



# TRADITIONAL METHODS AND NEW APPROACHES FOR PROFICIENCY TESTING OF WASTEWATER SAMPLING

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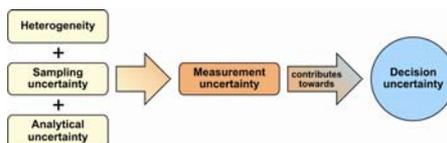
## INTRODUCTION

With the support of the Environment Agency of the Republic of Slovenia, the Laboratory for Environmental Sciences and Engineering at the National Institute of Chemistry will organize a collaborative field trial on wastewater sampling. Since sampling errors were recognized as an important factor affecting the quality of an analytical result, the needs for consistency of data arising from the European Water Framework Directive 2000/60/EC rendered enhancement of metrological knowledge in this step of the measurement chain more significant. The sampling method used depends largely on the types of analyses to be run, and the nature of the waste stream being sampled. The aim of this study will be to evaluate several sampling procedures, including standardized, to determine the variability induced by sampling operations in subsequent analytical processes. Experimental determination of sampling uncertainty contribution is very costly and time intensive, especially for a single laboratory experiment. The most convenient and robust way to estimate sampling uncertainty is thus participation in proficiency testing organized in agreement with international guides (Nordtest Report TR 604).

## SAMPLING

### Wastewater sampling targets:

- > Investigations related to specific control limits (industrial wastewater).
- > Supervision of inlet to wastewater treatment plants for optimization of the wastewater treatment process.
- > Surveillance of the outlet from an industry or wastewater treatment plant related to allowable limits.
- > Supervision of treatment processes.



### Decision chain and uncertainty

### Wastewater sampling procedures:

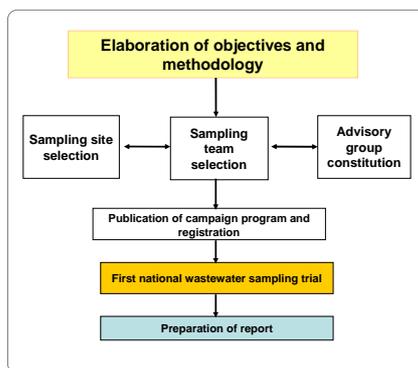
- > Samples being collected must be representative of the waste stream being tested.
- > Samples shall be collected in uncontaminated containers and preserved properly.
- > Samples should be of sufficient volume for the subsequent analyses.
- > Samples should be stored in a manner which does not alter the properties of the sample prior to chain of custody transfer.
- > Samples should be properly and completely identified by marking them with proper information.
- > Sample lines should be as short as possible with the smallest practical diameter to facilitate purging, reduce lag time, and give adequate consideration to maximum transport velocity.

## PROCEDURES

ISO 5667-10 Water quality – Sampling Part 10: Guidance on sampling of wastewaters

- It describes :
- manual sampling
  - automatic sampling.

The principle of using automatic equipment is that the sampler takes a series of discrete samples at fixed intervals that are held in individual containers. In practical cases the same design is used when carrying out 24-hour studies to identify peak loads.



The standard gives guidance on the selection of the sampling point to assure representative sample.



### Automatic wastewater sampling equipment

#### Monitoring parameters:

- field parameters: pH, oxygen, temperature and conductivity
- parameters to be analyzed in a laboratory, also called non-field parameters: chemical oxygen demand (COD), suspended solids and anions.

#### Sulphate in wastewater

Number of results	31
Number of excluded results	0
Mean	261 mg/L
Median	258 mg/L
Standard deviation	19 mg/L
Robust standard deviation	14 mg/L
Result range	229.14 to 325.16 mg/L
Number of results reporting MU	21
Extended MU (k=2) range	0.8 to 74 mg/L

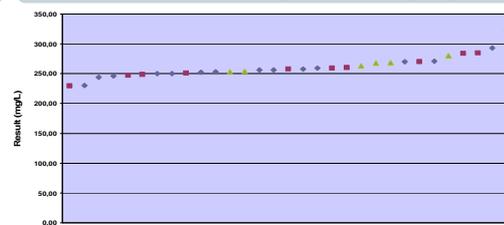
### Overview chart of wastewater sampling



Assigned value is established with reference measurements performed at the Laboratory for Environmental Sciences and Engineering (NIC) using ion chromatography

Assigned value	263 mg/L
Extended MU of assigned value (k=2)	15.0 mg/L

### Wastewater treatment plant near Ljubljana



Method	Number of Results	% of Total	Median	Robust SD	Range	Sat.
			mg/L			%
Ion chromatography	14	45	255	11	230 – 293.2	100
Gravimetric method using barium chloride	7	23	268	15	253 – 325.16	85.7
Other	10	32	259	19	229.1 – 284	100

### Results of sulphate measurements in wastewater

## SUMMARY

This trial will be the first national attempt to improve knowledge of the effect in wastewater sampling undertaken as part of regulatory monitoring. It is planned that over twenty sampling teams will take part in the trial in a sampling site on municipal wastewater treatment plant near Ljubljana. Flow-proportional 24-h composite samples are required, particularly where the monitored discharge is intermittent or variable; such samples are preferred over time composite samples. The sampling site is appropriate for collecting samples as long as it is representative of the discharge and has no bypass capabilities. The monitoring parameters selected will be field parameters (pH, dissolved oxygen, temperature and conductivity) and chemical oxygen demand, suspended solids and anions. Metrological traceability of analytical results of participants will be verified with the use of reference materials.

## REFERENCES

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- M.P. Strub, B. Lepot, A. Morin, *Trends in Analytical Chemistry*, 2009, 28, No. 2, 245-263
- SIST ISO 5667-10 (1992) Water quality – Sampling – Part 10: Guidance on sampling of waste waters. International standard Organization- Geneva