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ESTIMATION OF AMMONIUM NITROGEN CONCENTRATION UNCERTAINTY IN WASTEWATER EFFLUENT ARISING FROM SAMPLING BY MEANS OF PROFICIENCY TESTING

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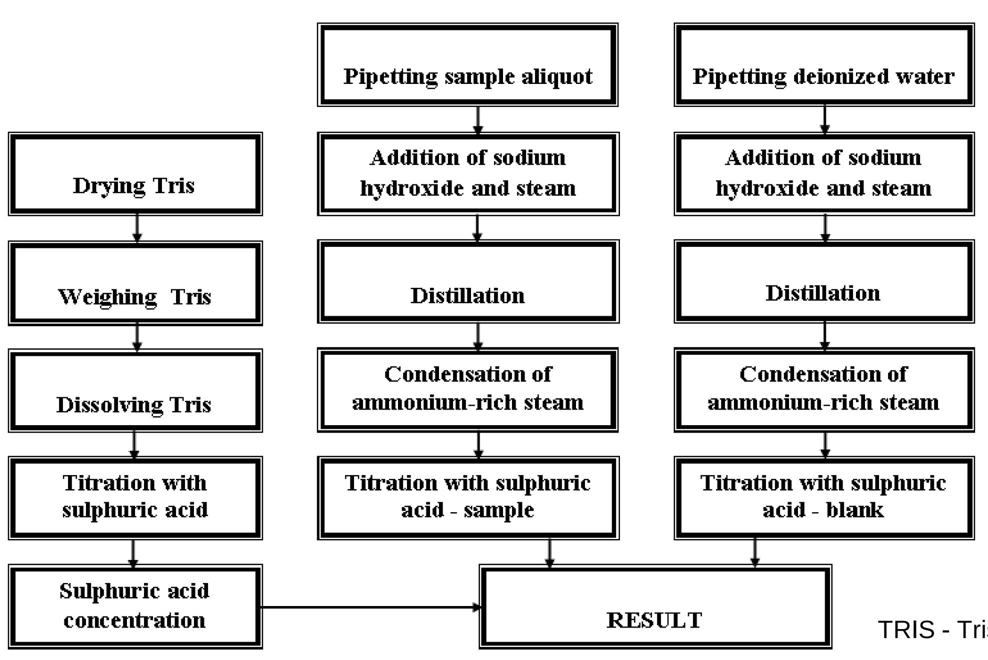
Introduction

- Reliable measurement results are highly important for environmental protection. Wastewater emissions as point sources of contamination are monitored with a goal to protect environment; therefore, only high quality analytical results can provide a basis for decision-making about the environmental pollution and the influence of existing or future potential contaminants.
- 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/EC2 rendered enhancement of metrological knowledge in this step of the measurement chain more significant.
- The most convenient way to estimate sampling uncertainty is participation in a proficiency testing scheme, organized in agreement with international guides.
- In this work, we developed a methodology for the determination of the SI traceable reference value of ammonium nitrogen concentration in wastewater.
- Later on, that reference value was used in wastewater sampling proficiency testing (SPT) which was performed on a real sampling site.

Reference measurements

Measurement procedure



TRIS - Tris(Hydroxy-methyl-amino-methane)

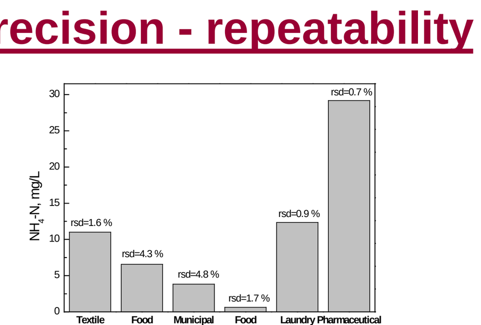
$$C_{NH_4\text{-}N} = \frac{M_N \cdot (V_2 - V_1) \cdot f \cdot C_{H_2SO_4}}{V_0}$$

M_N - molar mass of nitrogen
V_2 - volume of the sulphuric acid (sample)
V_1 - volume of the sulphuric acid (blank)
C_{H2SO4} - molarity
V_0 - volume of the sample

Trueness

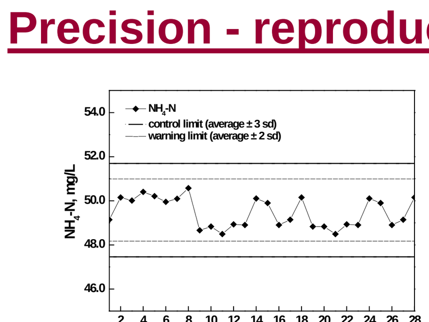
Recovery (R) = 102 %

Precision - repeatability



0.7 %

Precision - reproducibility



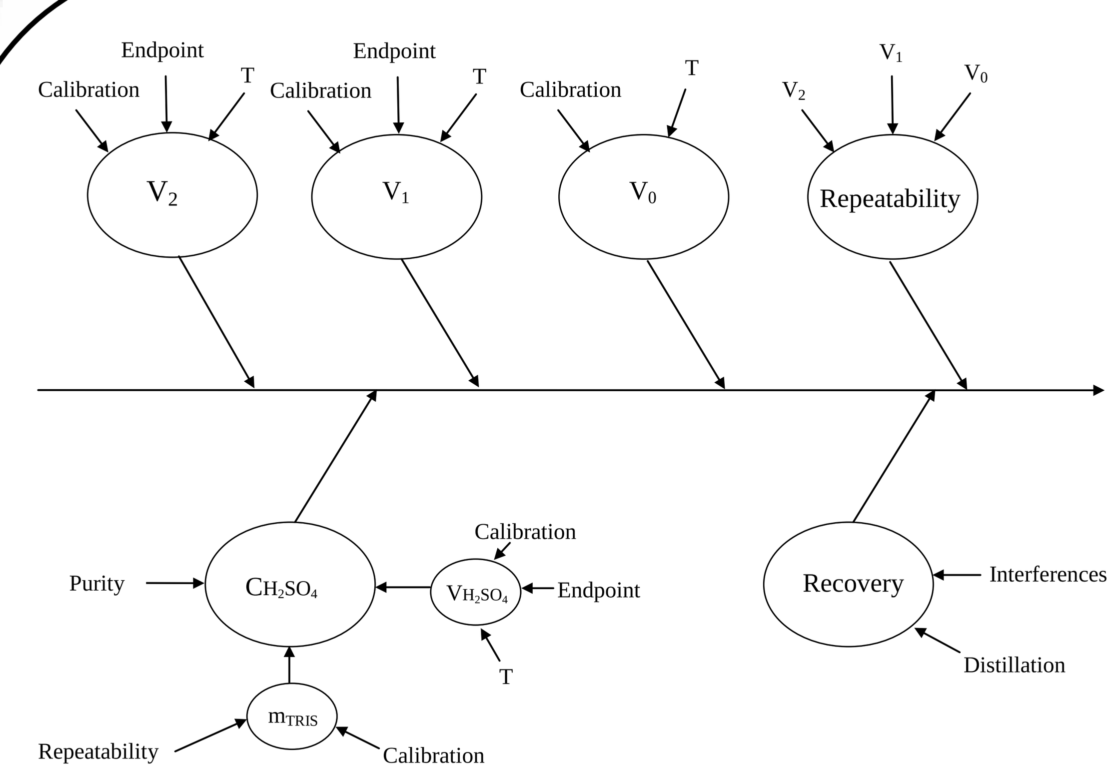
2.6 %

LoD/LoQ

Limit of detection (LoD): blank + 3 s
Limit of quantification (LoQ): blank + 10 s
Confirmation of limit of quantification (LoQ):
RSD < 10 %
LoD = 0.6 mg/L
LoQ = 1.9 mg/L

Measurement uncertainty evaluation

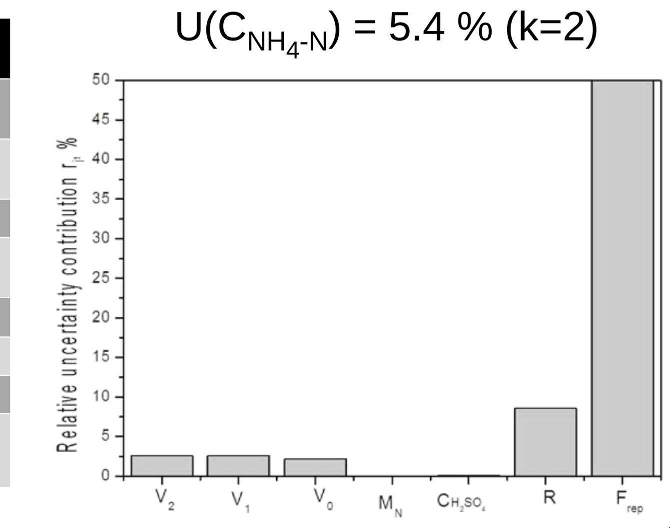
Cause and effects diagram



Quantity	Symbol	Unit	Value	Standard uncertainty	Relative variance contribution r_i, %
Volume of H_2SO_4 for titration of the sample	V_2	mL	1.501	0.003	2.6
Volume of H_2SO_4 for titration of the blank	V_1	mL	0.514	0.003	2.6
Volume of the sample	V_0	mL	5.00	0.02	2.2
Molar mass of nitrogen	M_N	g/mol	14.01	Constant	-
Conc. of H_2SO_4	$C_{H_2SO_4}$	mmol/L	10.01	0.01	0.1
Recovery	R	-	1.00	0.008	8.6
Repeatability	F_{rep}	-	1.00	0.025	84.0
Ammonium nitrogen concentration	$C_{NH_4\text{-}N}$	mg/L	38.5	1.1	100

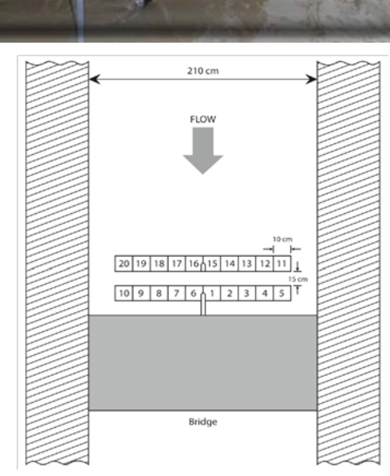
Measurement uncertainty

$U(C_{NH_4\text{-}N})$ = 5.4 % (k=2)



Sampling proficiency testing

Sampling site

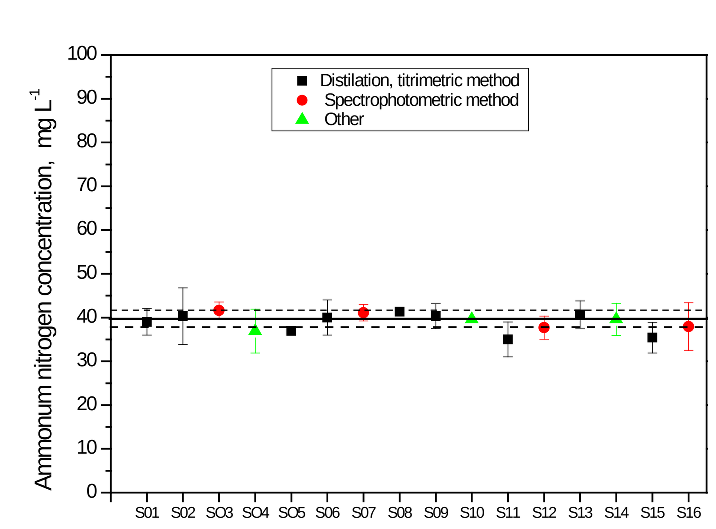


Equipment and methods used by samplers

Sampling team	Number on sampling site	Employed sampling equipment	Sampling method
S01	14	ISCO Glacier (V9)	Time-proportional sampling
S02	10	ISCO 6712	Time-proportional sampling (200 mL / 9 minutes)
S03	5	Sigma 900 MAX	Time-proportional sampling
S04	13	ISCO 6712	Time-proportional sampling (400 mL / 15 minutes)
S05	16	ISCO 6712	Time-proportional sampling (take off a sample every 15 minutes)
S06	15	Sigma 900 MAX	Time-proportional sampling
S07	20	ISCO 6712	Time-proportional sampling
S08	1	ISCO Glacier	Time-proportional sampling
S09	3	ISCO Glacier	Time-proportional sampling
S10	9	ISCO GLS sampler	Time-proportional sampling (take off a sample every 15 minutes)
S11	4	ISCO 6712	Time-proportional sampling (200 mL / 8 minutes)
S12	17	ISCO 3700	Time-proportional sampling
S13	6	ISCO AVALANCHE	Time-proportional sampling (250 mL / 15 minutes)
S14	8	ISCO 6712	Time-proportional sampling
S15	12	Sigma 900 MAX	Time-proportional sampling
S16	2	Sigma SD900	Time-proportional sampling

The participants used different sampling devices from well-known producers that were equipped with either peristaltic or vacuum pumps for aqueous-phase sample withdrawal. They used three different analytical methods for ammonium comcentration analysis.

Results of sampling proficiency testing



Measurement uncertainty arising from sampling

$$U_{global} = \sqrt{U^2_{sampling} + U^2_{analysis}}$$

The variability between reported results for ammonium nitrogen in the trial, expressed as CV, was found to be 5.4 %. For the analyses of wastewater monitoring, concentration of ammonium was above the LoQ. With this respect, all measured data were included in subsequent statistical analysis. Based on the values of uncertainties, one can conclude that sampling could significantly influence results of analytical measurements. Obviously, the contribution to uncertainty from sampling is in both cases (sample A and sample B) larger than the contribution resulting from analytical measurements.

	Samples A			Samples B			U_{global}	$U_{analytical}$	$U_{sampling}$
	Mean	Median	SD	Mean	Median	SD	(k=2), %	(k=2), %	(k=2), %
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
NH_4^+-N	39.0	39.6	2.10	38.5	38.0	1.46	10.80	2.60	10.40

Conclusions

- Metrological principles were integrated to the SPT in order to enable participating laboratories to evaluate sampling uncertainty contribution of their measurements. In this work, determination of SI traceable reference value of ammonium nitrogen concentration in wastewater was presented. Reference measurements based on distillation and titration method were developed, traceability to SI was established and measurement uncertainty evaluated by using modelling approach. This value was then used in wastewater SPT, which was performed on a real sampling site.
- The variability between reported results of participants in the SPT, expressed as CV, was found to be 5.4 % for ammonium nitrogen concentration.
- In contrast to the improvements that have occurred in analytical measurements, developments in the field of sampling are less active. With this respect, further SPT trials will be conducted on a regular basis, in which the used methodology for measuring uncertainty evaluation will be upgraded with other approaches.

References

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[3] Drolc A, Cotman M (2009) Integration of metrological principles and performance evaluation in a proficiency testing scheme in support of the Council Directive 98/83/EC. Accred Qual Assur 14:199-205.