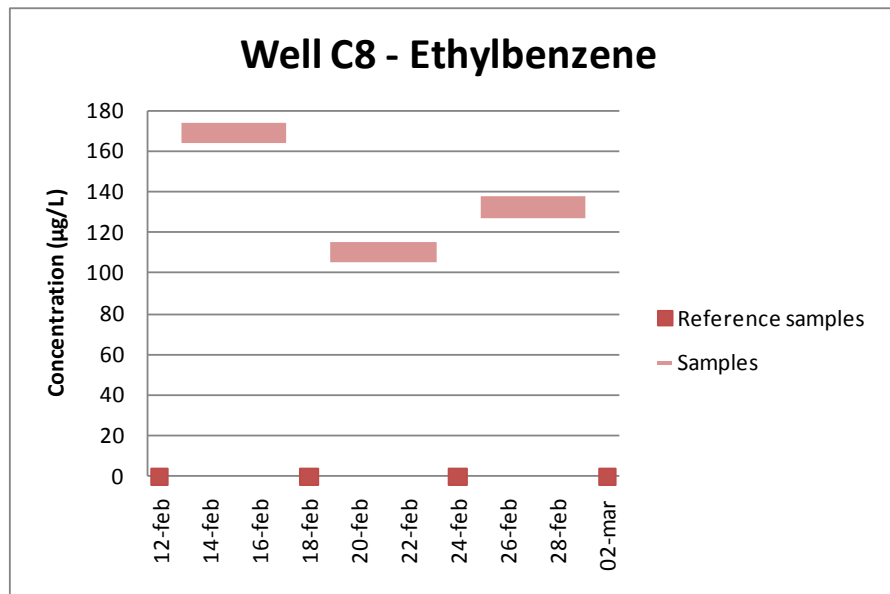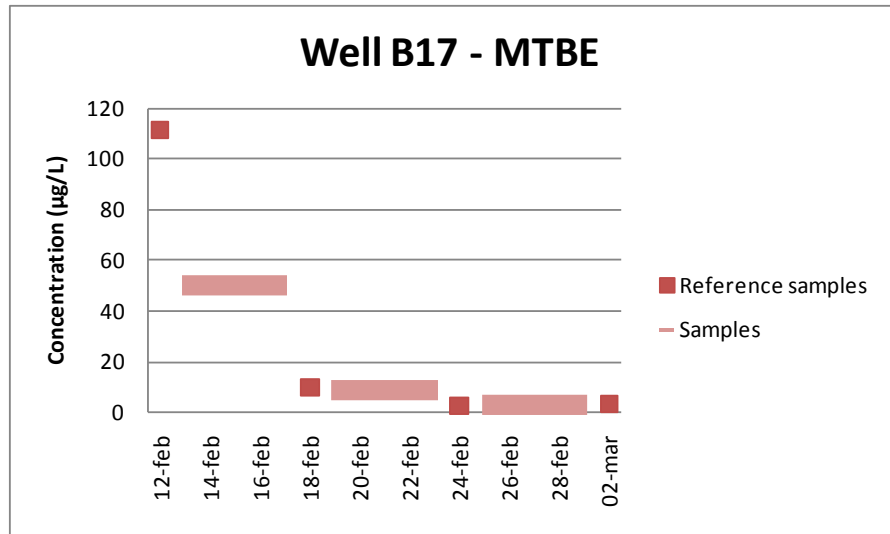
8.3 Evaluation of test quality

8.3.1 Sample analysis performance data

The performance of the sampler analysis has been reported by the vendor as given in Table 14, assuming a water volume sampled within the range used in the verification reported here. The performance reported by the vendor does therefore not include the trace salt measurements that are used for concentration calculations in routine application of the samplers.

Table 14   Performance parameters for sampler analysis reported by the vendor.

Compound	Limit of detection µg/L	Precision %	Recovery of spike to samplers %	Maximum concentration tested µg/L
Chloroethene	0.3	16	59	170
1,1-Dichloroethene	0.3	12	79	170
1,2-Dichloroethenes	0.2	11	82	170
Trichloroethene	0.2	11	92	170
Tetrachloroethene	0.2	19	103	170
Benzene	0.2	11	89	170
Toluene	0.1	10	87	170
Ethylbenzene	0.1	11	92	170
o-Xylene	0.2	10	93	170
m/p-Xylenes	0.3	10	92	170
MTBE	0.3	14	88	170

8.3.2 Reference analysis control data

The quality of the reference analyses is summarized in Table 15.

The three replicate reference analyses of the volatile halogenated organic compounds (VOX), standard dilution produced a trueness of 97-110% for the six compounds, in average 106%.

Out of 15 reference analyses of VOC stock solution, five were done on original 1.5 mL vials that had not been opened before. Those five analyses produced a trueness of 97-107%, for the 11 compounds, in average 101% of the true values stated in Table 15. The precision of these four analyses ranges from 3-11%, in average 5%.

During the test of the product's limit of detection in the standpipe, reference samples of groundwater with concentrations for all compounds around 2.5 µg/L were taken at three occasions as 2 or 3 replicates. From the triplicate, a conservative estimate of the LoD was derived, between <0.09 and <0.30 µg/L for the 11 compounds.

The laboratory provided data for participation in a proficiency test demonstrating that for chloroethene and 1,1-dichloroethene, a significant deviation from 100% trueness was found. The deviation for 1,1-dichloroethene was subsequently resolved and corrected as an analytical error.

The reference laboratory provided data from their routine quality control measures demonstrating limits of detection and trueness corresponding to the required analytical quality, see Table 6, but a precision slightly inferior to the requirement (5-11% RSD, requirement < 5% RSD).

Table 15   Summary of analytical reference performance control. Data given as range over the tested compounds, with average in parenthesis.

Control type	Limit of detection µg/L	Precision RSD %	Trueness %
VOX[1] standard solution	-	-	97-110 (106)
VOC stock solutions[2]	-	3-11 (5)	97-107 (101)
Groundwater	<0.09-<0.30	-	-
Laboratory quality control	0.008-0.01	5-11	93-110
Proficiency test	-	-	90-140 (106)

[1] Volatile halogenated organic compounds [2] From unopened stock solution vials only

Overall, the reference analysis quality data indicated precision and trueness satisfying the requirements for most compounds but with a concern for high results for chloroethene. For ethylbenzene, an error of preparation of the stock solution was indicated.

8.3.3   Test system
Reference analysis of the water used in laboratory test and water from the test system (dispenser, after 30 minutes and after 6 days) gave results below the LoD.

The field blank data did not indicate any substantial contamination with VOCs during field sample handling.

Over the test period, the stock solution concentrations varied considerably, and for 6 compounds the mean reference analysis measurements were significantly different from the true value calculated from added amounts and volumes of the prepared stock solutions. For these compounds, reference analysis measurements were assumed to be correct, see compounds listed as analyzed under Data source in Table 16.

Table 16 True concentrations in the stock solution.

Compound	True value g/L	Data source
1,1-Dichloroethene	9.7	calculated
trans-1,2-Dichloroethene	10.1	calculated
cis-1,2-Dichloroethene	7.70	calculated
Trichloroethene	9.79	analyzed
Tetrachloroethene	9.74	calculated
Benzene	8.98	analyzed
Toluene	9.04	analyzed
Ethylbenzene	13.9	analyzed
o-Xylene	8.90	analyzed
m-Xylene	10.4	calculated
MTBE	8.52	analyzed

The dispenser laboratory test system showed stable concentrations after 6 days and concentrations in the dispenser as measured by reference analysis corresponding to the true values.

Conversely, sample measurements were lower than the true values for most compounds. The deviations from 100% trueness were correlated to compound volatility, but not to compound polarity. In the dispenser, test solution was lead to the sampler through polymer capillaries supplied by the vendor. The plots of difference between sample measurement and true value (calculated from added amounts and volumes of the prepared stock solutions) against log K_{ow} (partitioning coefficient octanol water) and k_H (partitioning coefficient air water) did not support that loss through adsorption should be important (should exhibit inverse relationship between trueness deviation and partitioning coefficient), whereas loss of compounds by evaporation e.g. through the capillaries cannot be excluded (relationship between trueness deviation and Henry's law constant cannot be excluded). Accordingly, dispenser trueness data are not used independently but only as reference for robustness assessments.

The standpipe test system exhibited high reference sample measurements for the samples taken after two hours, followed by a lower and stable plateau. The initial high reference sample measurements were taken to reflect incomplete mixing in the test system and subsequently, the first reference samples were taken after four hours. The standpipe test system was made of the same materials as the dispenser test system with no adsorption observed, but adsorption to the sampling system with up to seven samplers suspended in the standpipe cannot be excluded. As reduced test solution concentrations in the standpipe due to adsorption could not be ruled out, reference sample based concentrations were used as true values in standpipe test.

8.3.4 Data transfer control

The spreadsheet used for the calculations were subject to control on a sample basis (>5% random test) without identifying any incorrect data transfers.

8.3.5 Amendments and deviations

No amendments to the verification protocol have been done. One deviation from the verification protocol has been done, implementing adaptation of calculation methods to the data characteristics to what is now shown in Table 7.

Four amendments have been done to the test plan. The amendments concerned change in field site, change in sample handling procedure and changes in test procedure (timing of reference sample, spike procedure). Totally 31 deviations from the test plan were observed. The deviations concerned laboratory, standpipe and field unforeseen incidents. Corrective and preventive actions were taken. To the degree that changes and incidents could impact the test and/or verification outcome, this has been discussed in the test and/or verification reports.

8.4 Additional parameters summary

8.4.1 User manual

The verification criterion for the user's manual is that it describes the use of the samplers adequately and that it is understandable to the typical sampler user and sampling planner. This criterion was evaluated by a number of specific points of importance, see Table 17 for the parameters included and the assessment outcomes.

A description was considered complete, if all essential steps were described, if they were illustrated with a figure or a photo, where relevant, and if the descriptions were understandable without reference to other guidance.

The user manual evaluation included four documents provided by the vendor:

- Sorbisense Product Sheet for Sorbisense GWS40 (shallow), version October 2008.
- GWS40 Users Manual, version October 2008.
- Sorbisense Product Sheet for SorbiCell (VOC), version October 2008.
- SorbiCell Users Manual, version October 2008.

The documentation given in the above documents described the method and covered the practical aspects of using the product.

Table 17   Criteria for user manual evaluation.

Parameter	Complete description	Summary description	No description	Not relevant
Product				
Principle of operation	√			
Intended use	√			
Performance expected	√			
Limitations		√		
Preparations				
Unpacking	√			
Transport				√
Assembly	√			
Installation	√			
Function test				√
Operation				
Steps of operation	√			
Points of caution	√			
Accessories				√
Maintenance			√	
Trouble shooting	√			
Safety				
Chemicals				√
Power				√

The information about the limitations of the application of the samplers was incomplete. The product sheet did not contain information about interfering substances. Also, neither the samplers nor the aluminum bags in which they were delivered carried a "best before date".

Information about the maintenance of the GWS40 reservoirs was missing. It was not stated in the user manual or product sheet if the reservoirs should be cleaned when moved between wells with different concentrations of contaminants, nor how they should be maintained between sampling campaigns.

8.4.2 Product costs

The capital investment costs and the operation and maintenance cost were itemized based upon a determined design basis /12/, see Table 18 for the items included. The design basis is monitoring at one site with 5 wells once a year over a five year period, totally 25 samples. It is presupposed that each sampling of the site should include all wells. Well establishment, equipment for well purging and reference sampling is not included.

Table 18   *List of capital cost items and operation and maintenance cost items per product unit (sample). Number stated is number needed for a total of 25 analyses.*

Item type	Cost item to include with example case design	Need
Capital		
Site preparation	Preparation of wells for access	5 days per 25 samples
Equipment	Samplers	5 per 25 samples
Start up/training	Sampling staff training (days/sample)	1 day per 25 samples
Operation and maintenance		
Materials, including chemicals	Samplers (number)	25 per 25 samples
Labor	Sampling without transport (days/sample)	2½ day per 25 samples
	Cleaning of samplers (days/sample)	2½ day per 25 samples

Note that the actual costs for each item were not compiled and reported.

8.4.3 Occupational health and environment

The risks for occupational health and safety and for the environment associated with the use of the product were compiled. The compilation emphasized chemicals used during product operation and classified as toxic, T, or very toxic, Tx, for human health and/or very environmentally hazardous (N) according to /13/. No consumption of hazardous chemicals was identified during sampling. The use of chemicals for sample analysis and reference sample analysis was not evaluated.

No risks from installing, operating and maintaining the product were identified, including risks for human health associated with power supply and danger of infections was considered. No additional risks compared to conventional groundwater sampling of contaminated samples were identified.

8.5 Operational parameters

The groundwater chemistry covered in the test is summarized in Table 19.

Table 19   Mean groundwater chemistry for standpipe and field sites, data for standpipe from /14/.

Site	Standpipe	Søborg (3 wells)		Farum (2 wells)	
	-	mean	st.dev.	mean	st. dev
	mg/L	mg/L	mg/L	mg/L	mg/L
Ca	76	233	15	125	7.1
Mg	27	25	3.1	8.0	1.1
K	4.8	4.7	0.4	1.7	0.14
Na	38	120	36	19	2.8
Fe	0.09	5.2	2.8	1.5	0.49
Ammonium	0.016	0.77	0.14	0.46	0.53
Nitrate	3.81	<0.5	-	<0.5-0.84	-
Chloride	51	340	62	53	22
Fluoride	0.91	0.30	0.015	0.28	0.042
Sulphate	10	157	40	75	23
Bicarbonate	369	482	81	315	28
NVOC[1] (DOC[2])	3.3	3.0	0.74	5.9	4.5
Ionic strength (moles/l)	0.011	0.028	0.0012	0.012	0.00055
pH	7.8	6.9	0.081	7.2	0.10
Conductivity (µS/cm)	740	2,020	156	733	32

[1] Non-Volatile Organic Carbon [2] Dissolved Organic Carbon

The sampler operational parameters tested in laboratory and field tests are summarized in Table 20.

Table 20   Parameters for sampler operation during testing.

Sampling Temperature[1]	Sampling depth	Sample volume	Sampling period
°C	m below water surface	mL	Days
9-22	0.5-5	80-620	3-9

[1] The temperature in the field could not be measured precisely, since the pump warmed the water in the well. First temperature measurement is used as estimate.
[2] For volumes over 500 mL, sample volumes measured manually were used

8.6 Recommendations for verification statement

The verification statement shall include the application definition as given in Table 1. The performance parameters verified shall be summarized as given in Table 21.

Table 21   Performance parameter summary.

Compound	Limit of detection	Precision		Trueness	Range of application	Robust-ness	Discrepan-cies positive/ negative
	LoD µg/L	Repeatability %	Reproducibility %	%	LoD- µg/L	%	%/%
Chloroethene	<30	>10	<51	65	n.d.[1]	n.d.[1]	0/0
1,1-Dichloroethene	<90	11	51	100	1,900	78-111	0/0
trans-1,2-dichloroethene	4	11	45	101	1,900	94-121	0/0
cis-1,2-Dichloroethenes	4	10.2	60	129	1,500	85-114	0/0
Trichloroethene	70	9.1	42	110	1,700	80-120	0/7
Tetrachloroethene	2	8.5	38	137	1,200	90-106	0/0
Benzene	3	10.0	70	135	1,600	80-108	13/0
Toluene	4	9.5	59	131	1,500	76-107	13/0
Ethylbenzene	5	8.6	46	153	1,600	75-101	20/0
o-Xylene	4	8.8	50	139	1,400	72-101	0/0
m/p-Xylenes	3	8.5	42	138	1,300	78-102	20/20
MTBE	6	10.6	95	147	1,700	67-100	0/0

[1] no data

The user manual and other instructions are described as complete, except for the description of product limitations, maintenance and storage.

The product costs are described in Table 18.

The risks for occupational health and environment are not associated with the use of hazardous chemicals or other additional risks, compared to conventional groundwater sampling

The operational parameters are described in Table 20 and Table 22, where Table 22 gives the full range of concentration measured.

Table 22   Range of water chemistry in test in standpipe and field. For the tests using the sample dispenser, (MilliQ) water was used with potassium chloride for adjustment of conductivity. The addition of potassium is not included in the table.

Parameter	Range mg/L	Parameter	Range mg/L (unless otherwise indicated)
Ca	76-250	Chloride	37-410
Mg	7.2-28	Fluoride	0.25-0.91
K	1.6-5.2	Sulphate	10-200
Na	17-160	Bicarbonate	295-575
Fe	0.09-7.1	NVOC (DOC)	2.4-9.0
Ammonium	0.016-0.89	Ionic strength	0.011-0.028 (moles/l)
Nitrate	<0.5-3.8	pH	6.8-7.8 (-)

9   VERIFICATION SCHEDULE

The verification was done in 2008-2010. The overall schedule is given in Table 23.

Table 23   Verification schedule 2008-2010

Task	Timing
Verification protocol with test plan	Approved January 2009
Test	January to April 2009
Test reporting	May to October 2009
Verification	August 2009
Verification reporting	September to October 2009
Report document draft	September to October 2009
Report document review	October 2009 to January 2010
Verification statement	February 2010

10   QUALITY ASSURANCE

The Quality Assurance (QA) of the verification is described in Table 24 and Figure 2, and the quality assurance of the tests in the test report but is summarized here, as well as in the process document /3/.

Table 24   QA plan for the verification.

	DHI		Battelle AMS Center TSA[1]	US EPA QA	Technical experts
Initials	ALJ	LSC	ZW	MH, JMK, EH	CP, DM, MS
Tasks					
Verification protocol, test plan and process document	Review	-	Review	Review	Review
Test system	-	Audit	Audit	-	-
Test report, verification report and verification statement	Review	-	Review	Review (excluding test report)	Review

[1] TSA = technical systems audit

DHI internal review of plan and report documents were done by chief engineer Anders Lynggaard-Jensen (ALJ), and test system audit (see test report) was done following the Good Laboratory Practice (GLP) audit procedure /15/ by a trained auditor: head of laboratory products Louise Schlüter (LSC). Reviews and audits were done using the NOWATECH review report template and audit templates. Document review comments were addressed and/or implemented in the documents as indicated in the review reports. The internal audit reported two comments: delay of standpipe tests and a changed sequence in a test process that was subsequently reported as deviation and implemented in the test procedure.

The Battelle quality manager, Zachary Willenberg (ZW), performed technical systems audit (TSA) during this verification and test, including audit of the ref-

erence laboratory used. The audit report included 5 comments, two deviations and two amendments were filed to address these.

EPA QA staff, Michelle Henderson (MH), John McKernan (JMK) and Evelyn Hartzell (EH) reviewed the planning documents, the verification report and statement. Document review comments were addressed and/or implemented in the documents as indicated in the review reports.

The expert group did review of the plan and report documents. Reviews and audits were done using the NOWATECH review report template and audit templates. Document review comments were addressed and/or implemented in the documents as indicated in the review reports.

A P P E N D I X   1

Terms and definitions used in the verification protocol

The abbreviations and definitions used in the verification protocol and the test plan are summarized below.

Word	NOWATECH
AMS Center	Advanced Monitoring Systems Center at Battelle
Analysis	Analysis of Sorbisense samplers at the vendor identified laboratory
Application	The use of a product specified with respect to matrix, target, effect and limitations
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
Direct application	A test design where a standard solution is applied directly to the Sorbisense samplers
Discrepancy	Positive discrepancy: sampler finds measurable concentration when average of reference samples are below the sampler limit of detection. Negative discrepancy: sampler does not find measurable concentration when average of the reference samples are above sampler limit of detection.
DOC	Dissolved Organic Carbon
Effect	The way the target is affected, in this verification the measurement of volatile organic contaminants
EN	European standard
ETV	Environmental technology verification (ETV) is an independent (third party) assessment of the performance of a technology or a product for a specified application, under defined conditions and adequate quality assurance.
EU	European Union
Evaluation	Evaluation of test data for a technology product for performance and data quality
Experts	Independent persons qualified on a technology in verification or on verification as a process
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
GLP	Good Laboratory Practice
Groundwater investigation	Investigation of groundwater contamination with measurements controlled against groundwater maximum concentrations
Groundwater monitoring	Baseline monitoring of groundwater quality
GRUMO	The Danish groundwater monitoring program
GWS	Groundwater sampler
ICP	Inductively Coupled Plasma
k_H	Partitioning coefficient air water
K_{ow}	Partitioning coefficient octanol water
Limit of detection, LoD	Calculated from the standard deviation of replicate measurements at less than 5 times the detection limit evaluated. Corresponding to less than 5% risk of false blanks
Limit of quantification, LoQ	Calculated from the detection limit, typically 3 times the LoD, the concentration, where the blank variation impacts the precision 20%
Matrix	The type of material that the product is intended for
mbgw	Meters below groundwater table
mbs	m below surface
Method	Generic document that provides rules, guidelines or characteristics for tests or analysis
MS	Mass Spectrometry
MTBE	Methyl-*tert*-butylether
NOWATECH ETV	Nordic Water Technology Verification Centers
NOWATECH WMC	NOWATECH Water Monitoring ETV Center, operated by DHI
NVOC	Non-Volatile Organic Carbon
P&T	Purge and Trap

Word	NOWATECH
Performance parameters	Parameters that can be documented quantitatively in tests and that provide the relevant information on the performance of an environmental technology product
Precision	The standard deviation obtained from replicate measurements, here measured under repeatability or reproducibility conditions
PVC	Polyvinylchloride
QA	Quality assurance
Range of application	The range from the LoD to the highest concentration with linear response
Ratio	The ratio between one sample measurement and the mean of the reference sample measurements before and after the sample measurement
Reference analyses	Analysis by a specified reference method in an accredited (ISO 17025) laboratory
Reference samples	Samples taken for and analyzed by a specified reference method in an accredited (ISO 17025) laboratory
Repeatability	The precision obtained under repeatability conditions, that is with the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time
Reproducibility	The precision obtained under reproducibility conditions, that is with measurements that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects
Robustness	% variation in measurements resulting from defined changes in matrix properties
RSD	Relative standard deviation in %
Sample dispenser	Test device designed for controlled exposure of Sorbisense samplers to test solutions
Sampler	Sorbisense sorbent cartridge
Samples	Samples taken with and analyzed after the Sorbisense method
Sampling system	The sampling reservoir and venting system used to operate the Sorbisense samplers
SIM	Selected Ion Monitoring
Standard	Generic document established by consensus and approved by a recognized standardization body that provides rules, guidelines or characteristics for tests or analysis
Standpipe	Test device designed to simulate a groundwater well
Target	The property that is affected by the product, in this verification the target performance parameters measured
(Environmental) technology	The practical application of knowledge in the environmental area in a technology whose use is less environmentally harmful than relevant alternatives
Trueness	The % recovery of true value obtained either from knowledge on the preparation of test solutions or from measurements with reference methods
TSA	Technical system audit
US EPA	United States Environmental Protection Agency
Vendor	The party delivering the product or service to the customer
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance
VOC	Volatile organic compounds, here the compounds listed as target compounds/analytical parameters
VOX	Volatile halogenated organic compounds, here the halogenated compounds listed as target compounds/analytical parameters
WQS	Water Quality Standard
WS	Workshop (under CEN)

A P P E N D I X   2

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A P P E N D I X   3

Application and performance parameter definitions

This appendix defines the application and the relevant performance parameters application as input for verification and test of an environmental technology following the NOWATECH ETV method.

1 Applications

The intended application of the product for verification is defined in terms of the matrix, the targets and the effects of the product.

The Sorbisense GWS40 passive sampling system with samplers (cartridges) and analysis of the samplers is provided by the vendor as one product, and the verification shall accordingly see these two investigation steps as one.

1.1 Matrix/matrices

The matrix of the application is groundwater and the field of application is investigations of (potentially) contaminated groundwater (groundwater investigations). In groundwater investigations, the groundwater composition generally varies considerably, and the pressure on samplers will vary with depth to the sampling positions. The varying ionic strength, contaminant concentration and water pressure may impact the performance and this impact shall be evaluated as part of the verification.

1.2 Effects

The effect of the application is measurement of volatile organic contaminants, here mono-, di-, tri- and -tetrachloroethenes, BTEX and MTBE, in the defined matrix.

1.3 Target(s)

The targets of the application are the performance parameters for measurement of volatile organic contaminants in the defined matrix.

The performance parameters of monitoring devices are generally reported in terms of limit of detection (LoD), precision, trueness, range of application and robustness. The effects claimed by the vendor are given in Appendix table 1 for all target compounds.

The robustness is the change in trueness within the range of application for defined variations in water pressure, contaminant concentration, groundwater ionic strength and sampling time.

Investigations of contaminated groundwater generally include both uncontaminated and strongly contaminated groundwater. The concentrations verified shall accordingly reflect the range from uncontaminated groundwater to highly contaminated groundwater. With the claimed application at sampling depths from 0.5 mbs to 5 mbs (m below surface), pressure variation in the range 1.05 to 1.5 atmosphere shall be verified. Furthermore, with the claimed application, groundwater ionic strengths within the range 10 to 100 mS/m shall be verified, corresponding to the 5 to 95 percentile of Danish groundwaters /6/.

Appendix table 1   Vendor claim of performance, general terms.

Compound	Limit of detection	Precision	Trueness	Range of application	Robustness
	µg/L	%	%	µg/L	%
Chloroethene	0.5	<20	>80	LoD-2000	100±30
1,1-Dichloroethene	0.5	<20	>80	LoD-2000	100±30
1,2-Dichloroethenes	0.5	<20	>80	LoD-2000	100±30
Trichloroethene	0.5	<20	>80	LoD-2000	100±30
Tetrachloroethene	0.5	<20	>80	LoD-2000	100±30
Benzene	0.5	<20	>80	LoD-2000	100±30
Toluene	0.5	<20	>80	LoD-2000	100±30
Ethylbenzene	0.5	<20	>80	LoD-2000	100±30
Xylenes	0.5	<20	>80	LoD-2000	100±30
MTBE	1	<20	>80	LoD-2000	100±30

1.4 Exclusions

Passive sampling at waste disposal sites is excluded from the defined application and is thus not covered by the verification, as the conditions with respect to ionic strength and DOC are outside the ranges covered by the verification conditions. Groundwater baseline monitoring and drinking water control are excluded as well, as the passive sampler will not satisfy the detection limit requirements for this purpose, see Appendix Section 2.1.

2   General performance requirements

No formal performance requirements for the application have been identified in the European Union or the US.

The conventional performance parameters of analytical and monitoring methods and equipment are limit of detection (LoD), precision (repeatability and reproducibility), trueness, specificity, linearity and matrix sensitivity. The uncertainty of measurements may be used to summarize the performance. Parameters may be added to characterize e.g. on-line or on-site monitoring instruments. The listed parameters cover the requirements set or implemented in international standards or by testing the verification operators /16-20/.

2.1 Regulatory requirements

The general requirement for analytical quality in water monitoring in Europe will be established with the adoption of the Commission Directive on technical specifications for chemical analysis and monitoring of water status /21/ requiring no more than 25% relative standard deviation at the level of the relevant water quality standards. The Limit of Quantification (LoQ) must be at or below 30% of the relevant Water Quality Standard (WQS), corresponding to a limit of detection at or below 10% of the WQS. The LoQ is as defined in ISO 6107-2: 2006 /22/. The Groundwater Directive /23/ only sets an absolute requirement for monitoring of tri- and tetrachloroethene during groundwater monitoring without stating the water quality standard and the quality requirement.

The European Directive on drinking water /24/ defines performance requirements for methods used for control of drinking water quality for the VOCs benzene, tri- and tetrachloroethene, among others. These values cover the

chemical analysis only, and quality requirements for drinking water control would mostly be seen as stricter than for groundwater investigations. The drinking water based performance requirements for analysis only should, therefore, be seen as strict compared to groundwater monitoring including also sampling, see Appendix table 2.

Appendix table 2   Regulatory requirements from the European drinking water directive.

Compound	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L	Robust-ness %
Trichloroethene	1	25	75-125	-[3]	-
Tetrachloroethene	1	25	75-125	-	-
Benzene	0.25	25	75-125	-	-

The Monitoring Certification Scheme of the British Environment Agency does not provide performance standards for groundwater or drinking water monitoring /16/.

The Danish statute on quality requirements for environmental control /25/ specifies the requirements for control and monitoring of mono-, di-, tri- and – tetrachloroethenes and benzene in groundwater as shown in Appendix table 3. The detection limits stated are not justified by the maximum concentrations for groundwater, except for chloroethene, see Section 2.2.

Again, it should be noted that the requirements cover analysis only and must thus be seen as stricter than required for methods including sampling.

Appendix table 3   Regulatory requirements for groundwater monitoring and control from the Danish analytical quality requirement statute.

Compound	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L	Robust-ness %
Chloroethene	0.03	5	100±10[4]	-	-
1,1-Dichloroethene	0.03	5	100±10	-	-
1,2-Dichloroethenes	0.03	5	100±10	-	-
Trichloroethene	0.03	5	100±10	-	-
Tetrachloroethene	0.03	5	100±10	-	-
Benzene	0.03	5	100±10	-	-

2.2 Application based requirements

The application of the samplers in groundwater investigations further defines performance requirements in terms of the contaminant concentrations monitored and controlled during investigations in general. The lower limit of concentrations to be monitored will in most cases be defined by the groundwater maximum concentrations (and as a lower limit the drinking water maximum concentrations) for the compounds in question, see Appendix table 4.

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[3] -: no requirement.
[4] Assuming a 5% relative standard deviation.

Appendix table 4   Summary of groundwater and drinking water maximum concentrations, as summarized in /26/ and /27/.

Compound	Groundwater Denmark µg/L	Drinking water		
		EU µg/L	US µg/L	WHO µg/L
Chloroethene	0.2	0.5	2	0.3
1,1-Dichloroethene	1	-	7	30
1,2-Dichloroethenes	1	-	70-100	50
Trichloroethene	1	10	5	70
Tetrachloroethene	1	10	5	40
Benzene	1	1	5	10
Toluene	5	-	1000	700
Ethylbenzene	-	-	100	300
Xylenes	5	-	$10*10^3$	500
MTBE	2-5	-	20-40	-

A general requirement for the limit of detection of 1/10 of the maximum concentration is applied widely, and the derived limits of detection are compiled in Appendix table 5. Required detection limits for both drinking water and groundwater control are in the same ranges in Austria.

For the Danish Groundwater Monitoring Program (GRUMO), requirements for detection limits are as given in Appendix table 5 /28/. It should be noted, that the detection limits required here for groundwater monitoring do not comply with those required in Danish statute on quality requirements for environmental control /25/ covering also monitoring of the compounds in groundwater as shown in Appendix table 5.

Appendix table 5   Summary of detection limit requirements derived from the groundwater and drinking water maximum concentrations and for the Danish groundwater monitoring program, 2003.

Compound	Groundwater maximum concentration based Denmark µg/L	Drinking water maximum concentration based			Groundwater monitoring based Denmark µg/L
		EU µg/L	US µg/L	WHO µg/L	
Chloroethene	0.02	0.05	0.2	0.03	0.05
1,1-Dichloroethene	0.1	-	0.7	3	-
1,2-Dichloroethenes	0.1	-	7	5	-
Trichloroethene	0.1	1	0.5	7	0.02
Tetrachloroethene	0.1	1	0.5	4	0.02
Benzene	0.1	0.1	0.5	1	0.04
Toluene	0.5	-	100	70	0.04
Ethylbenzene	-	-	10	30	-
Xylenes	0.5	-	1000	50	0.02
MTBE	0.2	-	2	-	-

Application based requirements for trueness and precision have generally not been stated to the same degree as for the limits of detection, mainly because regulatory compliance rules in most cases do not consider the uncertainty of control results.

No requirements for range of application and robustness have been identified. In practical performance of site investigations, the dissolved concentrations range from below detection limit to the limit of solubility. The upper limit of concentrations to be monitored will thus in most cases be defined by the solubilities of the target compounds are summarized in Appendix table 6.

Appendix table 6   Summary of target compound solubilities.

Compound	Water solubility µg/L
Chloroethene	$2.8*10^6$
1,1-Dichloroethene	$3.3*10^6$
1,2-Dichloroethenes	$3.5-6.3*10^6$
Trichloroethene	$1.4*10^6$
Tetrachloroethene	$0.24*10^6$
Benzene	$1.8*10^6$
Toluene	$0.55*10^6$
Ethylbenzene	$0.17*10^6$
Xylenes	$0.16-0.20*10^6$
MTBE	$1.8*10^6$

3   State-of-the-art performance

Whereas a broad range of studies on the performance of analytical methods and sampling methods for VOC in groundwater have been published, independent and comparative studies of passive samplers used for VOC monitoring in groundwater are scarce. Examples of reported performances (sampling and analysis) are compiled in Appendix table 7.

Appendix table 7   Summary of state-of-the-art performance for passive samplers.

Sampler	Limit of Detection µg/L	Precision %	Trueness %	Range of application[5] µg/L	Robust-ness %	Refer-ence
GORE-SORBER	-	14-21	-	5-2000	-	/29/
USGS PDB	-	0.9-4.3	86-118	2-500	-	/30/
Dialysis membrane sampler	0.1-5	17	100%	$0.2-25*10^3$	-	/31/
USGS PDB		21			-	

Reported performance (sampling and analysis) as obtained with reference sampling is given Appendix table 8.

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[5] Verified range of application, practical range may differ.

Appendix table 8   Summary of state of the art performance for reference samplers.

Sampler	Limit of detection	Precision	Trueness	Range of application	Robust-ness	Refer-ence
	µg/L	%	%	µg/L	%	
Grab sampling	-	12%	-	5-2000	-	/29/
Grab sampling	-	1.1-9.8	-	2-500	-	/30/
Low purge pump sampling	-	15	-	$0.2\text{-}25*10^3$	-	/31/

The precision results obtained with the passive samplers do not greatly differ from the precision values obtained with reference sampling methods. As the precision data obtained with the reference methods will generally be accepted for groundwater monitoring and control, the precision data obtained with the passive samplers should also be considered acceptable.

4   Performance parameter definitions

The statement of regulatory and application based requirements in terms of the analytical quality rather than the combined quality of analysis and sampling, as relevant for passive samplers, makes the identification of relevant performance parameters and ranges difficult for passive samplers.

Only a limited number of studies on the contributions of sampling and analysis, respectively, to the limit of detection, precision and trueness of groundwater monitoring and control have been published. Therefore, the regulatory and application based requirements identified for analytical performance cannot be directly translated into the combined sampling and analysis performance parameters and ranges relevant for passive samplers.

The discrepancies between requirements based upon different approaches when comparing Appendix table 2, Appendix table 3 and Appendix table 5, further hampers the identification of relevant criteria.

Therefore, relevant performance parameters and ranges for the application are set in Appendix table 9 based upon regulatory, see Appendix tables 2 and 3, and application based, see Appendix table 5, requirements and state-of-the-art performance, see Appendix table 7.

In order to address the general definition of performance parameters in terms of analytical quality only, information on this using the sampler should be obtained from the responsible laboratory for comparison, if possible.

In addition to the straight forward performance parameters of limit of detection, precision, trueness and range of application, the robustness shall be tested for the critical parameters identified here: variations in water pressure, contaminant concentration, groundwater ionic strength and sampling time.

Appendix table 9   *Relevant ranges of performance parameters for groundwater investigations.*

Compound	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L	Robustness %
Chloroethene	0.02-0.05	<25	75-125	LoD-1*10^6	100±15
1,1-Dichloroethene	0.1-1	<25	75-125	LoD-1*10^6	100±25
1,2-Dichloroethenes	0.1-1	<25	75-125	LoD-1*10^6	100±25
Trichloroethene	0.1-1	<25	75-125	LoD-1*10^6	100±25
Tetrachloroethene	0.1-1	<25	75-125	LoD-1*10^5	100±25
Benzene	0.1-1	<25	75-125	LoD-1*10^6	100±25
Toluene	0.5-5	<25	75-125	LoD-1*10^5	100±25
Ethylbenzene	0.5-5	<25	75-125	LoD-1*10^5	100±25
Xylenes	0.5-5	<25	75-125	LoD-1*10^5	100±25
MTBE	0.2-2	<25	75-125	LoD-1*10^6	100±25