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Introduction

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The ZDHC Roadmap to Zero Programme takes a holistic approach to tackling the issue of hazardous chemicals in the global textile, apparel, footwear and leather industry. This holistic approach starts with the management of input chemistries, the management of day-to-day chemical use at production facilities, and the management of effluent generated and discharged by facilities.

With regards to effluent management, the ZDHC Wastewater Guidelines are in place to harmonise wastewater parameters, limit values and test methods. This is an attempt to encourage and enable the industry, in particular brands, suppliers (manufacturing facilities) and testing laboratories, to work towards the same set of expectations.

This ZDHC Wastewater Laboratory Sampling and Analysis Plan (SAP) document is one of the key elements to support the implementation of the ZDHC Wastewater Guidelines through standardising procedures for laboratories to conduct sampling and analysis.

It's important to note that the Sampling and Analysis Plan (SAP) for Sludge was in development at the time of this document's release. It will be provided as a separate document.

Purpose

This SAP provides a detailed framework for laboratories to conduct wastewater sampling and analytical services.

Data uses

Wastewater test data helps to promote the implementation of sustainable chemistry and best practices in the industry.

The laboratory must be aware of the importance of maintaining the integrity of test data generated under the ZDHC Programme. The test data may be used to make major decisions regarding manufacturing facilities.

1.0.0 Sampling

1.1.0 Types of Samples and Sampling Points/ Locations

Please refer to the ZDHC Wastewater Guidelines (WWG) for types of samples and sampling points/locations. The types of samples to be collected will depend on the testing option decided upon by the brand and supplier (manufacturing facility), but limited to the two testing options identified in the WWG. The WWG acknowledges the difference between facilities with a direct discharge, indirect discharge and on-site zero liquid discharge treatment plant. Important to note: to streamline efforts within the value chain, sampling, testing and reporting as per the WWG and as requested by one ZDHC Brand is a valid test. This test will and should be accepted by all ZDHC Brands.

1.2.0 Sample Collection

1. Samples shall be taken by qualified laboratory personnel. Wastewater samples shall be collected as composite samples following ISO 5667 - 10 guidelines: "Water Quality Sampling Guidance for the preservation and handling of water samples".
2. Sampling using calibrated and refrigerated auto samplers is preferred. To ensure representative samples, composite sampling must be performed for no less than six (6) hours, with no more than one (1) hour between discrete samples. Each discrete sample shall be of equal volume. The composite sample container must be cooled during sampling.
3. If necessary, laboratory personnel can collect discrete samples by hand for no less than six (6) hours, with no more than one (1) hour between discrete samples. Each discrete sample shall be of equal volume and combined to produce one composite sample. The composite sample container must be cooled during sampling.

4. All of the laboratory sample containers will be filled from the same bulk composite sample. A minimum sample volume of 20-liters is needed to fill all the containers. The laboratory may require extra volume for QA samples. The sampler shall coordinate extra volume requirements with the laboratory.
5. Samples must be taken during a time that represents continuous and normal production and continuous and normal wastewater treatment. For example, if the facility starts production, and the wastewater treatment system doesn't reach equilibrium for one hour, then wastewater sampling must be delayed for that length of time.
6. Samples must not be taken if the wastewater is diluted, for example, by heavy rainfall.
7. Wastewater flow data (volume/time) must be collected and reported with the laboratory test results.

1.3.0 Sample Containers and Preservatives

1. *Figure 1* presents standard sample collection containers and preservatives for the wastewater parameters specified in the ZDHC Wastewater Guidelines.
2. The appropriate sample collection container and preservative can vary depending on the standard test method used. Therefore, verify the proper container and preservative with the test method being used at the laboratory.

Figure 1: Sample Containers and Preservatives

Wastewater Parameter	Sample Container Minimum Size	Standard Preservative (verify with lab method to be used)
Conventional		
Temperature	NA	Measured in the field
TSS	P, G 200-ml	cool < 6°C
COD	P, G, FP 100-ml	H2SO4 < pH 2 cool < 6°C
Total-N	P, G, FP 100-ml	H2SO4 < pH 2 cool < 6°C
pH	NA	cool < 6°C
Colour [m-1] (436nm; 525; 620nm)	P, G, FP 500-ml	cool < 6°C
BOD5	P, G, FP 1,000-ml	cool < 6°C
Ammonium-N	P, G, FP 500-ml	H2SO4 < pH 2 cool < 6°C
Total-P	P, G, FP 100-ml	H2SO4 < pH 2 cool < 6°C
AOX	P, G, FP 500-ml	0.1 ml of 10% Sodium Thiosulfate, H2SO4 < pH 2, cool < 6°C
Oil and Grease	Glass, wide mouth PTFE lined lid 1,000-ml	HCl or H2SO4 < pH 2 cool < 6°C
Phenols	P, G PTFE lined lid 500-ml	H2SO4 < pH 2 cool < 6°C
Total Coliform [bacteria/100ml]	P, G clean, sterile, non-reactive, 125-ml	0.1 ml of 10% Sodium Thiosulfate cool < 6°C do not freeze
Persistent foam	NA	Measured in the field
Cyanide	P, FP 1,000-ml	NaOH > 12 pH, 0.1 ml of 10% Sodium Thiosulfate, cool < 6°C

Sulfide	P, FP 100-ml	4 drops 2N zinc acetate, NaOH > pH9 cool < 6°C
Sulfite	P, G, FP 100-ml	1-ml 2.5% EDTA, 0.5 g zinc acetate cool < 6°C
Shipping temperature indicator bottle	calibrated thermometer to +/- 1C°	room temperature water
Metals		
Antimony, Chromium-total Cobalt, Copper, Nickel Silver, Zinc, Arsenic Cadmium, Lead	P, G, FP acid washed 250-ml	HNO3 < pH 2
Chromium (VI)	G acid washed 40-ml Brown Glass VOA vial	0.45µm filter in field, add buffer * to pH 9.0-9.5, cool < 6°C
Mercury	P, G, FP acid washed 500-ml	HNO3 < pH 2 cool < 6°C
ZDHC MRSL		
AP and APEOs: Including All Isomers	G 1,000-ml PTFE lined lid	cool < 6°C
Chlorobenzenes and Chlorotoluenes	G 1,000-ml PTFE lined lid	cool < 6°C
Chlorophenols	G 1,000-ml PTFE lined lid	cool < 6°C
Dyes – Azo (Forming Restricted Amines)	G 1,000-ml PTFE lined lid	cool < 6°C
Dyes – Carcinogenic or equivalent Concern	G 1,000-ml PTFE lined lid	cool < 6°C
Dyes – Disperse (Sensitising)	G 1,000-ml PTFE lined lid	cool < 6°C
Flame Retardants	G 1,000-ml PTFE lined lid	cool < 6°C
Glycols	G 1,000-ml PTFE lined lid	cool < 6°C

Halogenated Solvents	Three x 40-ml amber VOA vial no headspace	HCl < pH 2 cool < 6°C
Organotin Compounds	G 1,000-ml acid washed PTFE lined lid	1M HCl to pH 2-3 cool < 6°C
Perfluorinated and Polyfluorinated Chemicals (PFCs)	P 1,000-ml no PTFE lined lid	cool < 6°C
Otho-Phthalates – Including all ortho esters of phthalic acid	G 1,000-ml PTFE lined lid	cool < 6°C
Polycyclic Aromatic Hydrocarbons	G 1,000-ml PTFE lined lid	cool < 6°C
VOC	Three x 40-ml amber VOA vial no headspace	HCl < pH 2 cool < 6°C

* Buffer = EPA Method 218.6. Dissolve 33g of ammonium sulphate in 75-ml of ASTM D1103 Type 1 or ISO 3696 water, add 6.5-ml of ammonium hydroxide. Dilute to 100-ml with ASTM D1103 Type-1 or ISO 3696 water.

P= plastic G= amber glass FP= fluoropolymer

- A temperature indicator bottle shall be included with each shipping container. The temperature indicator bottle will be clearly labelled.
- Field blanks shall be collected for the following parameters:
 - Total-Phosphorus
 - Coliform
 - Mercury
 - Halogenated Solvents
 - Volatile Organic Compounds (VOC)
- The field blanks shall use the same containers as the samples and will be filled with ultra-pure laboratory grade water (ASTM D1193 or ISO 3696).

1.4.0 Sample Custody

All samples shall have a Chain-of-Custody log that is maintained from the time of collection, during the entire analytical process, and until sample disposal. An example Chain-of-Custody form is presented in *Appendix A*. The sampling team must maintain physical custody, or use custody seal tape on the cool boxes, until the samples are handed off to the shipping company or laboratory.

1.5.0 Sample Shipments

- Use an overnight delivery service for samples that are shipped to a laboratory.
- To avoid shipping delays and compromising sample holding times, contact the shipping company prior to sample collection. The shipping company can help determine the appropriate customs arrangements that must be made.
- Appendix B* provides wastewater sample and shipping forms that may help to avoid delays in customs.
- Samples will be shipped in cool boxes with sufficient insulation and artificial refrigerant ("blue ice"), or ice contained in double zip-lock bags, to maintain a sample temperature of less than 6°C for the duration of transportation. Containers should be shipped upright. Use bubble wrap around individual glass containers and use adequate packing material to prevent movement during shipment, cushion from shock, and reduce the risk of leakage.
- The sampler shall be responsible for all handling, processing, and custody of the samples, including taking samples to the nearest servicing airport, bus station, or other carrier.

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2.0.0 Laboratory Analysis/Testing

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2.1.0 Sample Receipt, Handling, and Custody

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1. The laboratory shall be available to receive sample shipments at any time the delivery service is operating, including weekends.
2. The sample temperature shall be measured and recorded immediately upon opening the shipping container, and prior to unpacking the samples or removing the packing material.
 - a. The laboratory shall use the shipping container temperature indicator bottle reading as the sample temperature.
 - b. To determine the temperature, invert the bottle several times, remove the cap, and insert a calibrated thermometer.
 - c. Allow a minimum of 3 minutes, but not greater than 5 minutes prior to taking the measurement. The thermometer used shall be calibrated and capable of measuring within an accuracy of $\pm 1^{\circ}\text{C}$.
 - d. If a temperature indicator bottle is not present in the shipping container, an alternative means of determining shipping container temperature can be used.
 - e. Under no circumstances shall a thermometer or any other device be inserted into a sample bottle for the purpose of determining shipping container temperature.
 - f. Other devices (e.g. infrared thermometer), which can measure temperature may be used if they are calibrated to $\pm 1^{\circ}\text{C}$
 - g. If the sample temperature is not less than or equal to 6°C the laboratory shall note the issue and provide this information in the test report.
 - h. If the temperature exceeds 10°C the laboratory shall contact the client and inform them of the temperature deviation. The client may decide not to perform testing on these samples.
3. The pH for all aqueous/water sample containers received by the laboratory shall be measured and recorded at the laboratory to demonstrate that proper preservation was performed.

- a. Measure pH using test strips, an electronic hand-held pen, or pH meter. To prevent sample contamination, measure the pH on a small aliquot of the sample removed from the container.
- b. Under no circumstances shall a strip or any device be inserted into a sample bottle for the purpose of determining pH.

4. If the laboratory encounters problems with samples or related documentation [e.g. mixed media, sample pH, sample documentation and paperwork such as Traffic Report/Chain of Custody], the laboratory shall immediately contact the sampler for resolution.

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2.2.0 Sample Holding Time

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1. In general, minimising the time between sample collection and analysis will provide more reliable and representative analytical data.
2. *Figure 2* presents both the recommended and maximum holding times for each of the wastewater testing parameters.
3. If a sample exceeds the holding time the test results will be reported. However, any test results that exceed the holding time must be flagged with the following data qualifier.
 - a. Maximum holding time exceeded. Red flag in the ZDHC Gateway - Wastewater Module. Probable error in results due to the holding time.

Figure 2: Sample Holding Times

Wastewater Parameter	Recommended Holding Time	Maximum Holding Time
Conventional		
Temperature	measure in the field	15 minutes
TSS	24 hours	7 days
COD	7 days	28 days
Total-N	-	28 days

pH	measure in the field	6 hours
Colour [m-1] (436nm; 525nm; 620nm)	-	48 hours
BOD5	6 hours	48 hours
Ammonium-N	7 days	28 days
Total-P	-	28 days
AOX	-	6 months
Oil and Grease	-	28 days
Phenols	24 hours	28 days
Total Coliform [bacteria/100ml]	6 hours	24 hours
Persistent foam	measure in the field	-
Cyanide	24 hours	14 days
Sulfide	-	7 days
Sulfite	-	48 hours
Metals		
Trace Metals	28 days	6 months
Chromium (VI)	24 hours	28 days
Mercury	-	28 days
ZDHC MRSL		
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers	-	7 days to extract
Chlorobenzenes and Chlorotoluenes	-	7 days to extract
Chlorophenols	-	7 days to extract
Dyes – Azo (Forming Restricted Amines)	-	7 days to extract
Dyes – Carcinogenic or Equivalent Concern	-	7 days to extract
Dyes – Disperse (Sensitizing)	-	7 days to extract
Flame Retardants	-	7 days to extract

Glycols	-	7 days to extract
Halogenated Solvents	-	14 days
Organotin Compounds	24 hours	7 days
Perfluorinated and Polyfluorinated Chemicals (PFCs)	-	7 days to extract
Otho-Phthalates – Including all ortho esters of phthalic acid	-	7 days to extract
Polycyclic Aromatic Hydrocarbons (PAHs)	-	7 days to extract
VOC	7 days	14 days

2.3.0 ZDHC Wastewater Parameters

The wastewater parameters are listed in the ZDHC Wastewater Guidelines document, *Appendix A*, Table 1 and Table 2.

2.4.0 Standard Test Methods

1. The ZDHC approved standard test methods are presented in the ZDHC Wastewater Guidelines document, *Appendix A*, Table 1 and Table 2.
2. The methods are based on requirements in the European Union, the United States of America, and China. Alternate methods, such as those required by the regulatory agency in the region in which the wet processing/manufacturing occurs, may be used with prior approval from ZDHC.

2.5.0 Required Reporting Limits

1. The minimum required reporting limits are presented in the ZDHC Wastewater Guidelines document, *Appendix A*, Table 1 and Table 2. They are also based on the ZDHC discharge limits, which were established with consideration to achieving these levels with good laboratory practices. If the ZDHC reporting limits cannot be achieved, an alternate method or a sub-contract laboratory must be used.
2. The Method Detection Limit (MDL) for each parameter must be determined first and is used to establish the reporting limit. The MDL will be established using ISO/TS 13530:2009 4.4.3.
3. The Reporting Limit (RL) will be established using ISO/TS 13530:2009 4.4.7.
4. Non-detected test results will be reported using the calculated RL for each parameter and not the ZDHC discharge limit.

2.6.0 Quality Systems

1. The minimum quality assurance measures for organic chemical analysis of wastewater are presented in *Figure 3*.

Figure 3: Minimum Quality Assurance Measures for Organic Chemical Analysis

Measure	Description	Target value	Frequency	Points to be checked (examples)	
Routine					
Method blank	Covering sample preparation and measurement	< MDL	1 per batch	cleanliness of laboratory glassware and equipment	
Calibration Check	An independently sourced/prepared standard	± 20 %	1 per batch	Instrument condition/ drift, stability of standards	
Internal Standard	For GC methods. Substance with physico-chemical properties similar to the analyte	50 – 150%	every sample	Correction of injection error. Method specific: surrogate as alternative	Choice of internal standard or surrogate or a combination thereof is method/ analyte dependent
Surrogate	Substance which has similar physico-chemical properties as the analyte	method specific	every sample	Check sample preparation procedure and internal standard correction	

Problematic samples (e.g. internal standard recovery too low, phase separation issues etc.)				
Duplicate	duplicate undergoing complete process	< 35 % RPD	problematic samples only	flag results
Matrix Spike	spike onto sample			
Matrix Spike	matrix (duplicate)	method specific	problematic samples only	flag results
Duplicate	undergoing complete process			
Method validation				
Multi-Point Calibration	Min. 5-point calibration excl. origin	$r^2 \leq 0.995$	validation	linearity, working range
Recovery (LCS)	Extract the standard through the test procedure without matrix	method and analyte specific	validation	recovery without influence of matrix
Repeatability (matrix spike replicate)	Matrix spike replicates under repeatability conditions	method and analyte specific	validation	robustness, recovery with matrix influence, UoM, general fitness for use
Limit of Detection	ISO/TS 13530:2009 4.4.3 4.4.7	\leq WWG RL $\leq \frac{1}{2}$ WWG RL	validation	MDL RL

- Note:**
- General suitability of the analytical approach is demonstrated via method validation.
 - Specific, problematic sample matrices, which are not covered by the validation, require additional QC measures.
 - In case of conflict, quality assurance measures specified by the applied standard, the accreditation body or local authority shall prevail.

- The quality assurance testing in *Figure 4* is required for each of the ZDHC wastewater parameters. This data may be requested and used by ZDHC to assess data quality and validate the analytical results.

Figure 4: Required Quality Assurance Testing

Parameter	Field Blank	Method Blank	Calibration Check*	Lab Duplicate	ISTD and Surrogate
Frequency	1 per Batch	1 per Batch	1 per Batch	1 in 20	Every Sample
DQO	< MDL	< MDL	+/- 20%	+/- 35%	Method Specific
Conventional					
Temperature	-	-	-	-	-
TSS	-	-	X	X	-
COD	-	X	X	X	-
Total-N	-	X	X	X	-
pH	-	-	X	-	-
Colour [m-1] (436nm; 525; 620nm)	-	X	X	-	-
BOD5	-	X	X	-	-
Ammonium-N	-	X	X	X	-
Total-P	X	X	X	X	-
AOX	-	X	X	X	-
Oil and Grease	-	X	X	X	-
Phenols	-	X	X	X	-
Total Coliform [bacteria/100ml]	X	X	X	X	-
Persistent foam	-	-	-	-	-
Cyanide	-	X	X	X	-
Sulfide	-	X	X	X	-
Sulfite	-	X	X	X	-

Metals					
Metals	-	X	X	X	X
Chromium (VI)	-	X	X	X	X
Mercury	X	X	X	X	X
ZDHC MRSL					
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers	-	X	X	X	X
Chlorobenzenes and Chlorotoluenes	-	X	X	X	X
Chlorophenols	-	X	X	X	X
Dyes – Azo (Forming Restricted Amines)	-	X	X	X	X
Dyes – Carcinogenic or equivalent Concern	-	X	X	X	X
Dyes – Disperse (Sensitising)	-	X	X	X	X
Flame Retardants	-	X	X	X	X
Glycols	-	X	X	X	X
Halogenated Solvents	X	X	X	X	X
Organotin Compounds	-	X	X	X	X
Perfluorinated and Polyfluorinated Chemicals (PFCs)	-	X	X	X	X
Otho-Phthalates – Including all ortho esters of phthalic acid	-	X	X	X	X
Polycyclic Aromatic Hydrocarbons (PAHs)	-	X	X	X	X
VOC	X	X	X	X	X

* calibration check conducted with a second source standard

2.7.0 Sample Storage

1. All samples will be stored under custody at less than 6°C and above freezing 0°C (unless otherwise specified by the standard test method).
2. The samples may be disposed of 60 days after the final laboratory report is issued.

2.8.0 Reporting and Deliverable Requirements

1. All test data must be reported using the ZDHC Electronic Data Reporting format available in the ZDHC Gateway - Wastewater Module platform. **Important to note:** at the time of the release of this document in June 2019, this feature is not yet ready. Announcement to follow.
2. The use of formats other than those approved will be deemed as non-conformance. Such data is unacceptable and resubmission in the specified format will be required.

3.0.0 Data Validation

1. ZDHC routinely requests laboratory QA/QC information in accordance with *Figure 3* and *Figure 4* from randomly selected laboratories. The following information may be requested for data review:
 - a. Calibration Curves
 - b. Method Blank Instrument Reports
 - c. Calibration Check Sample Instrument Reports
 - d. Laboratory Control Sample Instrument Reports
 - e. Laboratory Duplicate Instrument Reports
 - f. Matrix Spike and Matrix Spike Duplicate Instrument Reports
 - g. Sample Custody Documentation
2. Failure to meet the ZDHC quality assurance objectives may result in the rejection of a data set.

Appendix A

Example Chain of Custody Form

[illegible]

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Appendix B

Shipping and Customs Forms

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If the following forms are completed, and accompany the samples during international shipment, the chance for shipping delays in customs will be minimised:

- 1. Safety Data Sheet (SDS) for water samples. This illustrates that the wastewater samples are not some type of known hazardous material. You can use Google to find some publicly available examples
- 2. Customs declaration forms for various countries, such as the one presented below, can be found at this link: <https://www.bing.com/images/search?q=Customs+Declaration+Form+PDF&FORM=IDINTS>

CUSTOMS DECLARATION		May be opened officially		CN 22	
Designated operator		Important! Read instructions on the back			
<input type="checkbox"/> Gift	<input type="checkbox"/> Commercial sample				
<input type="checkbox"/> Documents	<input type="checkbox"/> Other	(tick one or more boxes)			
Quantity and detailed description of contents (1)		Weight (in kg) (2)	Value (3)		
For commercial items only: If known, HS tariff number (4) and country of origin of goods (5)		Total weight (in kg) (6)	Total value (7)		
I, the undersigned, whose name and address are given on the form, certify that the particulars given in this declaration are correct and that the item does not contain any dangerous article or articles pro- hibited by legislation or by postal or customs regulations. Date and sender's signature (8)					

- 3. Toxic Substance Control Act (TSCA) Certification. This form certifies the sample is not a material which is hazardous to ship by air freight.

TOXIC SUBSTANCE CONTROL ACT (TSCA)
CERTIFICATION

Date: _____

(CHECK ONE SECTION ONLY)

POSITIVE CERTIFICATION:

_____ “I CERTIFY THAT ALL CHEMICAL SUBSTANCES IN THIS SHIPMENT
COMPLY WITH ALL APPLICABLE RULES OR ORDERS UNDER TSCA AND
THAT I AM NOT OFFERING A CHEMICAL SUBSTANCE FOR ENTRY IN
VIOLATION OF TSCA OR ANY APPLICABLE RULE OR ORDER THEREUNDER.”

- OR -

NEGATIVE CERTIFICATION:

_____ “I CERTIFY THAT ALL CHEMICALS IN THIS SHIPMENT ARE NOT
SUBJECT TO TSCA.”

COMPANY NAME: _____

COMPANY ADDRESS: _____

AUTHORIZED NAME: _____

AUTHORIZED SIGNATURE: _____

TITLE: _____

FEDERAL EXPRESS AWB#: _____

RETURN TO: _____

IF THE CERTIFIER IS UNSURE IF THEIR CHEMICAL SUBSTANCE IS SUBJECT
TO TSCA COMPLIANCE, CONTACT THE ENVIRONMENTAL PROTECTION
AGENCY, TSCA, ASSISTANCE OFFICE, WASHINGTON, D.C. (202) 544-1404
BETWEEN 8:30 AM AND 5:00 PM EST.

REVISED May 7, 1990

Toxic.392

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