MDA Arsenic Reduction

Test plan

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

MicroDrop Aqua Aps
February 2012

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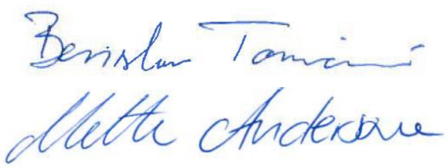

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Test plan

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

Prepared for MicroDrop Aqua Aps

Represented by Mr Idar Beck and Mr Krzysztof Piotr Kowalski

Iron generator and MDA

Project No	11520012
Classification	Open

Authors	Anke Oberender

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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 in drinking water.

1.1 Verification protocol reference

This test plan is prepared in response to the test design established in the MDA Arsenic Reduction verification protocol [1].

1.2 Name and contact of proposer

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Contact:
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Mr Krzysztof Piotr Kowalski, e-mail kk@microdropaqua.net, phone+45 52 48 31 92,
Microdrop website: http://microdropaqua.net/

1.3 Name of test body/test responsible

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

DHI
Agern Allé 5
2970 Hørsholm
Denmark

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

2 Test design

2.1 Test site

The verification of the MDA Arsenic Reduction will be carried out at one test sites in Denmark - Utterslev-Kastager water works (island of Lolland).

2.1.1 Types

The tests comprise on-site measurements (i.e. on-line measurement of relevant performance parameters and operational parameters) and laboratory analysis of grab samples.

2.1.2 Addresses

Utterslev Kastager water works

Højagervej 20

4913 Horslunde, Denmark

2.1.3 Descriptions

Utterslev-Kastager waterworks draws water from two groundwater wells – both situated at the site of the waterworks. When the wells were established in 1963, their capacity was estimated to be around 14 and 25 $m^3/t/m$. The geology at the site of the groundwater wells is dominated by lime and as a result of calcination the specific capacity of the groundwater wells might be reduced over time. The rate of groundwater abstraction was reported to be $5m^3/h$ per well [2].

Selected results for the groundwater quality (feed water quality) are shown in Table 2-1. The groundwater quality at Utterslev-Kastager water works is such that the concentration of ammonium, iron and arsenic is above the regulatory requirements. The level of iron and ammonium in the groundwater is not problematic with respect to treatment achievability of normal water treatment, but the arsenic concentration is well above the level where ordinary precipitation can achieve concentrations below regulatory requirements [2].

Table 2-1 Groundwater (feed water) quality at Utterslev-Kastager groundwater wells – data from ALECTIA A/S [2]

Parameter	Well 1 DGU no. 229.0172	Well 2 DGU no. 229.0173	Comments (ALECTIA A/S [2])
Date	10/12/2007	23/11/2006	
Arsenic	20-24 µg/l	20-24 µg/l	Very high concentration, above regulatory requirement
Iron	0.15-0.24 mg/l	0.15-0.24 mg/l	Low concentration, but above regulatory requirement
Chloride	67 mg/l	67 mg/l	Elevated concentration
Sulphate	33 mg/l	33 mg/l	
Hardness	17-18 °dH	17-18 °dH	
Nitrate			Low concentration
Ammonium			Above regulatory requirement
Aromatic hydrocarbons, chlorophenols, chlorinated solvents, pesticides (and degradation products) [2]			Not detected

Utterslev-Kastager waterworks has provided drinking water (treated water) data for the last couple of years. Data with relevance for the verification testing are shown in Table 2-2. With regard to arsenic the data included only two results for drinking water that has been sampled before the MDA Arsenic Reduction was installed at the waterworks. Please note, that those results represent concentrations in drinking water at the user´s tap whereas the remaining results are for drinking water sampled directly at the waterworks.

The transport of water from the waterworks through the drinking water pipeline and to the user´s tap may affect some parameters – especially temperature, which may explain the relatively large variations in results (see Table 2-2).

Table 2-2 Characteristics of feed water and drinking water quality (initially collected data) (values in italics represent drinking water sampled at the users tap)

Parameter	Unit	Initially collected data – treated water (drinking water)						
Selected performance parameters								
Date		*02/09/2008*	13/01/2009	*05/10/2010*	27/01/2010	13/01/2011	04/10/2011	31/10/2011
Comment		Before installation of MDA Arsenic Reduction					After installation of MDA Arsenic reduction	
Sampling point		*User´s tap*	waterworks	*User´s tap*	waterworks	waterworks	waterworks	waterworks
As	µg/l	*12*		*9.1*			5.3	5.7
Fe	mg/l	*< 0.005*	< 0.005	*< 0.01*	< 0.005	< 0.01		
Mn	mg/l		< 0.005		< 0.005	< 0.005		
Oxygen content	mg/l	*7.0*	4.4	*6.6*		8.2		
Operational parameters								
Turbidity	FTU		0.099			0.21		
Colour	(mg Pt/l)		3.6			1.3		
Conductivity	mS/m	*77*	77	*77*	75.5	76		
pH	-	*7.3*	7.5	*7.4*	7.4	7.6		
Tempera-ture	°C	*16.8*	9.5	*13.0*	7.6	9.0		
Ni	µg/l	*0.39*		*0.14*				

Table 2-3 contains information regarding Utterslev-Kastager waterworks (test site and facility). The information was collected during the preparation of the test plan and was provided by the board of the waterworks, MicroDrop representative and the producer of the sand filters that are installed at the test site. Additional information was collected during a site visit the 26th October 2011. Figure 2-1 and Figure 2-2 show some of the pictures that were taken during the site visit.

Table 2-3 Description of test site and characteristics of the facility

Parameter	Information
General	
Name and site location	Utterslev-Kastager waterworks, Højagervej 20, 4913 Horslunde
Contact person (testing)	Mogens Popowitz
Pattern of operation	Continuous, but stopped when max. level in drinking water tank is reached
How many households does the waterworks supply water to?	219
Average range of production (min-max per day)	Ca. 35 – 50 m^3
How much water is abstracted per groundwater well and day?	Waterworks operates with approx. 4m^3/h flow. With average production of 35-50 m^3 per day approx. 17.5-25 m^3 is abstracted per day.
Is water abstracted from both groundwater wells at the same time or alternating?	From both wells at the same time
MicroDrop iron generator	
Iron generator capacity	Approx. 0,75 m^3 The iron anode is arranged around a centre cathode. The release of iron may be enhanced by an electric current that may be varied by a constant current generator.
How often are the iron anodes replaced?	Approx. once a year
MicroDrop aerator	
Aerator capacity	Set at 10 m^3/h (range of capacity is 10 to 30 m^3/h) Size: approx. 80 cm in width, 120 cm in height, but depending on the number of modules (50 cm in height per module)
Operating principle (e.g. diffusers)	Aeration due to gravity
How is the aeration rate controlled?	Indirectly via water flow through the aerator system
Typical aeration rate (e.g. air pressure)	Normal pressure (1 bar)
Regular maintenance/cleaning required (e.g. precipitated sludge etc.? How often on average?	1-2 times a year
Sand filter	
Filter type	Two closed pressure filters; Silhorko – Eurowaters A/S (contact person: Thomas Reuter, telephone: +45 4820 1003), Eurotank Modul NSB 130, nr. 43094 Filters nr. 3915 and 3916; 1015 litre each and 7,8 m^3/h (when installed in series), max. 6 bar
Filter capacity /average filtration rate	Filters are set up in parallel and filtration rate is ca. 3.9 m^3/h
Filter height	2.3 m
Filter cross section	80 cm
Height of filter bed	1.3 m
Maximum head loss	0.5 bar
Structure and composition of filter bed (no of layers/size fractions and particles sizes, type of material)	Three layers: Top layer: Nevtraco filter media (1-3 mm), 540 litre Middle layer: gravel /sand (1.6 – 2.5 mm), 52 litre Bottom layer: gravel / sand (3.5 mm), 50 litre
Filter age	10 years
Average length of operating cycle/filter run	235 m^3 (approx. 59 hours)
What defines the length of one filter run - turbidity break through, terminal head loss, time?	Drinking water production (235 m^3) in combination with time: After flow through of 235 m^3 backwashing is started for one filter. After an additional flow

	through of 235 m³ backwashing is started for the second filter. This means that the filter run for each filter is approx. 470 m³. Backwashing is started during the night (around 1 or 2 am) after the flow through of 235 m³ is reached.
Is the backwash started automatically or manually?	Automatically
Average duration of backwashing and backwash rate (flow)	Back wash procedure (per filter): 5 min flushing with air 2 min break 5 min flushing with water; water flow is approx. 8.4 m³/h (700 l/ 5 min)
Where is the backwash water discharged to?	Desludging tanks
Average water consumption for backwash	ca. 700 l
How long is the turbidity spike on average, i.e. time after backwash before turbidity levels are back to normal for filter operation mode?	Has not been measured previously
Do you redirect the first portion of filter water after backwash to the desludging tank/sewerage until the turbidity spike subsides?	No
Drinking water	
Is the drinking water fed directly into the drinking water system or is it stored, i.e. in a buffer tank beforehand?	Stored in a buffer tank (drinking water tank) of 17 m³
Desludging tank	
Tank capacity	Two plastic tanks, 600 litre each
Is the decantate (partly/all) used for backwashing the filter (i.e. recycling of backwash water)?	No
How often is the desludging tank emptied?	Approx. once a year
How is the tank emptied?	Mechanically – Sludge can be drained at the bottom of each tank, and the decantate is discharged once it reaches the level of the connected sewage pipes.
Where is the sludge disposed of?	Community waste deposit
Where is the backwash water (decantate) disposed of?	Backwash water is pumped into the desludging tanks where the solids settle. The decantate is discharged into the sewer.
In-line measurement	
Do you have in-line measurement equipment installed?	Yes
If yes, what kind (e.g. turbidity meter, pH meter)?	One flow meter
If yes, where is it installed?	Drinking water pipe to buffering tank
Is there a possibility for on-line logging of measurement data?	No (Water production is recorded continuously in a printing recorder and can be set to record once per hour. However, the smallest unit recorded is 1 m³, i.e. water production below this value will be recorded as "0".)
Sampling	
Describe potential sampling points for: a) Feed water (groundwater) b) Filtered water c) Backwash water (decantate) d) Sludge from desludging tank e) Turbidity spike (filtrate produced after backwash)	 a) Tap b) Tap c) Desludging tank d) Bottom tap at desludging tank e) Desludging tank or from tap at each sand filter
Identification of sampling principle for: a) Feed water (groundwater) b) Filtered water c) Backwash water (or decantate) d) Sludge from desludging tank e) Turbidity spike (filtrate produced after backwash)	 a) Grab sampling b) Grab sampling c) Grab sampling d) Grab sampling e) Grab sampling and/or on-line measurements

Figure 2-1 Pictures take during the site visit 26th October 2011: Top left - of iron generator; top right - iron generator and aerator; bottom left – groundwater pumps and red/orange tap for groundwater and blue tap for drinking water; bottom right – inside the waterworks

Figure 2-2 Pictures take during the site visit 26th October 2011: from left to right 1) first desludging tank with backwash water inlet through the top of the tank 2) second desludging tank with outlet for decantate discharge to sewerage 3) desludging tanks with connecting pipe and bottom taps for sludge discharge; tank to the right with inlet pipe through the top of the tank and tank to the left with big outlet pipe to sewerage

2.2 Tests

The test design for the verification testing of the MDA Arsenic Reduction is described in the following sections.

2.2.1 Test methods

In accordance with the verification protocol [1], the test design has been divided into four main tasks - site characterization, equipment set-up and initial operations, verification testing and documentation of verification.

1. Site characterization

A number of information regarding site characterization was collected during the preparation of the test plan and this information is given in section 2.1.3 Descriptions. Table 2-1 and Table 2-2 contain feed water quality data for the groundwater drawn at the Utterslev-Kastager waterworks as well as data on quality of treated water (drinking water). Additional data will be collected during the verification testing.

Table 2-3 was sent to the relevant contact persons at the Utterslev-Kastager waterworks and MicroDrop, respectively, and necessary information was filled in. The producer of the sand filters that are installed at the waterworks contributed with information about the filter design and capacity and additional information was collected during a site visit 26th October 2011.

2. Equipment set-up and initial operations

During a two week period equipment set-up and initial operations are carried out to ensure that on-line 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 in order to avoid technical problems during the verification testing – which means the following tasks:

- 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 (i.e. adjustment of length of filter run)
- Identification of optimal operational conditions for the iron generator and MicroDrop aerator
- Adjustment of backwash flow and backwash time
- Final selection of sampling points and sampling method/equipment for feed water, filtered water, backwash water (decantate), sludge from the desludging tank, turbidity spike (filtrate produced after backwash)

Once the optimal operational conditions have been identified they will be summarized (see Table 2-8). The verification testing will be conducted under the identified operational conditions.

3. Verification testing

Verification testing will be conducted over a two-week period. Based on the results from sampling and analysis conducted during the verification testing, the treatment capability will be evaluated and verified. Furthermore, the response of the equipment and treatment process to changes in feed water quality can be evaluated.

The verification testing shall include at least three full filter runs. A filter run is determined by the drinking water production in combination with a timer. As specified by Utterslev-Kastager water works backwashing is started during the night once 235 m^3 of drinking water has been produced. The length of the filter runs and timer settings will be adjusted during equipment set-up and initial operations so that sampling can be done during normal working hours. The operational conditions for the verification testing are described in Table 2-8.

The following tasks will be carried out during verification testing:

- 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, as well as backwash water, sludge and turbidity spike
- On-line measurement of selected parameters in feed water and treated water during the verification cycles, as well as in turbidity spike

4. Documentation of verification

Appendix E contains report forms to be used for data from sampling and analysis of feed water and treated water samples during the verification testing. Furthermore, tables for data on sludge and decantate (backwash water) from the desludging tank and turbidity spike can be found.

On-line measurements of feed water, treated water and turbidity spike will include the parameters shown in Table 2-4. The results will be reported in a data table with information on average value, standard deviation, confidence interval and min/max values, see Appendix E.

Table 2-4 Operational parameters - on-line measurement of feed water, treated water and turbidity spike

Parameter	Unit
Oxygen content	mg/l
Turbidity	FTU
Redox	mV
Conductivity	mS/m
pH	-
Temperature	°C

2.2.2 Test staff

Test responsible is Anke Oberender, DHI (initials: AOB). The daily operation and sampling at the Utterslev-Kastager waterworks will be performed by a representative of the waterworks.

2.2.3 Test schedule

The test schedule can be seen in Table 2-5.

Table 2-5 Test schedule

Task	Week																							
	2012																							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Test plan																								
Euipment set-up and initial oparations																								
Verification testing																								
Data handling																								
Test report																								

2.2.4 Test equipment

MDA Arsenic Reduction is installed at the Utterslev-Kastager waterworks.

2.2.5 Type and number of samples

Table 2-6 shows the type and number of samples to be taken during the verification testing. A combination of grab sampling and on-line measurements will be used. Sample containers for grab samples will be provided by the analytical laboratory carrying out the chemical analysis.

All grab samples (apart from color) shall be taken in duplicates to ensure that there is a back-up sample, i.e. if a sample container breaks during transportation. One of each duplicate is stored as back-up whilst the other one is sent for analysis.

Grab samples of feed water and treated water will be taken from the sampling ports for groundwater (feed water) and drinking water (treated water). Sampling time, flow, iron generator settings and a number of other details will be recorded for each sample using the data report forms in Appendix E. When sampling, the valve at the sampling port should be opened for at least 30 seconds and the water collected will be discharged to the sewerage. Afterwards, the grab sample is filled into the appropriate sample container(s) and preserved if necessary. Samples are stored at 4 °C until chemical analysis.

Grab samples of backwash water/decantate will be taken from the desludging tanks after each backwash. Upon sampling one sample will be taken from each tank by lowering a beaker or bottle attached to a telescopic rod into the tank. The first volume of water sampled shall be discarded to the sewerage. The beaker/bottle will be lowered into the tank again and the actual sample will be taken. Water from the beaker/bottle will be transferred into the appropriate sample container(s) and preserved if necessary. Samples are stored at 4 °C until chemical analysis.

Grab samples of sludge can be taken in two different ways. Sludge can be drawn from the bottom outlet of each tank. Alternatively samples can be taken from each tank using sampling equipment such as a Coliwasa sampler, which allows sludge to be taken from a defined depth in the tank. Samples will be transferred into the appropriate sample container and will be stored at 4 °C until chemical analysis. Sampling time, flow, iron generator settings and a number of other details will be recorded for each sample of decantate and sludge using the data report forms in Appendix E. It can be assumed that most of the particles will settle in the first tank, where the backwash water enters the desludging tanks. If the level of sludge in the second tank is too low to take a sample, sampling of sludge will be limited to the first tank. The sampling method/equipment will be decided during equipment set-up and initial operations.

Table 2-6 Type and number of samples

Matrix	Type of sample	Number of grab samples to be sent for analysis	On-line measurement
Feed water	Grab sample and on-line measurement	10-12 (1-2 samples per filter run*)	Measurement over ca. 30 minutes (will be determined once the length of the turbidity spike is known)
Treated water	Grab sample and on-line measurement	10-12 (1-2 samples per filter run)	Measurement over ca. 200 minutes (will be determined once the length of the turbidity spike is known)
Decantate from de-sludging tank 1 and 2	Grab sample	5-6 samples from each tank (1 sample per filter run); Total of 10-12 samples	-
Sludge from desludg-ing tank 1 and 2	Grab sample	5-6 samples from each tank (1 sample per filter run); Total of 10-12 samples	-
Turbidity spike (fil-trate produced after backwash)	Grab sample and on-line measurement	10 samples per filter (sam-pling of two turbidity spikes per filter; 5 samples per sam-pling round); Total of 20 samples	Measurement over entire length of turbidity spike, one filter at a time (length to be determined during equipment set-up and initial operations

*Initially the average length of a filter run is approx. 59 hours (235 m^3 and 4 m^3/h) or 2.5 days. With 14 day operation during the verification run this should allow for 5-6 filter runs.

Turbidity spike is the first filtrate that is produced after backwash of the filters. Grab samples of this filtrate can be taken directly from a sampling port at each filter. During equipment set-up and initial operations the length of the turbidity spike will be determined based on on-line measurements of turbidity. Consequently, it can be determined at what intervals grab samples of the turbidity spike will be taken (e.g. after 1, 5, 10, 20 minutes). Details, such as sampling time, flow and turbidity meter reading are filled in using the data report form in Appendix E. Samples are filled into the appropriate sample container(s), preserved if necessary and will be stored at 4 °C until chemical analysis.

On-line measurements will be conducted for a number of parameters (see Table 2-6 and Table 2-7). The equipment for on-line measurement and data recording is installed in a trailer which will be placed at the water works. Water is pumped into the system and flows through the measurement equipment that is installed in series. The intake will shift between feed water and treated water, and directly after back wash of the sand filters, the intake will shift to the sampling ports at the sand filters to monitor the water quality of the turbidity spike. Monitoring of the turbidity spike is intended to take place one filter at a time.

Table 2-7 On-line measurements of feed and treated and turbidity spike during verification testing

Parameter	Unit	Recording
Oxygen content	mg/l	Data logger, 1-minute average
Turbidity	FTU	Data logger, 1-minute average
Redox	mV	Data logger, 1-minute average
Conductivity	mS/m	Data logger, 1-minute average
pH	-	Data logger, 1-minute average
Temperature	°C	Data logger, 1-minute average

2.2.6 Operation conditions

The MDA Arsenic Reduction installed at the Utterslev-Kastager waterworks will be operated at defined conditions. Operation conditions will be determined during equipment set-up and initial operations.

2.2.7 Operation measurements

During equipment set-up and initial operations the operations conditions, type of measurement and recording will be determined and will be summarized in Table 2-7. During verification testing the operations conditions will be measured (e.g. on-line) and recorded (e.g. manually or by data-logger) accordingly.

Table 2-8 Operational conditions for MDA Arsenic Reduction during verification testing and sampling points

Operational conditions	Unit	Set-up	Measurement	Recording
Flow	m^3/h			
Filtration rate	m/h			
Backwash frequency	No/days			
Duration of backwash	minutes			
Backwash rate (flow)	m^3/h			
Length of turbidity spike	minutes			
Sampling points and principle for:		**Sampling point**		**Sampling principle**
a) Feed water (groundwater) b) Filtered water c) Backwash water (decantate) d) Sludge from desludging tank e) Turbidity spike (filtrate produced after backwash)		a) b) c) d) e)		a) b) c) d) e)

2.2.8 Product maintenance

According to the information about the test site and MDA Arsenic Reduction plant product maintenance will not be relevant during the verification testing.

2.2.9 Health, safety and wastes

Work at the test site will be done according to the DHI rules for safe field work included in the DHI safety rules.

When handling sludge and water samples from the desludging tanks, care shall be taken, since the levels of arsenic and other metals can be expected to be elevated. The sampler is therefore advised to wear disposable gloves during sampling.

The analytical laboratory will provide sample containers. Some of the containers will contain preservation liquid, e.g. nitric acid. Care shall be taken when handling those sample containers and the sampler is advised to wear goggles and disposable gloves when handling the sampling containers.

3 Analysis and measurements

3.1 Analytical laboratory

The majority of chemical analyses will be carried out by ALS Scandinavia AB, Aurorum 10, SE-997 75 Luleå, Sweden.

Contact person: Anna Engberg, email Anna.Engberg@alsglobal.com, telephone +46 920 28 9963,

Homepage: http://www.alsglobal.se/

Analysis of colour in water samples will be carried out by Eurofins Miljø A/S, Ladelundvej 85, DK-6600 Vejen.

Contact person: Vivi Handberg, email vha@eurofins.dk, telephone +45 70 22 42 55

Homepage: http://www.eurofins.dk

3.2 Analytical and measurement parameters and methods

Table 3-1 gives a summary of the chemical analyses that will be conducted during the verification testing. The table show the name and type of the analysis and the parameters included. Furthermore, the name of the laboratory carrying out the analysis can be seen, the standard or analytical test method used and whether or not the analysis is accredited.

Table 3-1 chemical analysis – laboratory, standard/method and accreditation

Analysis	Type	Parameters	Laboratory	Standard/method	Accredited
V2	Water analysis	As, Fe, Mn, Cr, Ni	ALS	Analysis of acid sample without digestion. The analysis is performed by ICP-AES (according to EPA 200.7 modified), ICP-SFMS (EPA 200.8 modified)	Yes (inclusive tot- As)
Colour	Water analysis	Colour	Eurofins	DS/EN I 6271-2	Yes
M2	Solid analysis	As, Fe, Mn, Cr, Ni	ALS	The samples are digested in HNO3 in Teflon vessels in a micro oven and then analyzed with ICP-SFMS (according to EPA 200.8 modified).	Yes (inclusive As-tot)
Dry matter	Solid analysis	Dry matter	ALS	SS 02 81 13-1	Yes
LOI	Solid analysis	LOI	ALS	SS 02 81 13-1	Yes
pH	Solid analysis	pH	ALS	SS 02 81 22-2	No

3.3 Analytical and measurement performance requirements

3.4 Preservation and storage of samples

Table 3-2 shows an overview of preservation and storage requirements for the grab samples to be taken. Water samples for metal analysis are to be conserved by adding supra pure 1% HNO_3 to each sample (e.g. 1 ml HNO_3 to 100 ml water).

Chemical analysis of color for water samples needs to be performed within 24 hours. Therefore, water samples need to be sent to the analytical lab right after sampling (Daily pick up of samples by Eurofins-courier can be arranged). The samples cannot be frozen prior the analysis.

Sludge samples do not need to be preserved but stored in a plastic container and in a cold place.

Table 3-2 Preservation and storage of grab samples

Matrix	Parameter	Sample container	Sample amount	Preservation	Storage
Feed water	As, Fe, Mn, Cr, Ni	V2-analysis – acid washed bottles	50 ml	supra pure 1% HNO_3 (e.g. 1 ml HNO_3 to 100 ml water);	Stored at around 4 °C
	color	Orange cap plastic bottle (sample container no 4)	500 ml	No preservation required; Sample bottle is to be filled to the top	Immediate transport to lab
Treated water	As, Fe, Mn, Cr, Ni	V2-analysis – acid washed bottles	50 ml	supra pure 1% HNO_3 (e.g. 1 ml HNO_3 to 100 ml water);	Stored at around 4 °C
	color	Orange cap plastic bottle (sample container no 4)	500 ml	No preservation required; Sample bottle is to be filled to the top	Immediate transport to lab
Decantate from desludging tank	As, Fe, Mn, Cr, Ni	V2-analysis – acid washed bottles	50 ml	supra pure 1% HNO_3 (e.g. 1 ml HNO_3 to 100 ml water);	Stored at around 4 °C
	color	Orange cap plastic bottle (sample container no 4)	500 ml	No preservation required; Sample bottle is to be filled to the top	Immediate transport to lab
Sludge from desludging tank	As, Fe, Mn, Cr, Ni	M2- Plastic container	Min. 10 g	-	Stored at around 4 °C
Turbidity spike	As, Fe, Mn, Cr, Ni	V2-analysis – acid washed bottles	50 ml	supra pure 1% HNO_3 (e.g. 1 ml HNO_3 to 100 ml water);	Stored at around 4 °C
	color	Orange cap plastic bottle (sample container no 4)	500 ml	No preservation required; Sample bottle is to be filled to the top	Immediate transport to lab

3.5 Data management

Data management will follow the filing and archiving rules described in the DHI quality system. All relevant project documents, e-mail communication and data will be stored on the project SharePoint Site.

3.6 Data storage, transfer and control

Table 3-3 shows a summary of the type of data and recording/storage for the data from the verification. Data control will be performed as part of the test report review.

The test plan and test report will be compiled as protected PDF file and will be stored on the project SharePoint Site. Data from on-line measurements will be stored on a local data logger. After completion of the testing, on-line measurement data will be transferred to DHI and will be stored on the project SharePoint Site. Handwritten field data and completed data report forms will be scanned as PDF-documents and stored at the project SharePoint Site.

Any deviation from the test plan will be recorded into a field log book – with date, time, initials and description of the reason/event for deviation and actions taken.

Samples to be sent for (chemical) analysis by an external laboratory will be labeled in advance to ensure correct transfer of analytical data to relevant data report forms.

Table 3-3 Summary of data storage, transfer and control

Data type	Data media	Responsible for recording/storage of data	Timing of data recording/storage	Data storage
Test plan and report	Protected PDF files	Test responsible, DHI	When approved	Files and archives at DHI
On-line measurements	Excel files	Test responsible, DHI	During testing	Files and archives at DHI
Test details in laboratory and field	Log book and pre-prepared forms	Test responsible and technician, DHI; responsible from waterworks	During testing	Files and archives at DHI
Calculations	Excel files	Test responsible, DHI	During calculation	Files and archives at DHI
Analytical reports	Paper	Test responsible, DHI	When received	Files and archives at DHI

4 Quality assurance

4.1 Test plan review

The test plan will be put through an internal review by Morten Møller Klausen (MMK), DHI. The proposer, represented by Mr Idar Beck and Mr Krzysztof Piotr Kowalski will also carry out a review of the test plan.

4.2 Performance control – analysis and measurements

Chemical analyses are carried out by a laboratory with accreditation for the majority of parameters – measurement of pH in sludge is not accredited.

Both ALS and Eurofins are accredited for a number of analytical methods – ALS is accredited by SWEDAC (Swedish Board for Accreditation and Conformity Assessment) whilst Eurofins is accredited by DANAK (Danish Accreditation and Metrology Fund). Both laboratories comply with the international quality standard ISO 17025.

ALS will carry out the relevant water and sludge analysis of metals in accordance with two modified US EPA methods – the EPA 200.7 method describes analysis with ICP-AES and EPA 200.8 analysis with ICP-MS. There are several modifications done to meet the demands according to Swedish rules, regulations and directions, but also to fit the laboratory instrumentation on site and to fit sample types other than water, such as ash, biological samples and so on. Furthermore, ALS analyzes for more elements then mention in the EPA methods.

ALS has participated in several round robin tests, for example SYKE, and has provided documentation of that (Syke 3-2010 - Water and sediment, Syke 3-2011 - water and sludge).

The typical limits of quantification (LOQ) and measurement uncertainties (MU) for the relevant analyses can be seen below.

Table 4-1 Typical limits of quantification (LOQ) and measurement uncertainties (MU) for the relevant analyses

Parameter	LOQ	MU
Water analysis		
As	0.05 µg/l	
Fe	0.4 µg/l	
Mn	0.03 µg/l	
Cr	0.01 µg/l	
Ni	0.05 µg/l	
Colour	5 mg Pt/l	14% at 20 mg Pt/l
Solid analysis		
As	0.1 mg/kg DM	
Fe	10 mg/kg DM	
Mn	0.5 mg/kg DM	
Cr	0.1 mg/kg DM	
Ni	0.08 mg/kg DM	

4.3 Test system control

4.4 Data integrity check procedures

Deviations from the stated operating conditions (see Table 2-8) will be documented in a 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 a filter cycle to be included in the data evaluation, data has to be collected during minimum 70% of the duration of the filter cycle.

4.5 Test system audits

An internal audit of the test system will be performed by Bodil Mose Pedersen, DHI.

4.6 Test report review

The test report will be reviewed by Morten Møller Clausen, DHI as well as by the proposer, represented by Mr Idar Beck and Mr Krzysztof Piotr Kowalski.

5 Test report

The test report will be based on the template that can be found in the DANETV quality manual. The test report shall refer to the test plan and a summary of any amendments to and deviations from the test plan recorded during test from the plans shall be included. Templates for reporting amendments and deviations can be found in the DANETV quality manual.

The test data report shall include all analytical and calculated data as well as a reference to the staff performing the test. The methods of calculation, test measurement and performance parameters from raw data shall be described, unless they are given in the analytical and test methods used. If relevant, details on equipment and software used shall be included.

The test report shall be reviewed by the test center internal expert and the proposer and shall be approved by the verification responsible before the verification report is prepared.

5.1 Amendment report

The test report section on amendments will compile all changes to the test plan occurring before testing and will contain justifications of amendments and evaluation of any consequences for the test data quality.

5.2 Deviations report

The report section on deviations will compile all deviations from this test plan occurring during testing with justification of deviations and evaluation of any consequences for the test data quality.

6 References

1. DANETV (2011) MDA Arsenic Reduction. Verification protocol. DHI. September 2011.
2. ALECTIA A/S (2009) Ressource- og indvindingsvurdering, 29 vandværker i Lolland Kommune, bilag til vandforsyningsplanen

APPENDICES

APPENDIX A

Terms and definitions

The terms and definitions used by the DANETV test centres are derived from the EU GVP, ISO 9001 and, ISO 17020

Term	Definition	Comments
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	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 technology 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 technology 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	A change to a specific verification protocol or a test plan done during the verification or test step performance	None
Environmental technologies	Environmental technologies are all technologies whose use is less environmentally harmful than relevant alternatives	The term technology covers a variety of products, processes, systems and services
Evaluation	Evaluation of test data for a technology 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

Term	Definition	Comments
Innovative environmental technologies	Environmental technologies presenting a novelty in terms of design, raw materials involved, production process, use, recyclability or final disposal, when compared with relevant alternatives.	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.
Method	Action described by e.g. generic document that provides rules, guidelines or characteristics for tests or analysis	An in-house method may be used in the absence of a standard, if prepared in compliance with the format and contents required for standards, see e.g.: /8/
NOWATECH	Nordic Water Technology Verification Centres	
Operational parameter	Measurable parameters that define the application and the verification and test conditions. .	Operational parameters could be flow, pH, temperature, production capacity, concentrations of non-target compounds in matrix etc
(Initial) performance claim	Proposer claimed technical specifications of technology. 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 technology, the requirements of society (legislative regulations), customers (needs) and proposer initial performance claims.
Potential environmental impacts	Estimated environmental effects or pressure on the environment, resulting directly or indirectly from the use of a technology under specified conditions of testing or use.	None
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
Product	Ready to market or prototype stage product/technology, process, system or service based upon an environmental technology	Technology is used instead of the term product
Proposer	Any legal entity or natural person, 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	Can be vendor or producer

Term	Definition	Comments
	several technologies.	
Purpose	The measurable property that is affected by the technology 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.
Ready to market technology	Technology available on the market or at least available at a stage where no substantial change affecting performance will be implemented before introducing the technology on the market (e.g. full-scale or pilot scale with direct and clear scale-up instructions).	None
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 technology for measurement/para-meters defined for the application	None
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.
Vendor	The party delivering the technology to the customer. Here referred to as proposer	Can be the producer

Term	Definition	Comments
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

APPENDIX B

Reference methods

APPENDIX C

In-house test methods

APPENDIX D

In-house analytical methods and measurements

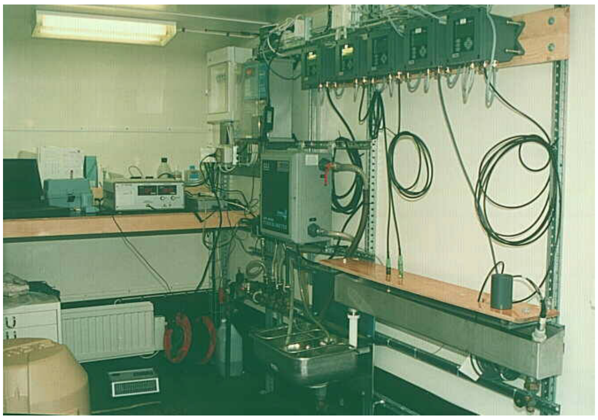
Description of DHI's trailer with on-line measurement equipment

DHI Sweden mobile equipment for on-line water quality parameters in water treatment plants and water distribution systems

The equipment

DHI Sweden has a mobile equipment for on-line measurement of water quality parameters in drinking water treatment plants and at water distribution systems. The instruments are assembled in a trailer transportable by a passenger car. The following instruments and equipment are available:

- UV-absorbance
- Turbidity
- Chlorine residual
- pH
- Redox-potential
- Conductivity
- Oxygen
- Temperature
- Water pressure
- Sample water flow meter
- Sample water valve controller
- Particle counter
- Datalogger with GSM-modem



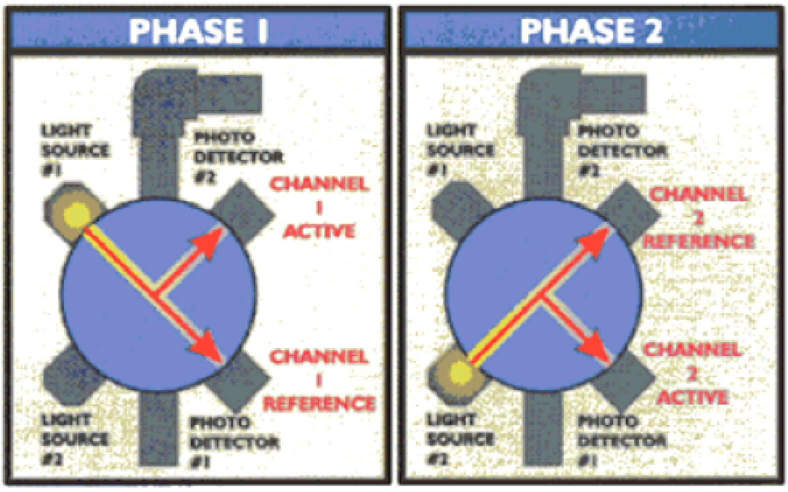
The sample water is led into the trailer normally from a fire hydrant or from a water tap in a plastic tube. The pressure is reduced and the water is led through a measurement channel where the electroanalytical electrodes are inserted, or through the different instruments of flow-through type. The total inflow can be controlled as well as the individual flows through the instruments. The total sample flow is normally 4-6 litres/min, or 8 m3/day. The water is finally discharged via a plastic tube to an appropriate sewer manhole or a drainage ditch.

For water treatment plant studies there are possibilities to use a special UV-absorbance meter together with a sample water valve controller with 4 different inlet sources, thus possible to collect water from various stages in the treatment process in a treatment plant. This equipment can also be combined with optional instruments which are normally used. Two pumps are available to transport water from treatment basins etc.

In the following, those instruments and signals that are relevant for the chemical coagulation treatment step in surface water treatment plants are described in more detail. (The particle counter, however, will be described separately).

Instruments - short description

<u>Turbidity</u> is measured by a GLI instrument (Swedish brand Satron) model Accu 4 with a range of measurements between 0.000-100.0 NTU with four significant digits. The measurement principle is a 4-beam radiometric method according to USEPA (GLI Method 2). The reflection of two different light sources is alternately detected at right angles to incoming light beam.



For calibration a glass cube, factory approved against a known USEPA formazine standard, is used.

Instrument performance

System error ±2% of measurement value for all ranges
Flow velocity 0.2-26.5 l/min
Sensibility 0,001 NTU
Stability 0,1% of measurement range
Integrated air bubble trap for 0.2-1.8 l/min

pH is measured by a GLI instrument (Swedish brand Satron) model P53.
Calibration is performed with buffer solutions with pH 9 and pH 6.

Instrument performance

Measurement range: pH -2.00 to 14.00 pH
Accuracy 0,1% of measurement range
Stability 0,05% of measurement range
Repeatability 0,1% of measurement range

Electrode:
Satron 970070 - for pH-measurements in cold waters with low ionic strength
Combination electrode with closed double KCl reference
0,1-mol KCl i reference part close to the media.
0-14 pH, max 7 bar, max 100 ^{o}C.

Conductivity is measured by a GLI instrument (Swedish brand Satron) model C53

The conductivity measurement cells with internal temperature compensation are at factory calibrated by 1 point so called dry calibration. That means that the cell at factory can be claimed to be exactly measured and marked when temperature- an cell constants are considered.

Measurement units: µS/cm, mS/cm, MΩ · cm, KΩ · cm, ppm, ppb, %

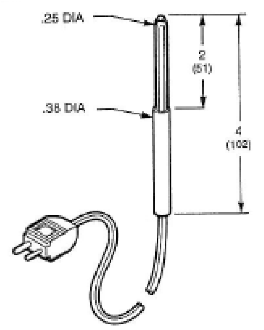
Instrument performance

Cell constants/measurement ranges:
C=0,5 0-1000 µS/cm, 0,001-20 MΩ · cm
Sensibiliy 0,05% av mätområde
Stability 0,05% av mätområde
Repeatability 0,1% av mätområde
Temperature compensation automatisc/manual -20 to +200oC

Temperature information can be fetched as a signal from the conductivity meter.

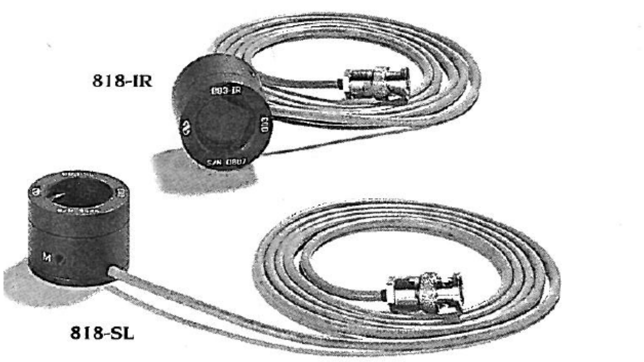
UV-absorbance

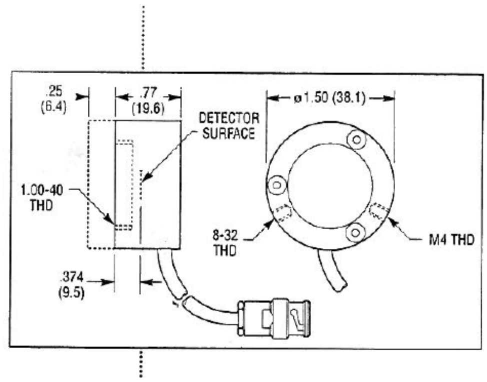
The measurement system for UV-absorbance is constructed by DHI. The sample water is continuously led through a cuvette with a measuring compartment of 4 cm from the light source window to the detector window.



The light source is a spectral calibration lamp Oriel 6035 HG(Ar) with irradiance more than 10 µW/cm^2 at 50 cm of wavelength 253.7 nm.

An Oriel UV-interference filter 254 nm with bandwidth 10 nm is placed before the detector to ensure that light of the right wavelength is measured.





The detector is a Newport 818-UV detector with an active area 1 cm^2.

The windows in the measurement cell are made of optical quartz glass to ensure that a minimum of the UV light is absorbed on the way.

From the detector a voltage signal is produced as a measure of the amount of transmitted light. The signal is amplified to a voltage of 0-10 V. The amplification can be adjusted by a potentiometer. Calibration is perfomed by putting the light off (0% transmission) and reading the response with the lamp on and the cuvette filled with ultra pure water (100% transmission). The absorbace during measurements is then calculated according to Beers law:

$$ABS_{4cm}=\log(V_{100\%transmission} / V_{Measuredt\ ransmission})$$

APPENDIX E

Data reporting forms

Sampling and analysis of feed water samples and treated water samples during the verification testing

Table cells marked with bold border are to be filled in manually during sampling.

Feed and treated water sampling			
Sample number			
Sampling date		**Sampling time**	
Initials		**Filter cycle No.**	
Comments:			
Field measurement			
Flow reading	**m^3/h**		
Total flow	**m^3**		
Water meter reading	**m^3**		
Iron generator			
Current (if applied)	**mA**		
Voltage (if applied)	**mV**		
Analytical results	**Unit**	**Feed water**	**Treated water**
As	µg/l		
Fe	mg/l		
Mn	mg/l		
Cr	µg/l		
Ni	µg/l		
Colour	mg Pt/l		

Sampling and analysis for operational parameters during verification testing - treatment sludge and decantate

Table cells marked with bold border are to be filled in manually during sampling.

Sampling of treatment sludge and decantate			
Tank no.		**Sample number**	
Sampling date		**Sampling time**	
Initials		**Filter cycle No.**	
Date and time of last backwash			
Comments			

Field measurement		
Flow reading	**m³/h**	
Total flow	**m³**	
Water meter reading	**m³**	
Iron generator		
Current (if applied)	**mA**	
Voltage (if applied)	**mV**	

Analytical data	Unit	Treatment sludge	Unit	Decantate
As	mg/kgDM		µg/l	
Fe	mg/kgDM		mg/l	
Mn	mg/kgDM		mg/l	
Cr	mg/kgDM		µg/l	
Ni	mg/kgDM		µg/l	
Colour	-	-	mg Pt/l	
pH	-		-	-
LOI	%		-	-
TS	%		_	_

Sampling and analysis for operational parameters during verification testing – turbidity spike (first filtrate produced after backwash)

Table cells marked with bold border are to be filled in manually during sampling.

Sampling of turbidity spike (first water produced after backwash)			
Sample number			
Sampling date		**Sampling time**	
Initials		**Filter cycle No.**	
Comments:			

Field measurement	Unit	Filtrate A	Filtrate B	Filtrate C	Filtrate D	Filtrate E
Sampling	**min**	t_0	t_0 + x min.	t_0 + x min.	t_0 + x min.	t_0 + x min.
Sampling time						
Flow reading	**m^3/h**					
Turbidity reading	**NTU**					
Analytical data						
As	µg/l					
Fe	mg/l					
Mn	mg/l					
Cr	µg/l					
Ni	µg/l					
Colour	mgPt/l					

Data table for on-line measurement results – not to be filled in manually during testing

Parameter	Unit	Number of observations	Min	Max	Average	Confidence interval	RSD
Oxygen content	mg/l						
Oxygen saturation	%						
Turbidity	FTU						
Redox	mV						
Conductivity	mS/m						
pH	-						
Temperature	°C						
Flow	m^3/h						