Sampling Protocol for Aqueous Samples Analysed for Melamine and Related Substances

Note: The following sampling protocol is based on ISO 5667 on water quality sampling. The relevant sections of the standard referring to general guidance on sampling as well as more specific guidance on sampling from different aqueous matrices are considered. While ISO 5667 aims at applicability to a wide variety of different parameters, this sampling protocol is tailored to analyses of melamine and related substances. To this end, information of ISO 5667 is selected and supplemented by information gained during the development and validation of an analytical method for melamine and related substances.

1 General Guidance on Design of Sampling Programmes and Sampling Techniques (Based on ISO 5667-1)

Safety and Environmental Considerations

- Ensure safety of sampling personnel, taking into account weather conditions (e.g. snow, ice)
- Avoid any environmental impact of sampling activities

Design of Sampling Programme

- Establish objectives of sampling programme before start of sampling; here: identification of discharges of melamine and related substances into the environment
- Collected samples should be as representative as possible to adequately represent the water quality
    - Ideally, take samples from well-mixed water bodies to ensure sample homogeneity → Choose sampling points accordingly
    - Take into account variability of the sampling locations (e.g. flow, meteorological conditions, expected variations (e.g. seasonal, weekly) of target analyte concentrations)
    - Sampling should be conducted under “normal” conditions, avoid extreme weather conditions (e.g. flooding)

Sampling Technique

- To investigate the discharge of melamine and related substances from several sources, spot samples are usually advisable (discrete samples, collected manually)
- Where possible, samples should be taken directly into the sample containers after rinsing: the sample container is opened and the lid kept away from contamination; then, the sample container is filled with the sample water and the water is discarded again up to three times (rinsing); finally, the sample container is filled again and the lid is replaced
- Sampling containers should be filled completely and sealed safely to avoid sample loss
- Sufficient sample volume for analyses and repetitions should be collected; for melamine and related substances, at least 10 mL of sample are required to allow for application of the developed analytical method including the evaporation step; in general, sampling of 50 mL is recommended to allow for replicate analyses
- Perform on-site measurements (e.g. temperature, pH) in a separate container, discard this water sample afterwards

Quality Assurance

- Avoiding contamination during sampling is essential, consider all possible sources of contamination (e.g. sample containers, personnel (e.g. clothing), vehicles)
    - Personnel should wear disposable gloves while sampling
- Avoid cross-contamination between samples

Possible quality control measures:

- Take field blank (de-ionized water from laboratory taken to the field and treated like a sample, i.e. filled from one bottle into a sampling container after rinsing the container with the de-ionized water, same sampling equipment used, transported with the samples under the same conditions)
- Take duplicate samples to check for sample precision

Documentation

- Provide clear record of the sample source and the conditions while sampling; attach report to samples; ensure that labelling of samples is resistant to weather conditions
- Usage of GPS data is recommended to describe sampling locations
- If on-site analysis was conducted (e.g. temperature, pH), include this information in the sample documentation
- Annex 4.1: general example of field documentation

2 General Guidance on Preservation and Handling of Water Samples (Based on ISO 5667-3)

Sampling Containers

- For melamine and related substances, sample containers consisting of glass, PE and PS can be used without limiting the stability of the target analytes
- PE and PS sampling containers are recommended to avoid glass breakage
- PE and PS containers should not be re-used
- Glass containers can be re-used, but should be cleaned thoroughly including pyrolysis
- Additionally, sample container packaging should be used to protect the samples from contamination during transport; the packaging material itself must not be a source of contamination

Sample Preservation and Stability

- For melamine and related substances, no addition of preservatives or on-site filtration is necessary; however, (on-site) filtration can be applied to remove suspended solids if necessary
- Cooling is generally not necessary, because the substances were shown to be stable at room temperature, but excessively high temperatures during sample transport should be avoided
- The sample transport should be started as soon as possible after sampling
- The target analytes were shown to be stable over a period of 28 days; therefore, ensure that the complete time between sampling and analysis does not exceed 28 days (time between sampling and transport + transport time to the laboratory + time between transport and analysis at the laboratory)

Documentation

- Document all steps of sample preservation and handling

3 Specific Guidance on Sampling from Different Water Matrices

3.1 Sampling from Natural and Man-Made Lakes (Based on ISO 5667-4)

Design of Sampling Programme

- Consider seasonal and daily water quality changes in lakes
- Depending on the specific question to be answered, samples can either be taken vertically at different layers of the lake stratification or just below the lake surface
- Samples can be taken by boat or from the lake shore; if a boat is used, collect samples either from multiple horizontal positions or just one sample above the deepest part of the lake; if samples are collected from the shore, they should ideally be taken at or near the outflow

Sampling Technique

- Usually, samples from lakes are grab samples
- Surface film of water should not be included → submerge the sampling container completely (at least few cm below the surface); to avoid sampling the surface layer, either open the sampling container under water or insert container upside down and then turn
- Attach sampling container to sampling pole
- Hold container in water at 45°C angle to let air bubbles escape while filling

Quality Assurance

- Avoid sampling through ice and under severe freezing conditions, if possible; when sampling through ice, ice and snow should not enter the sampling container
- Lake vegetation should not enter sampling container
- Consider possible sample contamination by boat/wading into the water → collect samples forward of the path/upwind

Documentation

- Annex 4.2: example of a sampling report from lake sampling

3.2 Sampling of Drinking Water from Treatment Works and Piped Distribution Systems (Based on ISO 5667-5)

Design of Sampling Programme

- Samples can be collected from service reservoirs, water treatment plants, disinfection/oxidation plants or distribution systems (domestic faucets, installed sampling faucets, fire hydrants)
- When sampling from faucets, it is preferred to sample from indoor, fixed style, non-threaded faucets

Sampling Technique

- Usually, composite samples are not recommended
- Recommended pre-collection cleaning and flushing measures:

    - For service reservoirs, allow 2-3 min free flow before sampling
    - For hydrants, clean surfaces
    - For faucets, depends on question to be answered whether samples should be taken before or/and after cleaning or flushing for 2-3 min (either to assess influence of faucet on drinking water quality or to measure water quality in general)

Documentation

- Document any taken cleaning and flushing measures

3.3 Sampling of Rivers and Streams (Based on ISO 5667-6)

Design of Sampling Programme

- Samples can be taken from bridges, while wading, from bank side or from a boat
- When choosing sampling locations for repeated sampling, consider seasonal changes in river volume (choose sites that are always accessible and do not fall dry during summer)
- Take samples at well-mixed and flowing sections of the river/stream; when evaluating the influence of discharges into the river/stream, select one sampling point before the discharge and one sampling point far enough downstream to ensure complete mixing; consider the following estimations concerning mixing:
    - Vertical mixing usually occurs within few 100 meters → sampling at different depths is therefore usually not necessary
    - Lateral mixing depends on sharp reverse bends of river, usually in kilometre range
    - Longitudinal mixing occurs last, depends on dynamics of discharge
- If non-homogeneous sampling sites cannot be avoided, ensure sufficient sampling points to achieve representative results
- Consider travel time of water through the river/stream when selecting sampling locations

Sampling Technique

- Depending on the sampling location, sampling containers can be attached to poles, or lowered to the water by rope or flexible wires
- Samples should be collected at least 30 cm below the surface and above the ground; if the river/stream is too shallow to achieve this, collect samples at mid-height
- To avoid sampling the surface layer, either open the sampling container under water or insert container upside down and then turn when the required depth is reached

Quality Assurance

- Avoid large particles in water samples
- Avoid sampling at/near the surface, bottom, bank, stagnant areas and pools

Documentation

- Annex 4.3: example of a sampling report from rivers/streams

3.4 Sampling of Wet Deposition (Based on ISO 5667-8)

Design of Sampling Programme

- Consider that electricity can be required depending on which type of sampling device is applied (e.g. power supply, battery)

Sampling Technique

- Direct sampling into sampling containers is usually not possible
- Usually, wet deposition is sampled by wet-only collectors or bulk collectors
- Recommendation: wet-only collectors with moisture sensing grids and solid state control circuits to operate motor driven covers
- Place collectors on grass-covered, undisturbed surfaces
- Preference is given to wind-sheltered areas
- For rain collection: select the size of the collection orifice depending on how much sample is to be generated from how much precipitation
- For snow collection: choose shielded deep cylinder as collector to avoid removal by wind
- Alternatively, precipitation can be collected in clean buckets which are removed immediately after the precipitation event, if the sampling personnel is on site

Quality Assurance

- Avoid contamination from ground by ensuring that collector intake is 1-2 m above ground
- Avoid contamination from above by incorporating some form of guard to collect larger particles
- Avoid contamination from trees and buildings by ensuring that collector is not placed closer to them than 5-10 times their height

Documentation

- Annex 4.4: example of a sampling report from wet deposition

3.5 Sampling of Wastewater (Based on ISO 5667-10)

Design of Sampling Programme

- Difficult to obtain representative samples because of spatial and temporal heterogeneity → still try to sample “normal” conditions (activity, flow, weather conditions)
- Consider variations (seasonal, weekly, daily) of the discharges
- When sampling influent and effluent of treatment plants, consider the travel time of the water through the plant to ensure comparability
- Samples can be taken from sewers, channels and manholes, wastewater treatment plants, industrial sites, cooling systems
- Obtain information about production processes / applied water treatments of sampled plants

Sampling Technique

- Sampled stagnant tanks can be mixed before taking samples to increase sample homogeneity, by e.g. mechanical agitators or bubbling
- Sampling points in water bodies should be halfway up the water column and at sufficient distance from the walls
- Both composite (manual or automatic) and spot (direct or indirect) samples can be taken
    - Composite samples can be either constant volume variable time samples (C.V.V.T), constant time variable volume samples (C.T.V.V) or constant time constant volume samples (C.T.C.V)
    - Time range for composite samples: from few hours up to one week
    - Usually, samples are repeatedly taken into the same container to create a composite sample
    - Automatic composite samplers should be equipped to avoid sampling of solid materials and the unit volume should be at least 25-50 mL
- If only a fraction of the collected sample is used for analysis, ensure homogenization before transferring

Quality Assurance

- Limit intermediate material to avoid contamination
- Avoid including suspended solids in the samples
- Avoid touching the walls of wastewater bodies with sampling containers

Documentation

- If automatic samplers are used, record sampling programme
- Annex 4.5: example of a sampling report from wastewater sampling

3.6 Sampling of Groundwaters (Based on ISO 5667-11)

Design of Sampling Programme

- Sampling can be conducted in the saturated (below water table) and unsaturated (above water table) zone

Sampling Technique

- Unsaturated zone sampling:
    - Solid sampling followed by extraction of groundwater (pore fluids)
        - Most widely used
        - Extraction from solid material by centrifuging or mechanical squeezing
    - Unsaturated pore-fluid sampling by percolate or vacuum soil water samplers
- Saturated zone sampling:
    - Most commonly, the saturated zone is accessed through boreholes and wells; spring discharge can also be sampled
    - Samples can be taken either by pumped sampling or depth sampling with a variety of different sampling systems
    - Depth sampler = grab sampler, sampling at specific depth
    - Pump sampling: water from different vertical layers will be combined in the sample
    - Before any sampling, the water at the sampling point should be purged → remove stagnant water to get a representative sample

        - Pump sufficient volume before water is taken (3x volume of borehole)
        - Monitor additional parameters during purging → purge until stable
    - Fill sample from sampling tubes into sampling container, without air bubbles, without submerging the tube into the filled sample

Quality Assurance

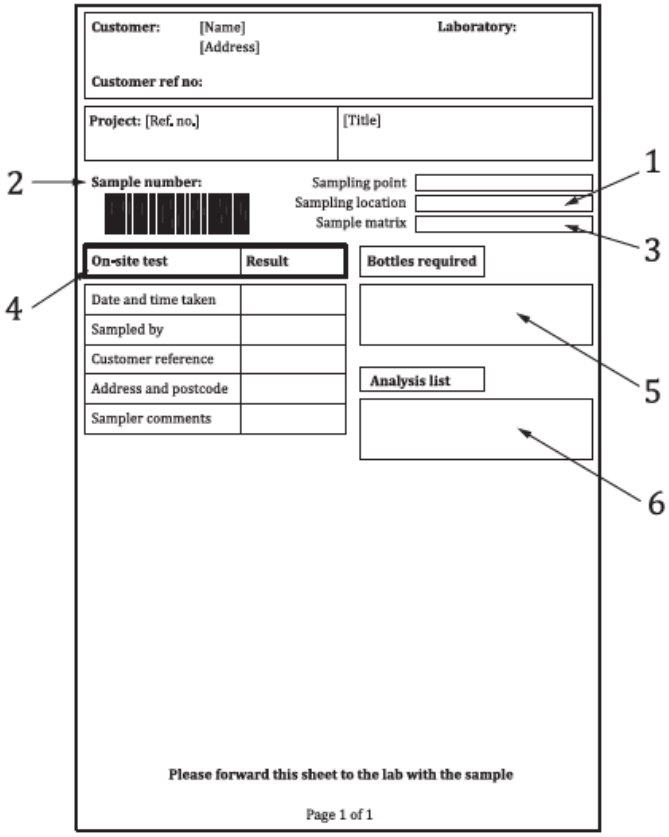
- Consider possible contamination from materials of the sampled wells

Documentation

- When sampling from wells, document material
- Annex 4.6: example of a sampling report from groundwater

4 Annex

4.1. General Example of Field Documentation (from ISO 5667-1)



Key

1 location of where the sample was taken (matches the sample text ID of the labels)

2 sample number needs to match the numbers on the labels used for this sample, to link the information in this sheet with the sample results; there is only one sheet per sample

3 type of water being sampled and tested

4 on-site test and results to be completed with the following:

a) date and time sample was taken (failure to record this constitutes deviation);

b) name of sampling operative;

c) any unique reference to be linked to this sample (this will be included in the test certificate);

d) address (including postcode) of sampling location if sample taken from a property;

e) any additional information to be linked to this sample (this will not appear in the test certificate, but will be stored)

5 bottle codes required for the sample, e.g. METALS (1); failure to enter any of these can result in some tests not being carried out or results being compromised

6 list of the tests assigned to this sample (e.g. COLOUR, METAL)

4.2 Example of a Sampling Report from Lake Sampling (from ISO 5667-4)

Sampling report for physical-chemical analysis from lakes, natural and man-made			
Project: Sample ID:			Date collected: Sampling time: Start: End:
Location:			UTM-coordinates: Easting: Northing:
Sample collector's name:			
Sampling method:	☐ Grab sample ☐ Depth profile samples ☐ Area profile samples ☐ Composite sample ☐ Integrated sample		Depth of the lake: Withdrawal depth: Depths for mixed samples:
Sampling equipment:	Integrated water samplers: ☐ Pipe: ☐ Horizontal water sampler ☐ Vertical water sampler ☐ Pump		Samples with ship:
Weather			In situ measurement data
Day of sampling	Wind:		
☐ Sunny ☐ Cloudy ☐ Changeable ☐ Rainy ☐ Hot ☐ Frosty	Force: Direction: Air temperature:	Ice cover: Ice thickness: Gauge level:	Turbidity and light by Secchi (cm): Aquatic vegetation: Submers/emers:
Remarks			
Date/signature _____			

In situ measurement data						
Sample ID	Withdrawal depth (m)	Water temperature (°C)	pH value	Conductivity (µS/cm at 25 °C)	Dissolved oxygen/% sat (mg/l/%)	Colour/ turbidity/ odour
Remarks						
Date/signature _____						

4.3 Example of a Sampling Report from Rivers/Streams (from ISO 5667-6)

Sampling report for physical-chemical river analysis					
River name	_____		Date	_____	
Identification area	_____		Time	_____	
Sampling point	_____		Easting	_____	
River (km)	_____		Northing	_____	
Kind of sampling	☐ discrete	_____	☐ Gauss-Krüger	☐ UTM	
Withdrawal depth	☐ sub-surface	_____	Sampling equipment	_____	
Sample collector's name			☐ bucket	☐ vessel	

Weather		River width	Discharge
Day of sampling	Previous day	Estimated value (m)	Water gauge _____
☐ sunny	☐ sunny		Staff reading (cm) _____
☐ cloudy	☐ cloudy	**Depth of water body**	Discharge (l/s) _____
☐ changeable	☐ changeable	Estimated average depth (m)	Estimated value (l/s) _____
☐ rainy	☐ rainy		
☐ hot	☐ hot	**Flow rate**	**Location of sampling**
☐ frosty	☐ frosty	Estimated value (m/s)	River bank ☐ right _____ ☐ left _____ ☐ middle _____

Character of the water sample				
Colour	**Foam formation**	**Odour**	***In situ* measurement data**	
☐ colourless	☐ none	☐ none	pH value	
☐ light	☐ light	☐ light		
☐ intense	☐ intense	☐ strong	Conductivity (µS/cm at 25 °C)	
☐ brown	**Turbidity**	☐ earthy		
☐ grey	☐ clear	☐ mildewed	Oxygen content/saturation (mg/l %)	
☐ yellow	☐ nearly clear	☐ putrid		
☐ green-blue	☐ light	☐ farm slurry	Water/air temperature (°C)	
☐ yellow-green	☐ intense	☐ fishy		
☐ yellow-brown		☐ aromatic		
		☐ sewage		
		☐ fuel/oil		

Remarks	
e.g. contamination, building measures, flow situations, etc.	
Date/signature	

Sampling report for physical-chemical river analysis					
Preservation measures					
Parameter (identification on sample container)	Sample container (number/material/volume)	Pre-treatment	Preservation	Preservation	
				On-site	In laboratory
				☐	☐
				☐	☐
				☐	☐
				☐	☐
				☐	☐
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				☐	☐
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				☐	☐
Remarks					
e.g. contamination, building sites, flow, etc.					
Date/signature					

4.4 Example of a Sampling Report from Wet Deposition (from ISO 5667-8)

Designation of samples: .....
Sampling point: .....
Reason for sampling: .....

Date:	Day	Month	Year	Time
	.....	.....	.....	.....

Operation time of collecting equipment: .....
With rain recorder: yes ..... no .....
Kind of sampling: .....
.....
.....

Designation of sampling instrument: .....
with measuring instrument for: pH yes ..... no .....
conductivity yes ..... no .....
Observation on site: .....
.....
.....

Stabilization
of parameter ..... Designation of sample .....
Kind and amount of chemical .....
of parameter ..... Designation of sample .....
Kind and amount of chemical .....
of parameter ..... Designation of sample .....
Kind and amount of chemical .....
Sample splitting: .....

Sampling was performed by:
Name/Institution .....
Signature .....
Remarks .....
.....
.....
The samples and the results of pH/conductivity measurements were given
to ..... on ....
(name) (date) (time)
Analytical index number: .....

4.5 Example of a Sampling Report from Wastewater Sampling (from ISO 5667-10)

SAMPLING IDENTIFICATION				
Sampling operative identity:			**Signature:**	
Date and time of beginning:			**Date and time of end:**	
Location of sampling:				
.....				
Exact sampling point Identification:				
.....				
Identification of client:				
Sampling purpose:				
waste water quality monitoring O			pollution identification O	
SAMPLING CONDITIONS				
Sampling type	Spot O		Direct O	Indirect O
	Composite O		Manual O	
	Automatic O			
Sampling location	Sewer O		Manhole O	
	Channel O		Reservoir O	
	Collector O		Other O	
Equipment used	Laboratory bottle O		Ballasted sample collector O	
	Sampling rod with a container O		Bucket O	
	Automatic sampler O		Pump O	
Material used	Glass O	PTFE O	Polyethylene O	Stainless O
MEASUREMENTS				
Physico chemical measurements		Continuous O		Spot O
	In-situ O	on site (spot sample) O		on site (Sub-sample of the volume collected) O
Temperature:		Water° C:		Air ° C:
pH (unity pH):	at °C	Conductivity 25 °C (µS/cm):		Redox potential (mV):
Turbidity:				
Other measurements:				
.....				
OTHER COMMENTS				

SPOT SAMPLING WITH PUMP

SAMPLING PROCEDURE

Pump type:	Date:	Start:	End:
Intake water positioning:		Intake water depth:	
Pumping flow (l/h):			
Duration of pump rinsing:		Duration of pumping for sampling:	

Other comments:

.....

.....

MANUAL COMPOSITE SAMPLING

Equipment type:			
Equipment cleaning before using	Yes O	No O	
Intake water positioning:		Intake water depth:	
Date:	Start:	End:	
Unit volume (ml):	Volume repeatability ≤ 5 %:		No O
Interval of subsamples:	Total composite sample volume:		Yes O

Other Comments: .....

.....

AUTOMATIC COMPOSITE SAMPLING

Automatic sampler type:	Reference:	
	Mono-flask O	Multi-flask O
Pumping type:	Peristaltic O	Vacuum O
Automatic sampler cleaning before using	Yes O	No O
Pipe purging before using	Yes O	No O
Intake water positioning:	Intake water depth:	
Speed suction (m/s):	Programming type:	
Flowmeter reference:	Date of last quality control:	
Running (date and hour):	Start:	End:
Suction pipe:	Diameter (mm):	Length (m):
Unit volume (ml):	Total composite sample volume:	
Volume repeatability ≤ 5 %:	Yes O	No O
Volume bias to ≤ 10 %:	Yes O	No O
Presence of a strainer:	Yes O	No O
Refrigerated automatic sampler:	Yes O	No O
Automatic sampler temperature:	Start value:	End value:

Other comments:.....

4.6 Example of a Sampling Report from Groundwater (from ISO 5667-11)

Reasons for sampling: .....

.....

Location of sampling point: .....

Nature of sampling point: .....

Nature of aquifer: .....

Date: .....
day month year

Weather conditions: .....

Water level (before purge): .....

Purging strategy: .....

Purge flow rate: .....

Purge time: .....

Purge volume: .....

Water level (before sampling): .....

Time: Start ..... End ..... of sampling

Sampling method: .....

Sample depth: .....

Sample pump flow rate: .....

Sample appearance: .....

.....

.....

.....

Details of preservation techniques employed: .....

.....

Details of sample storage method employed/required: .....

Name/initials of sample collector: .....

Other remarks, e.g. evidence of contamination: .....

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