Sorbisense GSW40 Passive Sampler

Joint verification protocol

Volatile organic compounds in groundwater

January 2009

Version approved

Sorbisense GSW40 Passive Sampler

Joint verification protocol

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Project	Project No
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	Approved by

Revision	Description	By	Checked	Approved	Date
	Joint verification protocol	CHG	ALJ	ALJ	

Key words	Classification
Environmental technology verification, passive sampler, groundwater	☒ Open ☐ Internal ☐ Proprietary

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DHI	CHG, GHE, MTA	
UBA-A	DM	
Battelle	AMG, ZJW	
US EPA	LD	

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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.

This verification is a joint verification with the US EPA ETV scheme and the Advanced Monitoring Systems Centre, Battelle, see the verification protocol /1/ for details on organization and implications. The compliance of the test with both scheme's requirements is ensured through a process document /2/.

2.1 Name of product

The product is the Sorbisense GWS40 passive sampling system (106-012-11) with samplers (cartridges) for analysis of volatile organic compounds (VOCs) (no. 043-0091-12, 043-0101-12, 043-0102-12). The analysis of the samplers is 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, +45 8999 2599.

Contact: Hubert de Jonge, e-mail hubert@sorbisense.com.

The laboratory responsible for the analysis of samples (subcontractor to the vendor) is: ALcontrol Laboratories, Steenhouwerstraat 15, 3194 AG Hoogvliet, Netherlands,

Contact: Jaap Willem Hutter, e-mail j.hutter@alcontrol.nl

2.3 Name of center/verification responsible

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

Verification responsible: Christian Grøn, e-mail chg@dhigroup.com, phone +45 95 16 95 70, mobile +45 29 65 34 47.

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 will be conducted as a joint verification between the Nordic Water Technology Verification Centers (NOWATECH ETV) and the U.S. En-

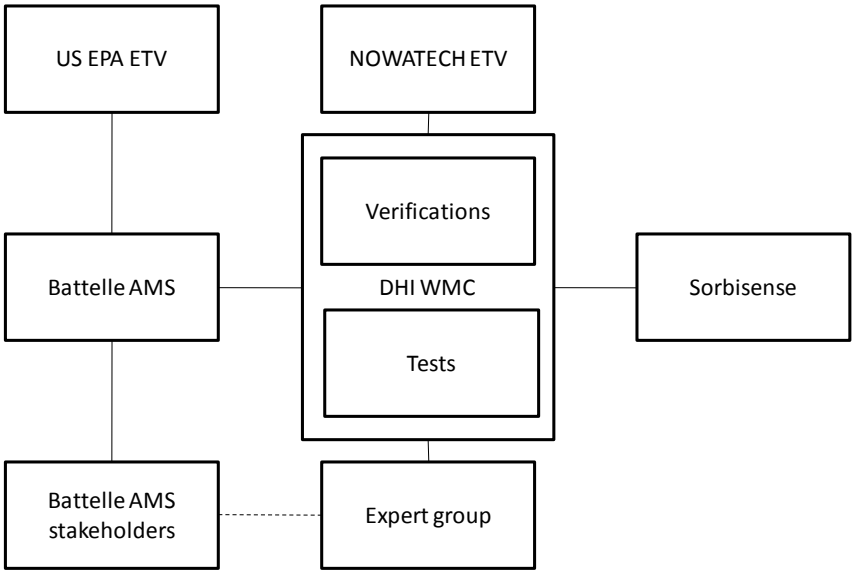
vironmental Technology verification (US ETV) Program. The verification is planned and conducted to satisfy the requirements of the ETV scheme currently being established by the European Union (EU ETV) and the US ETV program. Verification and tests will be performed by DHI as NOWATECH Water Monitoring Center (DHI WMC) under contract with Nordic Innovation Centre, Nordic Council of Ministers. Battelle will be participating as the manager of the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with the U.S. Environmental Protection Agency (EPA).

The day to day operations of the verification and tests will be coordinated and supervised by DHI personnel, with the participation of the vendor, Sorbisense. The testing will be conducted in the DHI laboratories, Hørsholm, Denmark and in the field in the Copenhagen area, Denmark. DHI will operate the samplers during the verification. Sorbisense will provide the sampling systems, the samplers and the analysis of samplers for the test. Furthermore, Sorbisense will provide user manuals and operation instructions, and will participate in development of protocol and plans with DHI. Battelle will ensure that the verification and tests is planned and conducted to satisfy the requirements of the US ETV program, including obtaining input and concurrence from its stakeholder group, as described in the process document /2/. Battelle will also participate in the development of the plan document for the verification and tests and perform quality assurance of the verification and tests. EPA will participate in quality assurance of the verification and tests.

An expert group is established to provide independent expert review of 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



2.5 Expert group

The expert group assigned to this verification and responsible for review of the verification plan and report documents includes:

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

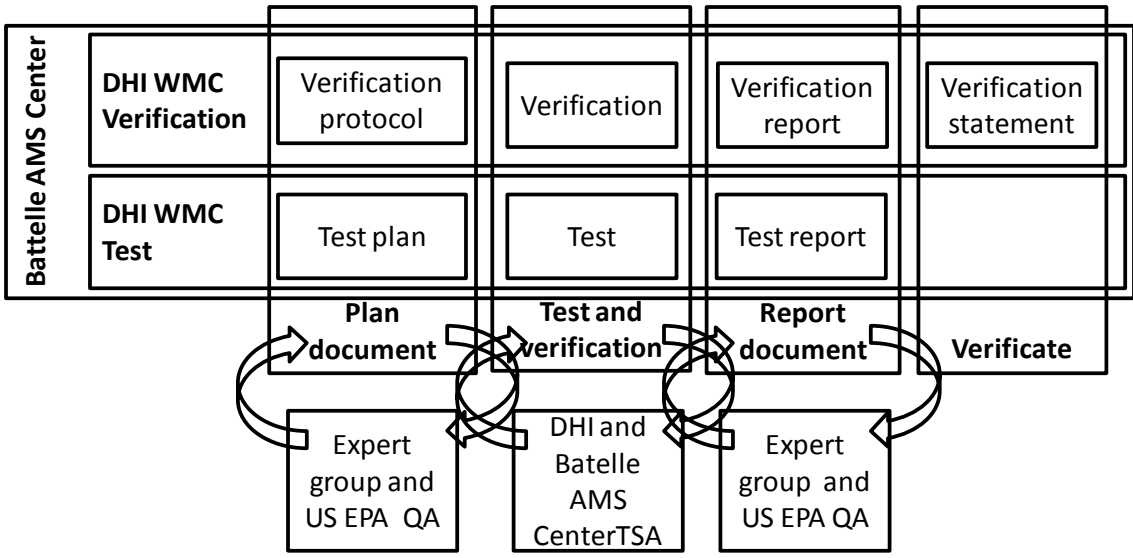
Mike Sherrier (MS), e-mail michael.p.sherrier@usa.dupont.com, DuPont, Barley Mill Plaza, Bldg 19-1132, 4417 Lancaster Pike, Wilmington, DE 19805, US, phone +1 302-892-1168

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 will be conducted in two separate steps, as required by the EU ETV. The steps in the verification are shown in Figure 2.

Figure 2 Verification steps



References for the verification process are the Quality Management Plan for the Battelle AMS /3/ and the Quality Manual for the ETV operations at DHI following the NOWATECH Quality Manual Template /4/.

A joint US EPA ETV and NOWATECH ETV verification statement will be issued after completion of the verification. Ensuring the compliance of the verification with the US ETV requirements is done following a process document developed by Battelle AMS.

This verification protocol, the test plan and the process document shall be seen as one consolidated verification description.

3 DESCRIPTION OF THE TECHNOLOGY

The technology product to be verified is applying the technology of passive sampling.

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 between the two media involved as obtained by *e.g.* experimental calibration of the device. 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.

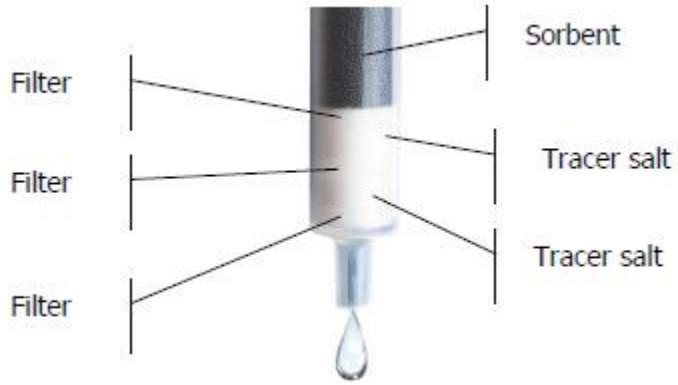
A wide range of products are available for passive sampling (equilibrium based and rate controlled) of solutes (inorganic and organic) from waters.

4 DESCRIPTION OF THE PRODUCT

The Sorbisense passive sampler combines the principle of passive sampling with a patented tracer based calculation of the amount 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 the sampler.
- Tracer salt that dissolves proportionally with the volume of water passing 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 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 GC-MS. The tracer salt (calcium citrate) is taken for extraction with 0.2 M HCl and quantification of extracted calcium with ICP.

The sampled water volume is calculated from:

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

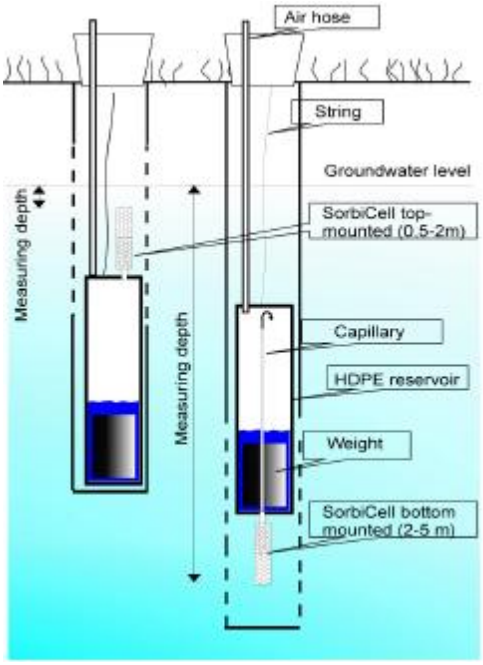
The solute water concentration is calculated from:

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

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 = VOC concentration in ug/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 to be verified here is the Sorbisense GWS40 sampling system intended for sampling of shallow groundwater and equipped with samplers for volatile organic compounds.

Figure 4 Mounting of the GWS40 sampling system



The GWS40 is mounted with air hose, safety string and Sorbisense samplers (can be mounted in top and 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.

5 APPLICATION AND PERFORMANCE PARAMETER DEFINITIONS

The application is defined as detailed in the application definition appendix, Appendix 3, in terms of matrix/matrices for use, targets of monitoring and effects.

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

5.1 Matrix/matrices

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

5.2 Target(s)

The targets of the product are volatile organic contaminants (VOC), here mono-, di-, tri- and –tetrachloroethenes, benzene, toluene, ethylbenzene and xylenes (BTEX) and methyl-*tert*-butylether (MTBE), see Table 1.

Table 1 Targets of the Sorbisense GSW40 VOC sampler

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

5.3 Effects

The effects for the application are set in terms of limit of detection (LoD), precision, trueness, range of application and robustness.

5.4 Performance parameters for verification

The ranges of performance relevant for the application, as derived in Appendix 3, are presented in Table 2. These ranges are used for planning the verification and testing only. For Sorbisense VOC sampling, concentrations above 2,000 µg/L are not likely to be measurable (vendor information) and are not included in the verification. The calculation of the performance parameters explaining their principle is given in Table 5.

Table 2 Ranges of performance parameters relevant 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-0.1*10^6	100±25
Benzene	0.1-1	<25	75-125	LoD-1*10^6	100±25
Toluene	0.5-5	<25	75-125	LoD-0.1*10^6	100±25
Ethylbenzene	0.5-5	<25	75-125	LoD-0.1*10^6	100±25
Xylenes	0.5-5	<25	75-125	LoD-0.1*10^6	100±25
MTBE	0.2-2	<25	75-125	LoD-1*10^6	100±25

Limit of detection shall be evaluated from the standard deviation of replicate measurements at less than 5 times the detection limit evaluated and will reflect a less than 5% risk of false blanks.

Precision shall be evaluated under repeatability and reproducibility conditions. Repeatability is 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 replicate measurements on the same or similar objects over a short period of time. Reproducibility is obtained as the standard deviation of measurements that includes different locations, operators, measuring systems, and replicate 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.

In addition to conventional trueness, the trueness of time-weighted averages obtained with the sampler shall be verified.

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

The parameters of robustness to be verified are sampling depth, sampling time, sampling concentration and groundwater ionic strength. Robustness is basically the trueness as found for different values of the robustness parameters.

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

Sampling time variations from 3 to 9 days shall be verified covering the different sampling times recommended by the vendor, as the exposure time may impact the performance.

In investigations of contaminated groundwater, both uncontaminated and strongly contaminated groundwater will be included. The concentrations verified shall 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 range 10-100 mS/m shall be verified, corresponding to the 5-95 percentile of Danish groundwaters /5/.

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

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

5.5 Additional parameters

Besides the performance parameters to be obtained by testing, compilation of parameters describing users manual, product costs and occupational health & safety issues of the product are required 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.

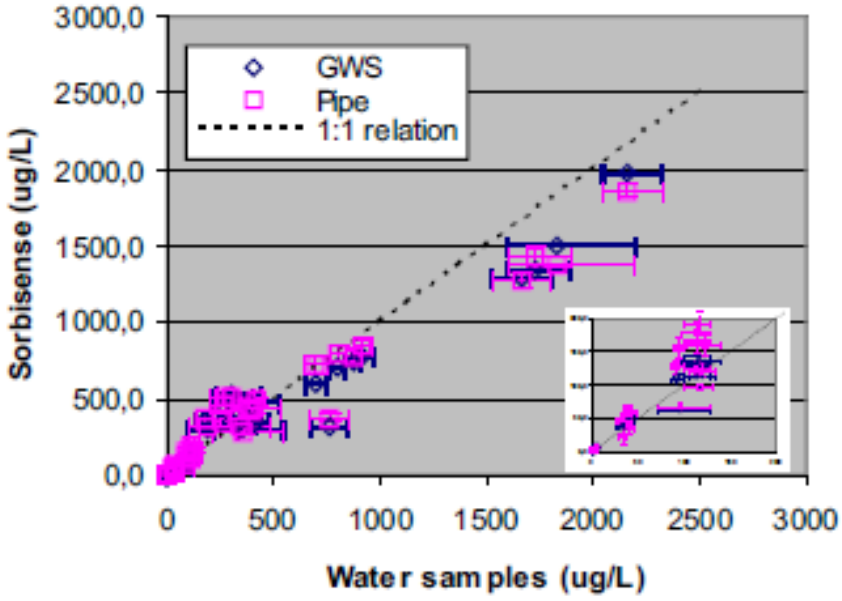
6.1 Summary of existing data

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”), Sorbisense samplers mounted in GWS samplers (“GWS”) and water samples taken directly from the pipe (“water samples”).

Figure 5 Summarized data on sampler test for selected VOC as provided by the manufacturer

Test parameter	Sorbisense	Water Samples
VOC Spike level: (average of results)	0, 6, 36, 120, 3000 ug/L	
VOC measuring range:	GWS: 0 – 1980 ug/L Pipe: 0 – 1860 ug/L	0 - 2160 ug/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 ug / V (V = volume sampled)	0.2 ug/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 /6/, the test laboratory can not 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 shall not be used as part of the verification due to the data quality issues, see Section 6.2. The data will be used as an indication of the performance range to be expected during planning.

7 TEST PLAN REQUIREMENTS

Based upon the application and performance parameter identification, Section 0, the requirements for test design have been set, see below. The detailed test

plan is prepared separately based upon the specification of test requirements presented below.

7.1 Test design

The outline of the required tests is shown in Table 3. The principle behind the design is that three test scales are used: laboratory tests, standpipe tests and field tests. Each scale is further described below and provides information on specified performance parameters, with the smallest scale chosen for each parameter in order to maintain simplicity and controlled conditions in the test.

Table 3 Test design scales and associated performance parameters

Laboratory	**Stand pipe**	**Field**
Limit of detection: best possible	Limit of detection: realistic	None
Precision and trueness: best possible	Precision (repeatability), trueness and range of application	Precision (reproducibility)
Robustness, sampling time and groundwater ionic strength	Robustness, sampling depth	General robustness
Trueness of time-weighted average concentration	None	None

As an example of the application of the scale principle, consider the test for evaluation of trueness and robustness. Trueness as best possible estimate is evaluated from direct application at the laboratory scale (chloroethene only). Trueness as realistic estimate is evaluated from the stand pipe scale simulating a groundwater well (all but chloroethene), and the variation in trueness between groundwater wells (robustness) is evaluated at the field scale. Combining the scales thus provides the best possible estimates of real conditions performance.

The laboratory tests shall apply direct application of standard solution to the samplers (best possible) or exposure of samplers to spiked water from a sample dispenser (robustness and trueness). The laboratory tests provides 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 can not be included in standpipe tests due to practical and health and safety considerations.

The standpipe test is intended to simulate ground water movement through a well established in the laboratory and to enable full control of solute concentrations. The standpipe test provides 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 shall provide 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 should be aimed at in order to allow for consideration of any impact of factors such as groundwater flow, well

construction or presence of other contaminants than the targets, as well as the impact of combined variation of robustness parameters.

7.2 Reference analysis

Reference analysis must be done under ISO 17025 accreditation /6/ using a GC-MS-SIM P&T method (EPA 624.2 or equivalent /7/) and must be documented to satisfy the analytical requirements set for groundwater investigations in Denmark, see Table 4 and the application and performance parameter definitions, Appendix 3.

Table 4 Required analytical quality for reference analysis

Compound	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L
All	0.03	5	90-110	0.03-2000

7.3 Data management

Data storage, transfer and control must be done in accordance with the requirements of ISO 9001 /8/ enabling full control and retrieval of documents and records. The filing and archiving requirements of the DHI Quality Manual must be followed (10 years archiving).

7.4 Quality assurance

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

The test plan and the test report will be subject to review by the expert group as part of the review of this verification protocol and the verification report, see Figure 2.

As this verification is a joint verification with the US EPA ETV, auditing from Battelle AMS Center is to be included in the test quality assurance.

7.5 Test report

The test report must follow the principles of template of the DHI NOWATECH verification center quality manual template /4/ with data and records from the tests presented. For this joint verification, the principles (contents) of the US ETV format must be complied with as well.

8 EVALUATION

The evaluation includes 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 /9/ and as described in Table 5, referring also to the test design shown in Table 3.

Table 5 Calculations used for the test results

Parameter	Calculation	Explanations
Limit of detection, LoD	$LoD = 2 \times t_{0.95}(f) \times s_r$	$t_{0.95}(f)$ 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	$D_i = \lvert x_{i\max} - x_{i\min} \rvert$ $\bar{x}_i = \frac{\sum x_i}{n}$ $d_i = \frac{D_i}{\bar{x}_i}$ $\bar{d} = \frac{\Sigma d_i}{m}$ $RSD = \frac{\bar{d} * 100}{1.693}\%$	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
Trueness, T	$\bar{x}_i = \frac{\sum x_i}{n}$ $\bar{y}_i = \frac{\sum y_i}{n}$ $T_i = \frac{\bar{x}_i}{\bar{y}_i} \times 100\%$ $T_i = \frac{\bar{x}_i}{y} \times 100\%$ $T = \frac{\Sigma T_i}{m}$	$\bar{x}_i$ is the mean of Sorbisense measurements at level i, x_i $\bar{y}_i$ is the mean of reference measurements at level i, y_i Ti is the trueness at level i y is the true value of the analyte T is the mean true value for all levels
Range of application	Visual identification of linear range, linear regression of results within linear range to yield slope, intercept and coefficient of regression (r^2).	
Robustness	See trueness, trueness reported for each specific parameter studied.	
Robustness, concentration integration	$y_T = \frac{\Sigma c_i \times t_i}{\Sigma t_i}$	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
Test of mean against true value	$\frac{\lvert \bar{x} - c \rvert \times \sqrt{n}}{s} > t_{0.975}(f)$	$t_{0.975}(f)$ is Student's t-factor for two-sided test at 95% confidence level, n is number of measurements and c is the true concentration.

Parameter	Calculation	Explanations
Test of mean against mean value	$\frac{\lvert\bar{x}_i - \bar{y}_i\rvert}{s_d} > t_{0.975}(v)$ $s_d = \sqrt{\frac{n+m}{n \times m} \times \frac{\sum(x-\bar{x})^2 + \sum(y-\bar{y})^2}{n+m-2}}$	The test requires that the variances are equal, v is n+m-2, and s_d is the standard deviation of the difference between the two means.

For field measurements, the reference measurements will be used as the true values.

For laboratory and standpipe measurements, concentrations obtained from preparation of the matrices are checked against the reference measurements (reference samples). If preparation based concentrations match the reference measurements, mean trueness within 100% ± 2 x RSD (relative standard deviation), these are used as true values for the test measurements. If not, the reference measurements are used as the true values.

Calculations will be performed in Excel 2007 set up for the purpose with the equations required.

8.2 Evaluation of test data quality

The information of the test report on the reference system, the test system and data quality and integrity control will be evaluated against the requirements set in this protocol and the objectives set in the test plan.

The spreadsheet used for the calculations will subject to control on a sample basis (spot validation).

The external audit reports prepared by Battelle AMS Center, see Section 7.4, will be evaluated and major findings compiled and reported.

8.3 Compilation of additional parameters

8.3.1 User manual

The verification criterion for the users manual is that it describes the use of the samplers adequately and understandable for the typical sampler and sampling planner. This criterion is evaluated through evaluation of a number of specific points of importance, see Table 6 for the parameters to include.

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

Table 6 Criteria for user manual evaluation

Parameter	Complete description	Summary description	No descrip-tion	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				√

8.3.2 Product costs

The capital investment costs and the operation and maintenance cost will be itemized based upon a determined design basis /10/, see Table 7 for the items that will be included.

Table 7 List of capital cost items and operation and maintenance cost items per product unit (sample)

Item type	Item	Number	None
Capital			
Site preparation			
Buildings and land			
Equipment			
Utility connections			
Installation			
Start up/training			
Permits			
Operation and maintenance			
Materials, including chemicals			
Utilities, including water and energy			
Labor			
Waste management			
Permit compliance			

The design basis will be described and the cost items relevant for the Sorbisense sampler listed. Note that the actual costs for each item is not compiled and reported.

8.3.3 Occupational health and environment

The risks for occupational health and safety and for the environment associated with the use of the product will be compiled. The compilation will list 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 /11/. The information will be given as amount used per product unit (sample), see Table 8 for format.

Table 8 Compilation of classified chemicals used during product operation

Compound	CAS number	Classification	Amount used per product unit

Additional risks from installing, operating and maintaining the product will be evaluated, compiled and reported, if relevant. In particular, risks for human health associated with power supply and danger of infections will be considered.

9 VERIFICATION SCHEDULE

The verification is planned for 2008-9. The overall schedule is given in Table 9.

Table 9 Verification schedule

Task	Timing
Application definition document	May 2008
Verification protocol with test plan	November 2008 to January 2009
Test	January to March 2009
Test reporting	March 2009
Verification	March 2009
Verification report	March 2009
Report document review	April 2009
Verification statement	April 2009

10 QUALITY ASSURANCE

The quality assurance of the verification is described in Table 10 and Figure 2, and the quality assurance of the tests in the test plan but summarized here, as well as in the process document /2/.

Table 10 QA plan for the verification

	DHI		Battelle AMS Center	US EPA ETV	Expert Group
Initials	ALJ	LSC	ZW	LD, JMK, EH	CP, DM, MS
Tasks					
Plan document with verification protocol and test plan	Review	-	-	Review	Review
Test system	-	Audit	Audit	-	-
Report document with test report and verification report	Review	-	-	Review	Review

Internal review of plan and report documents is done by chief engineer Anders Lynggaard Jensen (ALJ), and test system audit (see test plan) is done following the GLP audit procedure by a trained auditor: head of laboratory products Louise Schlüter (LSC).

The Battelle quality manager, Zachary Willenberg (ZW), will perform a technical systems audit (TSA) during this verification and test.

EPA QA staff, Lauren Drees (LD), John McKernan (JMK) and Evelyn Hartzell (EH) will do review of the plan and report documents.

The expert group will do review of the plan and report documents.

Reviews will be done using the NOWATECH review report template.

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.

Where discrepancies exist between NOWATECH and US EPA ETV terminology, definitions from both schemes are given.

Word	NOWATECH	US ETV
ADQ	Audit of data quality: An examination of a set of data after is has been collected and 100% verified by project personnel, consisting of tracing at least 10% of the test data from original recording through transferring, calculating, summarizing and reporting.	
AMS Center	Advanced Monitoring Systems Center at Battelle	
Analysis	Analysis of Sorbisense samplers at the vendor identified laboratory	
Analytical laboratory	Independent analytical laboratory used to analyze reference samples	
Application	The use of a product specified with respect to matrix, target, effect and limitations	
A-UBA	Umweltbundesamt Austria	
BTEX	Benzene, toluene, ethylbenzene and xylenes	
CEN	European Committee for Standardization	
CWA	CEN Workshop agreement	
DHI WMC	(ETV) Water Monitoring Center at DHI	
Direct application	A test design where a standard solution is applied directly to the Sorbisense samplers	
DOC	Dissolved organic carbon	
Drinking water control	Control of drinking water quality against drinking water maximum concentrations.	
DS	Danish Standard	
Effect	The way the target is affected, in this verification the way the target compounds are measured	
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.	EPA program that develops generic verification protocols and verifies the performance of innovative environmental technologies that have the potential to improve protection of human health and the environment
EU	European Union	
Evaluation	Evaluation of test data for a technology product for performance and da-	An examination of the efficiency of a technology

Word	NOWATECH	US ETV
	ta quality	
Experts	Independent persons qualified on a technology in verification or on verification as a process	Peer reviewers appointed for a verification
GC	Gas chromatography	
Groundwater investigation	Investigation of groundwater contamination with measurements controlled against groundwater maximum concentrations.	
Groundwater monitoring	Baseline monitoring of groundwater quality.	
GWS	Groundwater sampler	
ISO	International Standardization Organization	
Laboratory sample dispenser	Test device designed for controlled exposure of Sorbisense samplers to test solutions.	
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	
mbgv	m 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	
P&T	Purge and trap	
PE	Performance evaluation: A quantitative evaluation of a measurement system, usually involving the measurement or analysis of a reference material of known value or composition	
Performance claim	The effects foreseen by the vendor on the target (s) in the matrix of intended use	
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.	

Word	NOWATECH	US ETV
(Environmental) product	Ready to market or prototype stage product, process, system or service based upon an environmental technology	(Environmental) technology
PVC	Polyvinylchloride	
QA	Quality assurance	
Range of application	The range from the LoD to the highest concentration with linear response,	
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 %.	
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	
SM	Standard Methods for the Examination of Water and Wastewater, latest edition	
Stakeholder		Buyers and users of technology, technology developers/vendors, the consulting engineers, the finance and export communities, government permitters, regulators, first responders, emergency response, disaster planners, public interest groups, and other groups interested in the performance of innovative environmental technologies.
Standard	Generic document established by consensus and approved by a recognized standardization body that	

Word	NOWATECH	US ETV
	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 compounds measured.	
(Environmental) technology	The practical application of knowledge in the environmental area	An all-inclusive term used to describe pollution control devices and systems, waste treatment processes and storage facilities, and site remediation technologies and their components that may be utilized to remove pollutants or contaminants from, or to prevent them from entering, the environment.
Test/testing	Determination of the performance of a product by parameters defined for the application	
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	The technology developer, owner, or licensee seeking verification
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance	Establishing or proving the truth of the performance of a technology under specific, predetermined criteria, test plans and adequate data QA procedures
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	
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 on (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 Target(s)

The targets of the application are volatile organic contaminants, here mono-, di-, tri- and –tetrachloroethenes, BTEX and MTBE. 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 1-1.5 atmosphere shall be verified. Furthermore, with the claimed application, groundwater ionic strengths within the range 10-100 mS/m shall be verified, corresponding to the 5-95 percentile of Danish groundwaters /5/.

1.3 Effects

The effects for the application 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.

Appendix table 1 Vendor claim of performance, general terms

Compound	Limit of detection µg/L	Precision %	Trueness %	Range of application µg/L	Robustness %
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 Chapter 0.

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 and by testing and verification operators /12-16/.

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 /17/ requiring not 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 /18/. The Groundwater Directive /19/ 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 /20/ 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	**Robustness** %
Trichloroethene	1	25	75-125	-[1]	-
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 /12/.

Danish statute on quality requirements for environmental control /21/ 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 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	**Robustness** %
Chloroethene	0.03	5	100±10[2]	-	-
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

[1] -: no requirement
[2] Assuming a 5% relative standard deviation

maximum concentrations (and as a lower limit the drinking water maximum concentrations) for the compounds in question, see Appendix table 4.

Appendix table 4 Summary of groundwater and drinking water maximum concentrations, as summarized in /22/ and /23/

Compound	**Groundwater**	**Drinking water**		
	Denmark µg/L	**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 /24/. 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 /21/ 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 programme, 2003

Compound	**Groundwater maximum concentration based**	**Drinking water maximum concentration based**			**Groundwater monitoring based**
	Denmark µg/L	**EU** µg/L	**US** µg/L	**WHO** µg/L	**Denmark** 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	$3.5\text{-}6.3*10^6$
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	$0.16\text{-}0.20*10^6$
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**[3] µg/L	**Robustness** %	**Reference**
GORE-SORBER	-	14-21	-	5-2000	-	/25/
USGS PDB	-	0.9-4.3	86-118	2-500	-	/26/
Dialysis membrane sampler	0.1-5	17	100%	$0.2\text{-}25*10^3$	-	/27/
USGS PDB		21			-	

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

[3] 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 µg/L	Precision %	Trueness %	Range of application µg/L	Robustness %	Reference
Grab sampling	-	12%	-	5-2000	-	/25/
Grab sampling	-	1.1-9.8	-	2-500	-	/26/
Low purge pump sampling	-	15	-	$0.2\text{-}25*10^{3}$	-	/27/

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 criteria 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 needs identified for analytical performance can not be directly translated into the combined sampling and analysis performance requirements 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 for the application are set in Appendix table 9 based upon regulatory and application based requirements and state of the art performance.

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	85-115
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-0.1*10^6	100±25
Benzene	0.1-1	<25	75-125	LoD-1*10^6	100±25
Toluene	0.5-5	<25	75-125	LoD-0.1*10^6	100±25
Ethylbenzene	0.5-5	<25	75-125	LoD-0.1*10^6	100±25
Xylenes	0.5-5	<25	75-125	LoD-0.1*10^6	100±25
MTBE	0.2-2	<25	75-125	LoD-1*10^6	100±25