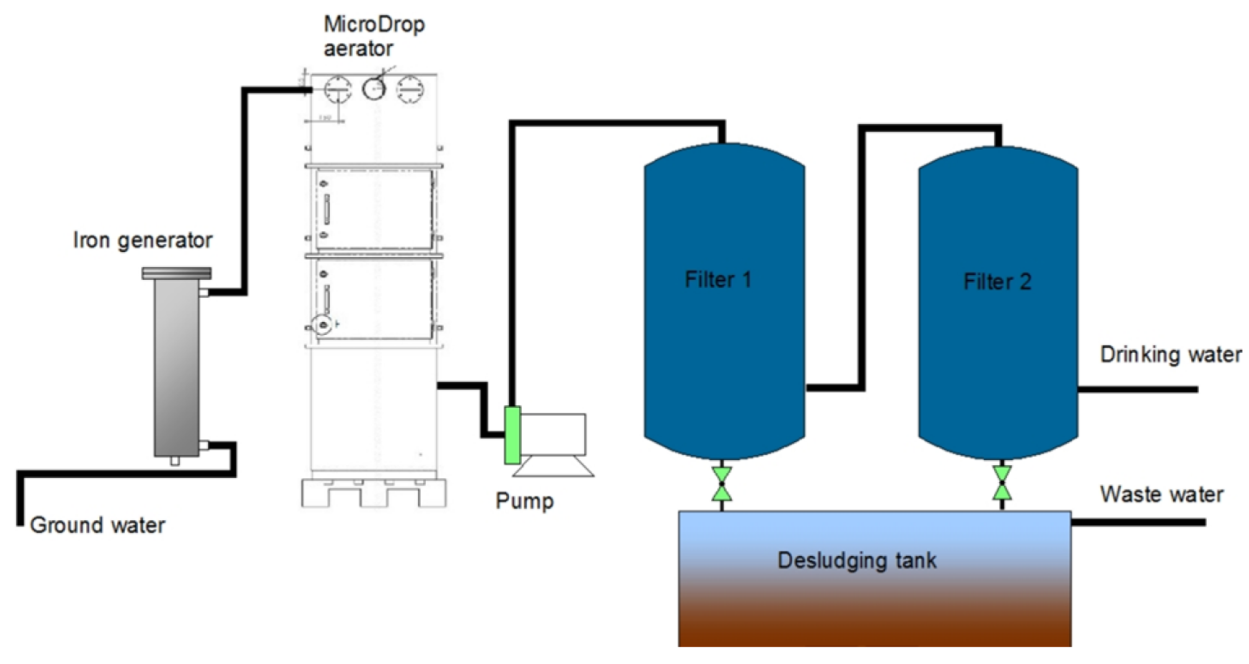
MDA Arsenic Reduction

Verification protocol

Arsenic removal from drinking water through oxidation and co-precipitation with subsequent removal by filtration



MicroDrop Aqua ApS
October 2011

Approved by Berislav Tomicic, (Head of Projects)
Berislav Tomicic

MicroDrop Aqua ApS
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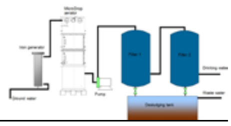
Prepared for MicroDrop Aqua ApS

Represented by Mr Andreas Guldager



MDA Arsenic Reduction

Project No	11520012
Classification	Open

Authors	Mette Tjener Andersson
	Gerald Heinicke

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Archiving: All standard project files (documents, etc) are archived in DHI project site.

1 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.

The objective of this verification is to evaluate the performance of an arsenic treatment technology that can be used to reduce arsenic concentrations in drinking water.

1.1 Name of technology

MDA Arsenic Reduction, produced by MicroDrop Aqua ApS (hereafter MicroDrop).

The technology to be verified consists of an iron generator, a MicroDrop aerator, sandfilters and a desludging tank.

1.2 Name and contact of proposer

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Skudehavnsvej 5
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Denmark

Contact: Andreas Guldager, e-mail ag@microdropaqua.net, phone +45 4371 2641, mobile +45 5358 2641, Microdrop website: http://microdropaqua.net/

1.3 Name of verification body/verification responsible

The Danish Centre for Verification of Climate and Environmental Technologies (DANETV), DHI DANETV Water Centre,

DHI
Agern Allé 5
2970 Hørsholm
Denmark

Verification responsible: Mette Tjener Andersson (initials MTA), e-mail mta@dhigroup.com, phone +45 4516 9148.

Test responsible: Anke Oberender (initials AOB), e-mail aob@dhigroup.com, phone +45 4516 9469.

1.4 Verification organization including experts

The verification will be conducted by the Danish Centre for Verification of Climate and Environmental Technologies, DANETV, which performs independent tests of technologies and products for the reduction of climate changes and pollution.

The verification is planned and conducted to satisfy the requirements of the ETV scheme currently being established by the European Union (EU ETV pilot programme) [1].

The verification and tests will be coordinated and supervised by DHI personnel, with the participation of the proposer, MicroDrop. The testing will be conducted at the Utterslev-

Kastager waterworks, Lolland, Denmark. The technical staff at the waterworks will operate the MDA Arsenic Reduction plant during the verification, supervised by MicroDrop Aqua and DHI.

An internal and an external expert are assigned to provide independent expert review of the planning, conducting and reporting of the verification and tests:

- Internal technical expert: Morten Møller Klausen (initials MMK), DHI, department Urban and Industry, e-mail mmk@dhigroup.com, phone +45 8620 5114
- External technical expert: Dr. Ali S. Amiri, Amiri (initials ASA), Clean Water Technologies, Oakville, Ontario, Canada, e-mail amiri.s.ali@gmail.com.

The tasks assigned to each expert are given in more detail in section 8 Quality assurance.

The relationships between the organisations related to this verification and test are given in Figure 1-1. The test centre is divided into two sub-bodies – one for verification and one for testing – and with different responsibilities during the verification process.

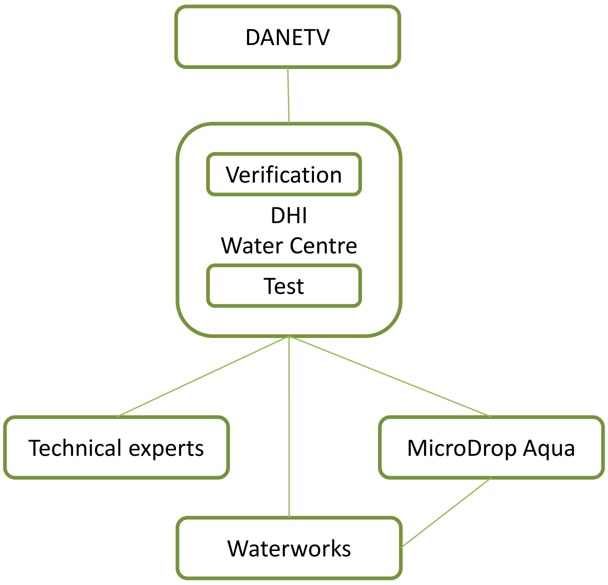


Figure 1-1 Organization of the verification and test

1.5 Verification process

The principles of operation of the DANETV verification process are given in Table 1-1. Verification and testing are, as seen, subdivided between two sub-bodies.

Table 1-1 Simplified overview of the verification process

Phase	Responsible	Document
Preliminary phase	Verification sub-body	Quick Scan
		Contract
		Verification protocol
Testing phase	Test sub-body	Test plan
		Test report
Assessment phase	Verification sub-body	Verification report
		Statement of Verification

Quality assurance (QA) is carried out by an expert group of internal and external technical experts. An audit will be performed internally by DHI. Reference for the verification process is the Quality manual for the ETV operations at DHI following the DANETV Centre Quality Manual – Water technology [2]. A Statement of Verification will be issued by DANETV after completion of the verification. The final verification report will include the other documents prepared as appendices.

2 Description of the technology

MicroDrop has developed a treatment system (method and device) for removal of contaminant trace species, especially arsenic, from water.

The method and device are used for purifying water from arsenic by co-precipitation of arsenic during oxidation and precipitation of iron compounds. The precipitate is subsequently removed by a separation process, normally rapid sand filtration. Precipitation is achieved by oxidising naturally occurring and/or added soluble iron (II) to insoluble iron (III). In MicroDrop' s treatment method, iron (II) is added by an electrolysis system, with several iron anodes arranged around a center cathode, with the possibility to enhance the process by an impressed current.

Concentration levels of arsenic and iron are often linked. Due to the affinity of arsenic for iron, iron oxides and iron hydroxides, arsenic removal by iron is popular [3, 4]. Arsenic removal can be achieved by use of iron, iron-based sorbents or by iron removal from water with elevated levels of dissolved iron. Three main mechanisms (precipitation, co-precipitation and adsorption) can independently contribute to arsenic removal. The formation of insoluble compounds (e.g. Fe(AsO4)) will result in precipitation of arsenic. Co-precipitation refers to the incorporation of soluble arsenic species into the structure of metal hydroxides. Adsorption on the other hand refers to the electrostatic binding of soluble arsenic to the external surfaces of insoluble metal hydroxides [3]. Although all three mechanisms play a role in arsenic removal, co-precipitation and adsorption are the most important ones.

The chemical and surface-complexation reactions that take place in arsenic removal by iron are complex and are influenced by a number of factors, such as pH, arsenic concentrations and competing ions. Figure 2-1 shows the number of different reactions that take place on iron-based filters and the majority of which also occur in the co-precipitation of arsenic.

When zero-valent iron Fe(0) is used as a sorbent, the formation of iron oxides and hydroxides on the surface will facilitate adsorption and formation of complexes with other ions, e.g. arsenic ions [4].

By oxidation of iron Fe(II) dissolved in (ground)water, insoluble ferric iron Fe (III) is formed. Oxidation of soluble iron can be achieved by aeration or addition of oxidizing agents.

In the presence of ferric iron Fe(III), hydrous ferric oxide (HFO) and hydrated iron (=FeOH) are formed, and As(V) species (arsenates) can be removed from water by surface complexation and precipitation on HFO and hydrated iron. Arsenates and arsenate-HFO-complexes also react with other soluble metals resulting in precipitation if solubility limits are exceeded [4].

Description	Reactions
Oxidation of soluble iron Oxidation of ferrous to ferric through active oxygen species	$Fe(II) + O_2 \rightarrow O_2^- + Fe(III)OH_2^+$ $Fe(II) + O_2^- \rightarrow Fe(III) + H_2O_2$ $Fe(II) + CO_3^- \rightarrow Fe(III) + HCO_3^-$
Oxidation of As(III) (Equations are balanced for reactive species only.)	$As(III) + O_2^- \rightarrow As(IV) + H_2O_2$ $As(III) + CO_3^- \rightarrow As(IV) + HCO_3^-$ $As(III)OH^- \rightarrow As(IV)$ $As(IV) + O_2^- \rightarrow As(V) + O_2^-$
Formation of HFO in the presence of Fe(III) Fe(III) complexation and precipitation	$=FeOH + Fe(III) + 3H_2O \rightarrow Fe(OH)_3$ $(s, HFO) + =FeOH + 3H^+$ (=FeOH is surface of hydrated iron)
Surface complexation of arsenates Surface complexation and precipitation of anionic species As(V) on HFO. log *K* values are shown in ( ). ψ is the surface potential.	$=FeOH + AsO_4^{3-} + 3H^+ \rightarrow = FeH_2AsO_4 + H_2O$ (29.31) $=FeOH + AsO_4^{3-} + 2H^+ - \exp(-F\psi/RT) \rightarrow$ $=FeHAsO_4^- + H_2O$ (23.51) $=FeOH + AsO_4^{3-} + H^+ - 2\exp(-F\psi/RT) \rightarrow$ $=FeAsO_4^{2-} + H_2O$ $=FeOH + AsO_4^{3-} - 3\exp(-F\psi/RT) \rightarrow$ $=FeOHAsO_4^{3-} + H_2O$ (10.58)
Precipitation of other metals Surface precipitation of arsenate with soluble metal ions if surface concentrations exceed solubility limits. Many metal ions are also quantitatively removed this way.	$=FeOHAsO_4^{3-} + Al(III) \rightarrow = FeOHAsO_4Al(s)$ $=FeOHAsO_4^{3-} + Fe(III) \rightarrow = FeOHAsO_4Fe(s)$ $=FeOH{\cdot}HAsO_4^{2-} + Ca(II) \rightarrow = FeOH{\cdot}HAsO_4Ca(s)$ $M(III) + HAsO_4^{2-} \rightarrow M_2(HAsO_4)_3$ (s), M = Fe, Al, $M(II) + HAsO_4^{2-} \rightarrow M(HAsO_4)$ (s) and other arsenates M = Ba, Ca, Cd, Pb, Cu, Zn, and other trace metals
Surface complexation of silicate species Reactions with iron surfaces and silicates can produce a porous solid matrix with extremely good mechanical stability for long-term use.	$=FeOH + Si(OH)_4 \rightarrow = FeSiO(OH)_3(s) + H_2O$ $=FeOH + Si_2O_2(OH)_5^- + H^+ \rightarrow = FeSi_2O_2$ $(OH)_5(s) + H_2O$ $=FeOH + Si_2O_2(OH)_5^- \rightarrow = FeSi_2O_3(OH)_4^-(s) + H_2O$

Source: Wilkie and Hering (1996), Dzombak and Morel (1990), Schecher and McAvoy (1998), MINTEQA2 Model System (2001), Stephen et al. (2001), and Davis et al. (2002). All surface species are indicated by = X.

Figure 2-1 Chemical and surface-complexation reactions in iron-based filters [4]

3 Description of the product

The product to be verified is the MDA Arsenic Reduction system which consists of MicroDrop's proprietary iron generator and aerator, combined with MicroDrop' s standard filtration system, i.e. at Utteslev-Kastager waterworks two parallel pressurised rapid sand filters (Figure 3-1 and Figure 3-2**Error! Reference source not found.**). MicroDrop's iron generator may be combined with alternative filtration techniques (e.g. membrane filtration), this would be regarded as different versions of the product and is not covered in this verification.

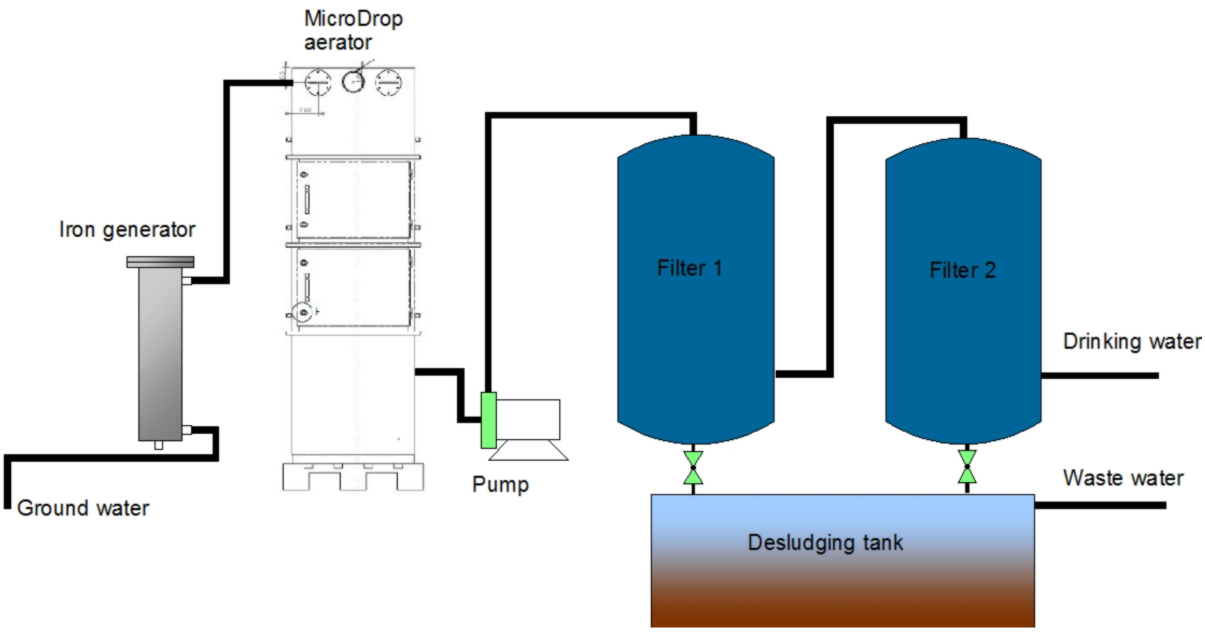


Figure 3-1 Schematic of MDA Arsenic Reduction plant (image provided by proposer). Notice, on the schematic the filters are in series and not in parallel as at the test site Utterselv-Kastager.

Well water is pumped from the groundwater well and flows through the iron generator. The groundwater pump is controlled to give a continuous flow rate. In the iron generator a number of iron anodes are arranged around a center cathode. The release of iron ions can be enhanced by connecting an electric current that may be varied by a constant current generator.

Some of the iron in the generator will be dissolved as Fe(II)ions. The water flows into the pressureless MicroDrop aerator, where Fe(II)ions due to aeration are oxidized to Fe(III)ions, which precipitate as insoluble hydroxide. Arsenic adsorbs to the surface of the iron hydroxide and is co-precipitated. Some of the precipitate settles at the bottom of the aerator and is removed at regular intervals.

The water from the aerator is pumped through sand filters, where the iron hydroxide flocs and the arsenic are retained. The filtrate from the filters is stored in a clean water tank and is distributed as drinking water, generally without disinfection. When the clean water tank is full the drinking water production is stopped, until water level in the clean water tank is below a certain level.

The sand filters are backwashed on a regular basis using filtrate. The backwash water is pumped into desludging tanks, where sludge is allowed to settle. Normal procedure is that the water is drained from the sludge, the sludge is dried and afterwards disposed of, e.g. at a landfill site. The precipitated iron hydroxide sludge may have a high content of arsenic, and may need to be disposed of as toxic waste. The decantate from the desludging tanks is discharged to the sewer.

Figure 3-2 Pictures from the Utterslev-Kastager water works: 1) picture to the left: Iron generator in the background and aerator in the foreground 2) top right picture: two sand filters 3) bottom right picture: iron anodes and centre cathode before installation in the iron generator

Figure 3-3 Desludging tanks at the Utterslev-Kastager water works

The MDA Arsenic Reduction system is currently available for smaller set-ups with a capacity of up to 10 m^3/h, but bigger system sizes are in the design phase. The system to be verified has a capacity of 10 m^3/h.

The MDA Arsenic Reduction system is protected by patent [12]. The patents title is "Method and device for removing contaminant trace species, especially arsenic, from water" and covers a system set-up that is different from the system to be verified. The patent covers a system with a bed of iron swarf arranged above an aeration device, and not for anodes as verified here as well it is also without electrical current to control iron release.

3.1 Application and performance parameter definitions

The intended application of the product for verification is defined in terms of the matrix and the purpose. MDA Arsenic Reduction is a combination of oxidation and co-precipitation of arsenic in groundwater with subsequent removal of arsenic from the water to produce drinking water.

3.1.1 Matrix/matrices

MDA Arsenic Reduction is used for the treatment of groundwater that contains dissolved arsenic. For this verification, the matrix is groundwater pumped at one test site in Denmark, Utterslev-Kastager water works (island of Lolland).

3.1.2 Purpose

MDA Arsenic Reduction is applied primarily to remove arsenic from groundwater. However, the process may also remove other ions prone to oxidation and/or (co-)precipitation. Furthermore, rapid media filtration will remove some suspended particles and colloids from the raw groundwater.

The main purpose of this process is removal of total arsenic (sum of As(III) and As(V)).

3.1.3 Exclusions

This verification covers the performance of the MDA Arsenic Reduction at a Danish test site with moderate arsenic concentrations. The investigated variation in raw water quality is limited to the natural variation occurring during a 2-week test period. No manipulation of the feed water quality (e.g. arsenic spiking) will be done during the test.

The verification only covers the specific set-up of the technology, as described, with MicroDrop iron generator and aerator, sand filters and desludging tank.

3.2 Performance parameters for verification

The performance parameters for the verification comprise parameters that e.g. describe the treated water quality, regulatory requirements, parameters that assess equipment performance etc. Performance or quality parameters may include chemical, physical and biological parameters.

The proposer has specific performance claims for a plant set-up with MDA Arsenic Reduction (iron generator, aerator and sand filter), see Table 3-1.

Table 3-1 Specific performance claims by the proposer

Parameter	Quality of groundwater intake to MicroDrop	Quality of outflow from MicroDrop
Oxygen content (in mg/l)	< 1	> 7
Oxygen content (in %)	2 to 5	> 95

Temperature (°C)	6 to 12	7 to 15
Colour, odour, taste		Acceptable to consumers and no abnormal change
Redox (mV)	(-30) - (-50)	>30 - 50
pH	6.5 - 9	Increases approx. 10%
Iron (mg/l)	0 - 4	0.1 - 0.2
Arsenic (µg/l)	< 50	5 - 10
Manganese (mg/l)	0 - 1	< 0.05
Ammonium (mg/l)	< 2	0.05 - 0.5
Nitrite (mg/l)	< 1	0.05 - 0.5
Methane (mg/l)	0 - 1	< 0.01
Hydrogen sulphide (mg/l)	0 - 0.5	< 0.02
NVOC (mg/l)	≤ 15-20	< 12
Aggressive CO_2 (mg/l)	≤ 25	< 2

3.2.1 Regulatory requirements

Regulatory requirements for the application are set by the EU drinking water directive [4] and the Danish implementation [6] of the directive. Both pieces of legislation include a number of microbiological, chemical (organic and inorganic) and physical/indicator parameters. The parameters with relevance for this verification are summarized in Table 3-2.

Table 3-2 Selected parameters from the EU drinking water directive and the Danish implementation (Statutory order no. 1449 of 11. December 2007 [6])

Parameter	Limit value – EU directive	Limit value – DK statutory order
Oxygen content (in mg/l)	5 mg/l (oxygen consumption)	Sufficiently high to ensure 5 mg/l at the users water tap
Temperature (°C)	-	<12 °C at the users water tap
Turbidity (FTU)	Acceptable for consumers and no abnormal change	<0.3
Colour (mg Pt/l)	Acceptable for consumers and no abnormal change	<5
Odour	Acceptable for consumers and no abnormal change	Water must not have different taste or odor; disinfectants are exempt
Taste		
Conductivity (mS/m)	≥25 at 20 °C	≥30
pH	6.5-9	7-8.5
Iron (mg/l)	<0.2	<0.1
Arsenic (µg/l)	<10	<5
Manganese (mg/l)	<0.05	<0.02
Chromium (µg/l)	<50	<20
Nickel (µg/l)	<20	<20
Ammonium (mg/l)	<0.5	<0.05

Nitrite (mg/l)	<0.1	<0.01
Methane (mg/l)	-	<0.01
Hydrogen sulphide (mg/l)	-	<0.05
NVOC* (mg/l)	-	<4
Aggressive CO_2 (mg/l)	-	<2

* Non-volatile organic carbon

For most parameters the Danish requirements are seen to be stricter than the EU regulatory requirements.

3.2.2 Application based needs

The speciation and reaction kinetic of arsenic and water need to be taken into account. In the presence of oxygen, As (III) is oxidised to As (V). At neutral pH this is a very slow process. In a catalytic process with oxygen and dissolved, reduced iron (Fe (II)) the oxidation to As (V) can be increased. The oxidation step of As (III) to As (V) is important since As (V) generally adsorbs better to iron oxides and is easier removed by sand filters than As (III). Unfortunately, the oxidation of iron on water works filters often occurs faster than the arsenic oxidation, and thus iron precipitates before the arsenic oxidation is complete [9]. Moreover, Danish groundwater typically consists of mainly As (III) and only little As (V) [9].

Aeration of ground water is essential, in order to ensure oxidation of arsenic and iron, and to meet the regulatory requirements for oxygen content. Oxygen content is therefore an important parameter for process control.

The concentration of iron is important both for the arsenic removal process, and because it is limited by drinking water regulations. Dissolved manganese as Mn(II) often occurs together with iron, and should be monitored as well.

3.2.3 State-of-the-art-performance

Water treatment in Denmark: In traditional water treatment, removal of arsenic relies on the raw water content of both arsenic and iron. For some Danish water works the iron content in the raw water is sufficiently high to remove arsenic to levels below the regulatory requirements. For Danish conditions it can be said that 50% of arsenic can be removed with an iron concentration of 1 mg/l in the raw water and 70% removal can be achieved with 2 mg/l iron concentration [7]. A Danish study of 4833 untreated groundwater samples established typical arsenic concentrations for Denmark - 83 % of the samples showed arsenic concentration below 5 µg/L. In 10 % of the samples the arsenic concentration was between 5 µg/L and 10 µg/L. The median value from 2 % of the samples exceeded a concentration of 20 µg/L [8].

In Denmark, supplementary drinking water treatment for arsenic removal was started around 2004 after the regulatory limit value for arsenic in drinking water was reduced from 50 µg/l to 5 µg/l in 2001. Removal of arsenic from Danish raw waters is typically achieved by [7]:

- Filtration through iron granulate that is placed into a pressure filter (i.e. iron granulate filter bed)
- Dosage of dissolved, reduced iron (iron chloride or iron sulphate coagulants)

Water treatment in other countries: Treatment methods, such as 1) addition of iron-containing coagulants, flocculation, settling and subsequent filtration, 2) iron-containing coagulants and direct filtration, 3) filtration on sorption media consisting of iron oxide granulates are commonly used in industrialised countries and have been since the 1990´s [9]. The use of granulates is relatively expensive – there is a need for an additional pressure filter in the system and the granulate needs replacement once the surface is saturated with arsenic. The addition of iron-based coagulants is relevant where raw water concentrations of iron are below 1 mg/l [7].

Disadvantages are, however, that in case of problems with ammionium removal the addition of iron may aggrevate the problem. Furthermore, undesirable impurities in form of heavy metals from the added iron product might be released to the raw water [9].

Treatment achievability: For treatment processes such as coagulation, ion exchange, precipitation or softening, activated alumina and membranes, arsenic removal of 80% or more to levels below 5 µg/l is achievable. However, this requires careful process control and optimization. It is more reasonable to expect 10 µg/l by conventional treatment[1] [10].

US EPA/NSF ETV verification testing for arsenic removal [11]*:* A protocol for equipment verification testing for arsenic removal highlights the range of feed water quality as one of the key aspects related to performance verification. According to the US protocol, important characteristics of feed water quality include:

- turbidity, suspended particles,
- arsenic concentration and arsenic species,
- other ions in solution (particularly sulphate, fluoride, silica)
- temperature
- dissolved organic carbon (DOC) and total organic carbon (TOC)
- pH, alkalinity, hardness
- iron and manganese
- total dissolved solids (TDS)

In Table 3-3 arsenic removal technologies verified under the US EPA ETV-programme are listed, and average concentrations in feed water and filtrate are shown.

Table 3-3 Results from US EPA ETV verifications on arsenic removal [15].

Technology	Product and vendor	Feed water conc. (µg/L)	Filtrate conc. (µg/L)
Ion exchange	High-Efficiency Ion Exchange Treatment System *Basin Water*	15	<1.0
Electroflocculation and filtration	ARS CFU-50 APC Electroflocculation and Filtration Water Treatment System *ARS USA, LLC*	12	6
Ozonation-filtration	CampWater Porta-5 System *Delta Industrial Services, Inc.*	18	9
Coagulation (NaOCl, $FeCl_3$) /filtration	Macrolite Coagulation and Filtration System, Model CPS100CPT *Kinetico, Inc.*	71.4	2.9
Coagulation (NaOCl, $FeCl_3$) and media filtration	KemLoop 1000 Coagulation and Filtration Water Treatment System *ORCA Water Technologies*	22	3
Coagulation (NaOCl, $FeCl_3$) and microfiltration	Microza Microfiltration System *Pall Corp.*	13	<2
Coagulation (NaOCl, $FeCl_3$) /filtration	eVOX Model 5 *Watermark Technologies, LLC*	77.6	4.1
Adsorption media filter	ADI Pilot Test Unit No. 2002-09 with MEDIA G2 *ADI International, Inc.*	21	7
Adsorption media filter	Para-Flo PF60 Model AA08AS With Actiguard AAFS50 *Kinetico, Inc., and Alcan Chemicals*	14	≤2
Reverse osmosis membrane filtration	Hydranautics ESPA2-4040 Reverse Osmosis Membrane Element Module *Hydranautics*	65	0.5

[1] In the water industry commonly defined as coagulation, settling and rapid media filtration

Reverse osmosis membrane filtration	TFC – ULP4 Reverse Osmosis Membrane Module, Park City, UT *Koch Membrane Systems*	60	0.9
Membrane filtration	M-Series M-15,000 Reverse Osmosis Treatment System *Watts Premier, Inc.*	14	<1.0

3.2.4 Selected performance parameters

Since the verification is carried out at a Danish site, the Danish requirements will be applied. Where the proposer's claim is stricter than the Danish requirements, the verification will be done for the proposer's claim. Table 3-4 shows the selected performance parameters for this verification.

Table 3-4 Selected performance parameters for this verification.

Parameter	Relevant ranges	Comments
Total arsenic (Sum of As (III) and As (V)) (µg/l)	<5 <10	If feed water concentration is <30 µg/l, regulatory requirement DK If feed water concentration is <200 µg/l, WHO recommendation
Iron (mg/l)	<0.1	Regulatory requirement
Manganese (mg/l)	<0.05	Proposer claim
Oxygen content (in mg/l)	>7 mg/l	Proposer claim

3.3 Operational parameters

3.3.1 Physico-chemical parameters on waters

It is relevant to know the physico-chemical properties of the raw water/feed water at the water works as well as the water quality of the filtered water. In addition to arsenic, iron, manganese and oxygen (selected performance parameters, see Table 3-4), the following physico-chemical parameters shall be determined. Parameters as turbidity, colour, redox, conductivity and pH give general information about the water quality. Chromium and nickel are associated to iron (impurities) and are analysed to monitor for any contamination of the treated water during the process. Table 3-5 lists relevant physico-chemical parameters.

The filtrate produced after backwashing shall be monitored to identify the period until the treated water meets drinking water standards. This will be based mainly on the results from online-measurements, supported by a predefined number of grab samples.

Water from the back-wash of the filters is pumped into the desludging tanks, where sludge settles. After the desludging the decantate will be discharged to the sewer. The physico-chemical parameters of this decantate will be analysed.

Table 3-5 Physico-chemical parameter to be measured in raw water, filtrate and decantate.

Parameter	Criteria	Comment
Turbidity (FTU)	<0.3	Regulatory requirement
Colour (mg Pt/l)	<5	Regulatory requirement
Redox (mV)	>30	Proposer claim
Conductivity (mS/m)	>30	Regulatory requirement

Temperature (°C)	7-15	Proposer claim
pH	7-8.5	Regulatory requirement
Chromium (µg/l)	<20	Regulatory requirement
Nickel (µg/l)	<20	Regulatory requirement

3.3.2 Arsenic content in sludge

The sludge that settles in the desludging tanks after back-wash contains the precipitated iron hydroxides, arsenic and potentially other precipitated metals. Representative sludge sample should be taken to determine the levels of arsenic (possibly other metal ions) in the sludge to decide whether the sludge is to be disposed of as toxic waste.

Table 3-6 Analyses on sludge from desludging tanks.

Parameter	Analyse
Sludge	Content in solid sample. As minimum arsenic, iron, chromium, nickel and manganese are included

3.3.3 Parameters of the equipment operation

Resources are limited to iron anodes that are installed in the iron generator, the lifetime of the anodes is expected to be more than one year. Electricity is needed for several processes in the system – pumps, the aerator and filters, and - in case an electric current is applied – the iron generator.

The kinetics of iron oxidation and the filter capacity for precipitated iron are important for a sand filter to work satisfactorily with regards to arsenic removal. In case of catalytic iron removal, where dissolved iron is aerated and precipitates when in contact with the filter material, oxygen content, pH, filter surface area and characteristics of precipitates on the filter surface are of importance for oxidation kinetics [9]. New (sand) filters initially do not have any film/incrustation on the surface, but over time precipitation occurs– the filter "matures" – and the filter surface may show a catalytic effect. It is assumed that iron oxides deposit first and that films of manganese oxides and biofilms are formed over time. Manganese is only to a lower extend removed by backwashing the filter, whilst up to 50% of precipitated arsenic and iron can be removed by backwashing [9]. Thus the amount of iron and arsenic precipitated on the sand surface will be highly dependent on the efficiency of backwashing. This in turn will have some influence on the filters ability to remove arsenic. Therefore, the cycle for backwashing, i.e. time between flushes, volume of water used for back-flush etc. (see Table 3-7) will be monitored.

Table 3-7 Operational performance parameters

Parameter	Definition
Filter rate and flow	An interval for flow (m^3/h) and filtration rate (m/h) acceptable in the verification testing has to be identified (to be specified in test plan)
Backwash	Backwashing frequency (No/day), rate (m/h), duration (min). From this, the ratio of filtrate used for backwashing (%) will be determined. Also the water and sludge phases from the desludging tank will be quantified. The time (min) until water quality is back to drinking water standard will be used to determine the fraction of filtrate that needs to be discharged during "filter to waste" operation.

In the test plan details of the equipment such as filter cross section, filter bed height, filtration rate (m/h), empty-bed contact time, type of filter media (one or several if multi-media), grain sizes (mm) and details about the previous operation of the filter media shall be specified.

3.4 Additional parameters

Besides the performance parameters obtained by testing, a compilation of parameters describing the ease of understanding the user manual, required resources, and occupational health and environmental issues of the product were included in the verification.

4 Existing data

4.1 Summary of existing data

The proposer has provided some data from the recent operation of the product/technology at the Danish water works "Bjergby Søndre Vandværk".

Table 4-1 Data from operation of MDA arsenic reduction at "Bjergby Søndre Vandværk" at 5 m^3/h and 60-100 m^3/day (water works consisting of Ø 315 mm iron generator, MicroDrop – MDA arsenic reduction - Ø 630 mm sand filter); Chemical analysis carried out by different analytical laboratories

Date	Parameter	Groundwater (feed water)	After iron generator	After treatment (drinking water)
15/04/2010	HCO_3^- (m/l)	200		
	Fe (mg/l)	0.25	1.6	0.021
	As (µg/l)	13		3.5
04/05/2010	Fe (mg/l)	0.25	1.4	0.0097
	As (µg/l)	12		5.6
02/09/2010	Fe (mg/l)	0.25	0.97	0.05
	As (µg/l)	13		8.3
10/10/2010	Fe (mg/l)	0.25	1.13	0.03
	As (µg/l)	13		7.6
04/10/2010	Fe (mg/l)	0.25	1.46	0.2
	As (µg/l)	13		<5

4.2 Quality of existing data

The data is relevant for this verification, since it covers both the operation of the product/technology and feed water quality.

However, the operational data is limited and stems from a different set-up and a different water works. Several analytical laboratories carried out the analysis and there is no information about QA of the results. Furthermore, no information on measurement uncertainties for the analysis is presented.

4.3 Accepted existing data

The existing data cannot be accepted for the verification, but will be used in the preparation of the test plan.

5 Requirements on test design and data quality

Based on the application and performance parameters identification the requirements for the test design have been set. A detailed test plan will be prepared separately based on the specification of the test requirements presented below.

5.1 Test design

The test design is partly based on the information given in US EPA/NSF ETV protocol for equipment verification testing for arsenic removal [11].

The outline of the required activities is given in Table 5-1 and consists of:

1. Site characterization
2. Equipment set-up and initial operation
3. Verification testing (Sampling and analysis)
4. Documentation

A more detailed description of each task in terms of work plan and objectives is given below. The results from each task will be reported in the verification report.

Table 5-1 Test design for this verification.

Task 1 Site characterisation	Task 2 Equipment set-up and initial operations	Task 3 Verification testing	Task 4 Documentation of verification
Description of the test site	Set-up of (online) measurement equipment and data logging	Verification testing - equipment and treatment capabilities	Data management
Characteristics of the facility	Check of operational conditions	On-line measurements	Data quality
Characteristics of feed water quality		Sampling on-site and external analysis	

5.1.1 Task 1 – Site characterisation

Objective: The objective of this task is to describe the test site, the facility and the feed water quality that is relevant for the operation of the MDA Arsenic Reduction process.

Work plan: The characterisation of the site comprises the following tasks:

- Description of the site and where the equipment is located
- Description of the facilities being used for handling the feed water, treated water and waste products from the testing program
- Pattern of operation (e.g. continuous or intermittent) of the feed water pumping system and the system itself and length of the operating cycle (feed water flow requirements, discharge requirements)
- Pre-selection of possible sampling points and suitable sampling principle (e.g. flow-proportional, time-proportional, spot samples)
- Characteristics of the feed water based on existing analytical data

5.1.2 Task 2 - Equipment set-up and initial operations

Objective: The objective of this task is to ensure that (online) measurement equipment and the treatment process are functioning as intended. This includes the determination of optimal operational conditions for the treatment process and the equipment to avoid technical problems during the verification testing.

Work plan: During the initial operations phase (two week period) the following tasks will be carried out:

- Set-up and testing of on-line measurement equipment, data logging and data communication
- Identification of optimal feed water flow and retention time in the system
- Identification of optimal operational conditions for the iron generator and MiroDrop aerator
- Adjustment of backwash flow and backwash time
- Final selection of sampling points and adjustment of sampling principle

5.1.3 Task 3 – Verification testing

Objective: The objective of this task is testing of the equipment. Based on sampling/analysis results (and online-measurements) the treatment capability is evaluated and verified. Furthermore, the response of equipment and treatment process to changes in feed water quality can be evaluated.

Work plan: The verification testing will be carried out over a two week period, including at least three full filter runs. A filter run is terminated either by reaching the maximum allowable head loss or the breakthrough of particles (turbidity).

The work plan comprises the following tasks:

- Monitoring and evaluation of the operational performance parameters during the verification filter cycles
- Sampling and analysis of feed water samples and treated water samples during the verification filter cycles
- Online-measurement of selected parameters in feed water and treated water during the verification filter cycles

5.1.4 Task 4 – Documentation of verification

Objective: The objective is to elaborate the protocol for the management of all data produced during testing.

Work plan: Deviations from the stated operating conditions (e.g. flow, pressure) will be documented in the field log book. Only filter cycles with deviation in operating conditions of less than +/-10% during 70% of the filter cycle will be included in the evaluation. For the filter cycle to be included in the data evaluation, data has to be collected during minimum 70 % of the duration of the filter cycle.

5.2 Reference analysis and measurements

Analysis and measurements will consist of:

- Sample analysis by external analytical laboratory
- On-line measurements at the test site

Table 5-2 Types of on-line measurements and analysis to be performed

On-line measurements	Water analysis	Solid analyses (sludge)
Oxygen content (mg/l)	Arsenic and arsenic species – As(III) and As(V) (µg/l)	Arsenic (mg/kg DM)
Oxygen saturation (%)	Iron (mg/l)	Iron (mg/kg DM)
Flow (m^3/h)	Manganese (mg/l)	Manganese (mg/kg DM)

Turbidity (FTU)	Chromium (µg/l)	Chromium (mg/kg DM)
Redox (mV)	Nickel (µg/l)	Nickel (mg/kg DM)
Conductivity (mS/m)	Colour (mg Pt/l)	
pH (-)		
Temperature (°C)		

5.3 Data management

Data storage, transfer and control must be in accordance with the requirements of the DANETV centre quality manual, [1], enabling full control and retrieval of documents and records. The filing and archiving requirements of the DHI quality manual must be followed; i.e. 10 years archiving.

On-line measurements are expected to be stored in a data-logger and retrieved by the test personnel via GSM modem. The data can then be transferred to Excel files for evaluation. The actual data handling will be specified further in the test plan.

5.4 Quality assurance

The quality assurance of the tests must include control of the test system (here the MDA Arsenic Reduction), the on-line measurement equipment (performance evaluation audit), control of analysis performed at external laboratory (results from proficiency tests) and control of the data quality and integrity.

The test plan and the test report will be subject to review by an internal expert as part of the review of this verification protocol and the verification report. Furthermore, test plan and test report shall be subject to review by the verification responsible.

A test system audit will be performed during the verification testing by an internal auditor.

5.5 Test report requirements

The test data provided in the test report must follow the principles of template of the DANETV centre quality manual [1], with data and records from the tests presented.

6 Evaluation

6.1 Calculation of performance parameters

Calculations are carried out according to generally accepted statistical principles. For all performance parameters (with at least three results), minimum, average and maximum values and precision will be stated. For arsenic the 95% confidence interval will be determined.

The following statistical calculations will be carried out: In order to evaluated effectiveness average is calculated

- *Average:*

  $$\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$$

  $\bar{X}$: average of values
  n: number of samples
  X_i: individual value

- *Precision:* In order to evaluate the precision, the standard deviation and relative standard deviation can be calculated

  $$SD = \sqrt{\frac{\sum_{i=1}^{n}(X_i - \bar{X})^2}{n-1}}$$

  $$RSD = \frac{SD}{\bar{X}}$$

  SD: standard deviation
  RSD: relative standard deviation
  n: number of samples
  X_i: individual value
  $\bar{X}$: average of values

- *Uncertainty:* For the analytical data produced during the verification the measurement uncertainty can be calculated for data based on at least 8 results and can be expressed with a 95% confidence interval around the sample mean value.

  Test if data are normally distributed.

  $$95\%\ \text{confidence interval} = \bar{X} \pm t_{n-1,0.975}\left(\frac{SD}{\sqrt{n}}\right)$$

  $\bar{X}$: mean of values
  $t_{n-1,\,0.975}$: Student´s distribution value with n-1 degrees of freedom and a significance level defined for 95 % confidence
  SD: standard deviation
  n: number of measurements included in data set

6.2 Evaluation of test quality

The test data provided in the test report will be evaluated against the requirements set in this protocol and the objectives set in the test plan. Only filter cycles with deviation in operating conditions of less than +/-10% during 70% of the filter cycle will be included in the evaluation. For the filter cycle to be included in the data evaluation, data has to be collected during minimum 70 % of the duration of the filter cycle.

Performance and test quality will be based on feed and treated water quality. Intermediate stages are not included.

The spreadsheet used for the calculations will be subject to control on a sample basis (spot validation of at least 5% of the data).

6.3 Operational parameter summary

Test data on operational parameters will be summarized in the test report (including minimum, average and maximum values).

6.4 Additional parameter summary

6.4.1 User manual

The verification criterion for the user manual is that the manual describes the use of the equipment adequately and is understandable for the typical laboratory technician and test coordinator. This criterion is evaluated through evaluation of a number of specific points of importance; see Table 6-1 for the parameters to be included.

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 6-1 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				

6.4.2 Required resources for operation

The capital investment and the resources for operation and maintenance, could be seen as the sustainability of the product, will be itemized based upon a determined design basis [13], see Table 6-2 for the items that will be included.

Table 6-2 List of capital cost items and operation and maintenance cost items per product unit.

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 MDA Arsenic Reduction technology will be listed. Note that the actual cost for each item is not compiled and reported.

Evaluation will also be done on the following subjects:

- Resources used during production of the equipment in the technology
- Longevity of the equipment
- Robustness/vulnerability to changing conditions of use or maintenance
- Reusability, recyclability (fully or in part)
- End of life decommissioning and disposal

6.4.3 Occupational health and environmental impact

The risks for occupational health and for the environment associated with the use of the products will be identified. A list of chemicals classified as toxic (T) or very toxic (Tx) for human health and/or environmentally hazardous (N) (in accordance with the directive on classification of dangerous substances [14]) will be compiled. The information will be given as amount used per product unit (sample), see Table 6-3 for format.

Table 6-3 Compilation of classified chemicals used during product operation.

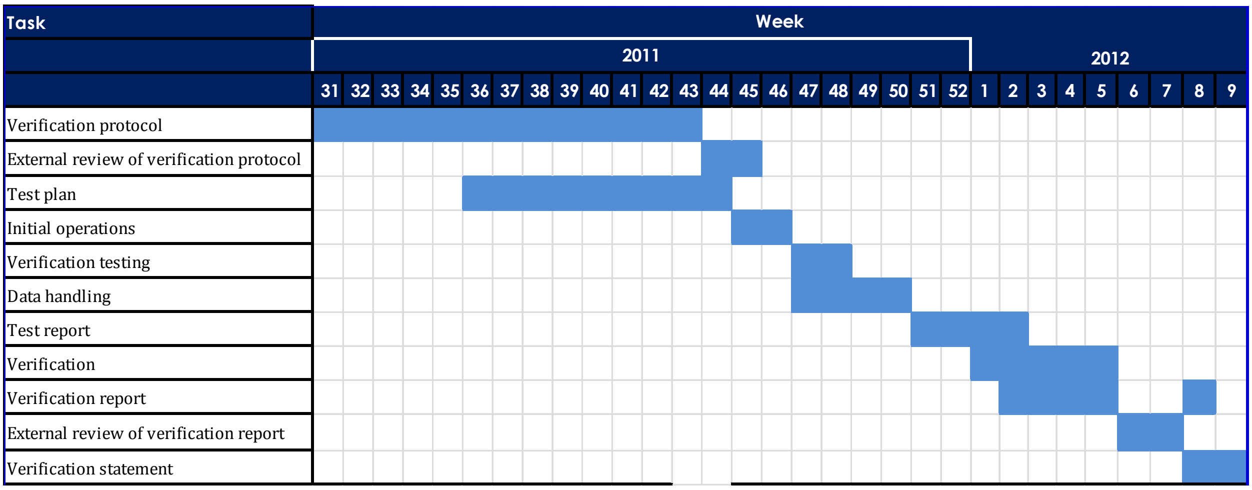
Compound	CAS number	Classification	Amount used per product unit

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.

7 Verification schedule

The verification is planned for 2011/2012. The overall and more detailed schedule is given in Table 7-1.

Table 7-1 Verification schedule (second half of 2011 and start of 2012)



8 Quality assurance

The personnel and experts responsible for quality assurance as well as the different quality assurance tasks can be seen in Table 8-1. All relevant reviews will be prepared using the DANETV review report template. In audit of the test will be performed, the relevant DANETV audit template will be used during the audit.

Table 8-1 QA plan for the verification.

	Internal experts (DHI)			Verification responsible	Proposer	External experts
Initials	MMK	BOP	MTA	MTA	MicroDrop	ASA
Tasks						
Verification protocol	Review				Review and approve	Review
Test plan	Review			Approve	Review and approve	
Test system at test site		Audit				
Test report	Review			Approve	Review	
Verification report	Review					Review

Internal review is conducted by Morten Møller Klausen (MMK) and a test system audit is conducted following GLP audit procedures by trained auditor Bodil Mose Pedersen (BOP).

Only verification protocol and verification report require external review according to EU ETV pilot programme GVP [1]. External review will be performed by Dr. Ali S. Amiri (ASA).

The verification responsible (MTA) does the approval of the test plan and test report.

9 References

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A P P E N D I C E S

APPENDIX A

Terms and definitions

Term	DANETV	Comments on the DANETV approach
Accreditation	Meaning as assigned to it by Regulation (EC) No 765/2008	EC No 765/2008 is on setting out the requirements for accreditation and market surveillance relating to the marketing of products
Additional parameter	Other effects that will be described but are considered secondary	None
Amendment	Is a change to a specific verification protocol or a test plan done before the verification or test step is performed	None
Analytical laboratory	Independent analytical laboratory used to analyse test samples	The test centre may use an analytical laboratory as subcontractor
Application	The use of a product specified with respect to matrix, purpose (target and effect) and limitations	The application must be defined with a precision that allows the user of a product verification to judge whether his needs are comparable to the verification conditions
DANETV	Danish centre for verification of environmental technologies	The centre comprises 4 centres covering: • Water technologies • Energy • Air • Agricultural technology
(DANETV) test centre	Preliminary name for the verification bodies in DANETV with a verification and a test sub-body	Name will be changed, when the final nomenclature in the EU ETV has been set
Deviation	Is a change to a specific verification protocol or a test plan done during the verification or test step performance	None
Evaluation	Evaluation of test data for a technology product for performance and data quality	None
Experts	Independent persons qualified on a technology in verification	These experts may be technical experts, QA experts for other ETV systems or regulatory experts
General verification protocol (GVP)	Description of the principles and general procedure to be followed by the ETV pilot programme when verifying an individual environmental technology.	None
Matrix	The type of material that the technology is intended for	Matrices could be soil, drinking water, ground water, degreasing bath, exhaust gas condensate etc.

Term	DANETV	Comments on the DANETV approach
Operational parameter	Measurable parameters that define the application and the verification and test conditions. Operational parameters could be production capacity, concentrations of non-target compounds in matrix etc.	None
(Initial) performance claim	Proposer claimed technical specifications of product. Shall state the conditions of use under which the claim is applicable and mention any relevant assumption made	The proposer claims shall be included in the ETV proposal. The initial claims can be developed as part of the quick scan.
Performance parameters (revised performance claims)	A set of quantified technical specifications representative of the technical performance and potential environmental impacts of a technology in a specified application and under specified conditions of testing or use (operational parameters).	The performance parameters must be established considering the application(s) of the product, the requirements of society (legislative regulations), customers (needs) and proposer initial performance claims
Procedure	Detailed description of the use of a standard or a method within one body	The procedure specifies implementing a standard or a method in terms of e.g.: equipment used
Proposer	Any legal entity or natural, which can be the technology manufacturer or an authorised representative of the technology manufacturer. If the technology manufactures concerned agree, the proposer can be another stakeholder undertaking a specific verification programme involving several technologies.	Can be vendor or producer
Purpose	The measurable property that is affected by the product and how it is affected.	The purpose could be reduction of nitrate concentration, separation of volatile organic compounds, reduction of energy use (MW/kg) etc.
(Specific) verification protocol	Protocol describing the specific verification of a technology as developed applying the principles and procedures of the EU GVP and this quality manual.	None
Standard	Generic document established by consensus and approved by a recognised standardization body that provides rules, guidelines or characteristics for tests or analysis	None
Test centre, test sub-body	Sub-body of the test centre that plans and performs test	None
Test centre, verification sub-body	Sub-body of the test centre that plans and performs the verification	None
Test/testing	Determination of the performance of a product for measurement/para-meters defined for the	None

Term	DANETV	Comments on the DANETV approach
	application	
Test performance audit	Quantitative evaluation of a measurement system as used in a specific test.	E.g. evaluation of laboratory control data for relevant period (precision under repeatability conditions, trueness), evaluation of data from laboratory participation in proficiency test and control of calibration of online measurement devises.
Test system audit	Qualitative on-site evaluation of test, sampling and/or measurement systems associated with a specific test.	E.g. evaluation of the testing done against the requirements of the specific verification protocol, the test plan and the quality manual of the test body.
Test system control	Control of the test system as used in a specific test.	E.g. test of stock solutions, evaluation of stability of operational and/or on-line analytical equipment, test of blanks and reference technology tests.
Verification	Provision of objective evidence that the technical design of a given environmental technology ensures the fulfilment of a given performance claim in a specified application, taking any measurement uncertainty and relevant assumptions into consideration.	None