Determination of chlorate in food and water: validation study and estimation of measurement uncertainty

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1. INTRODUCTION

Chlorate anion (ClO_3^-) is a known break down product of agents used for the chlorination of water using chlorine dioxide or the disinfection of surfaces and equipment using sodium hypochlorite (NaOCl). There are several possible pathways for contamination of food with chlorate; the use of contaminated water in plant cultivation and food processing (as chlorate can be formed when using chlorine, chlorine dioxide or hypochlorite, for the disinfection of drinking water), disinfection of food containers and the illegal use as a herbicide.

In order to ensure safe drinking water, disinfection must be applied. In Cyprus chlorination is used as the disinfection method, although no maximum levels for chlorate in drinking water have been established in the EU, while the World Health Organization (WHO) has established a guideline level of 0.7 mg/L for chlorate in drinking water.

In products of plant and animal origin, no specific Maximum Residue Levels (MRLs) have been established for Chlorate under Regulation (EC) No 396/2005. Therefore, the default MRL of 0.01 mg/kg could be applicable to all food commodities.

OBJECTIVES

- Method development and validation study for the determination of Chlorate in food samples based on QuPPe method
- Direct analysis of water samples for Chlorate using UPLC-MS/MS
- Estimation of measurement uncertainty

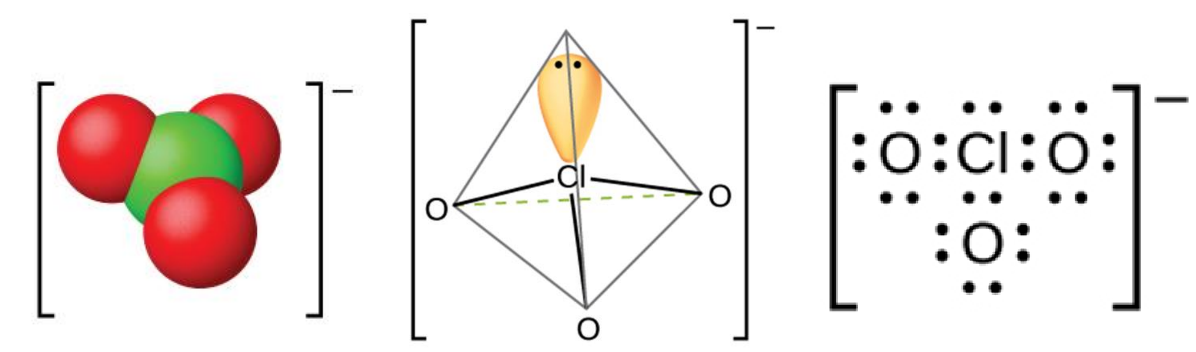
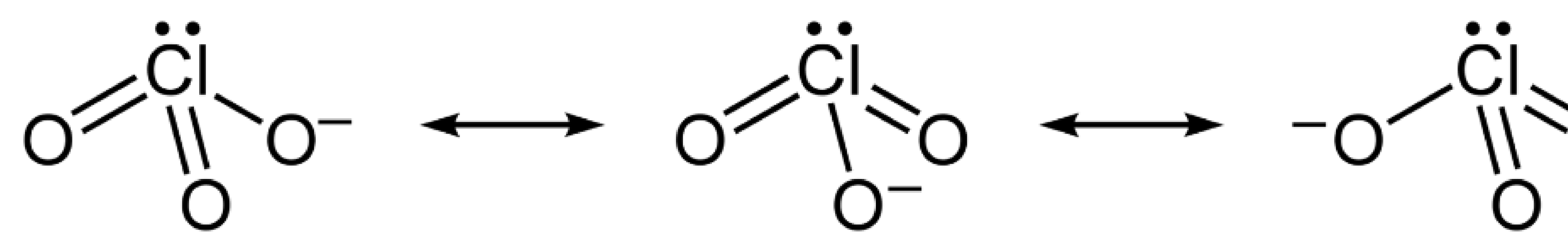


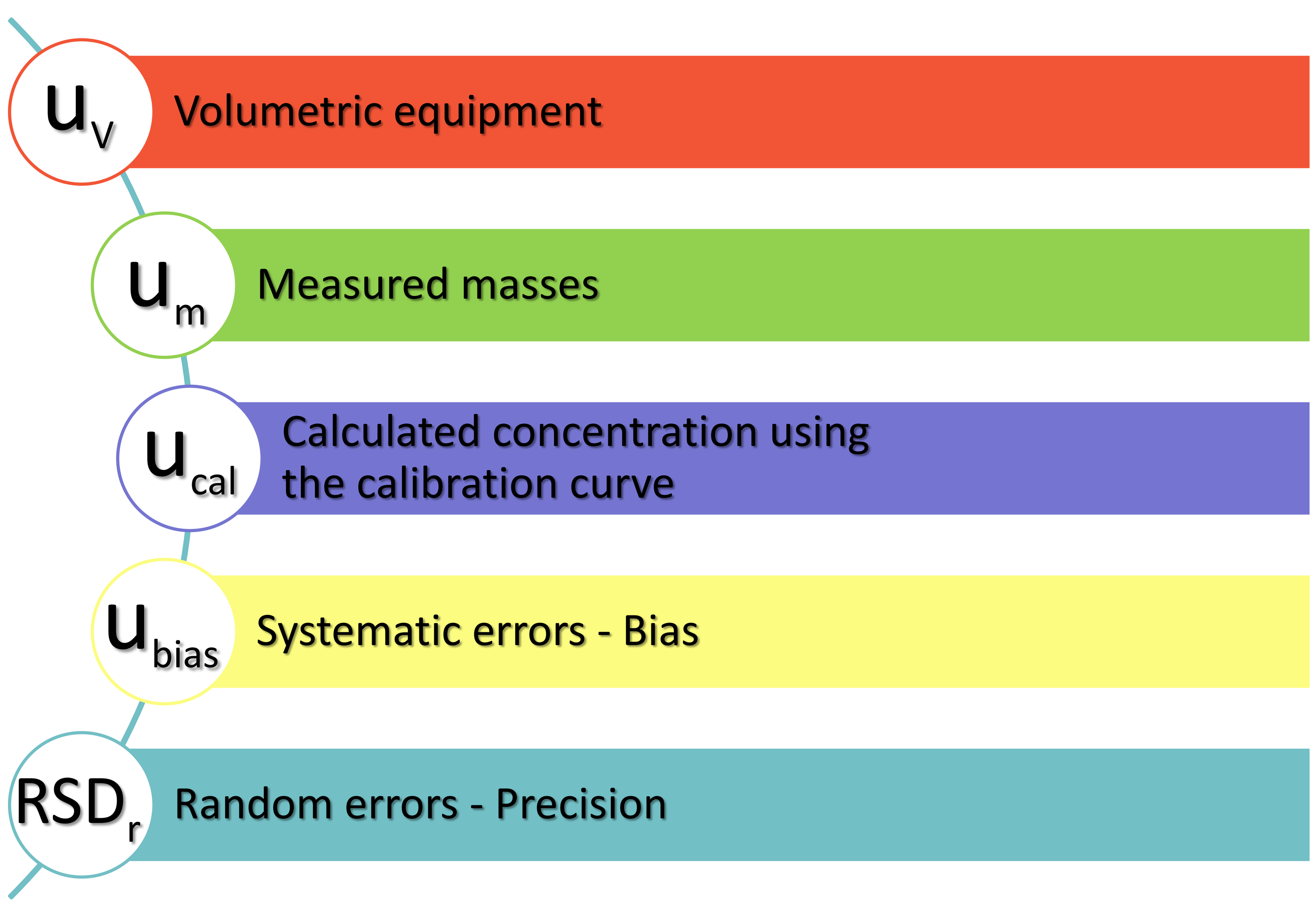
Figure 2: Chlorate ion molecular geometry and resonance structures.



2. EXPERIMENTAL PART

For the estimation of the overall uncertainty in Chlorate analysis, possible sources are identified and expressed as standard deviation i.e. **standard uncertainty (u).**

Each contribution to uncertainty is referred to as an uncertainty component.



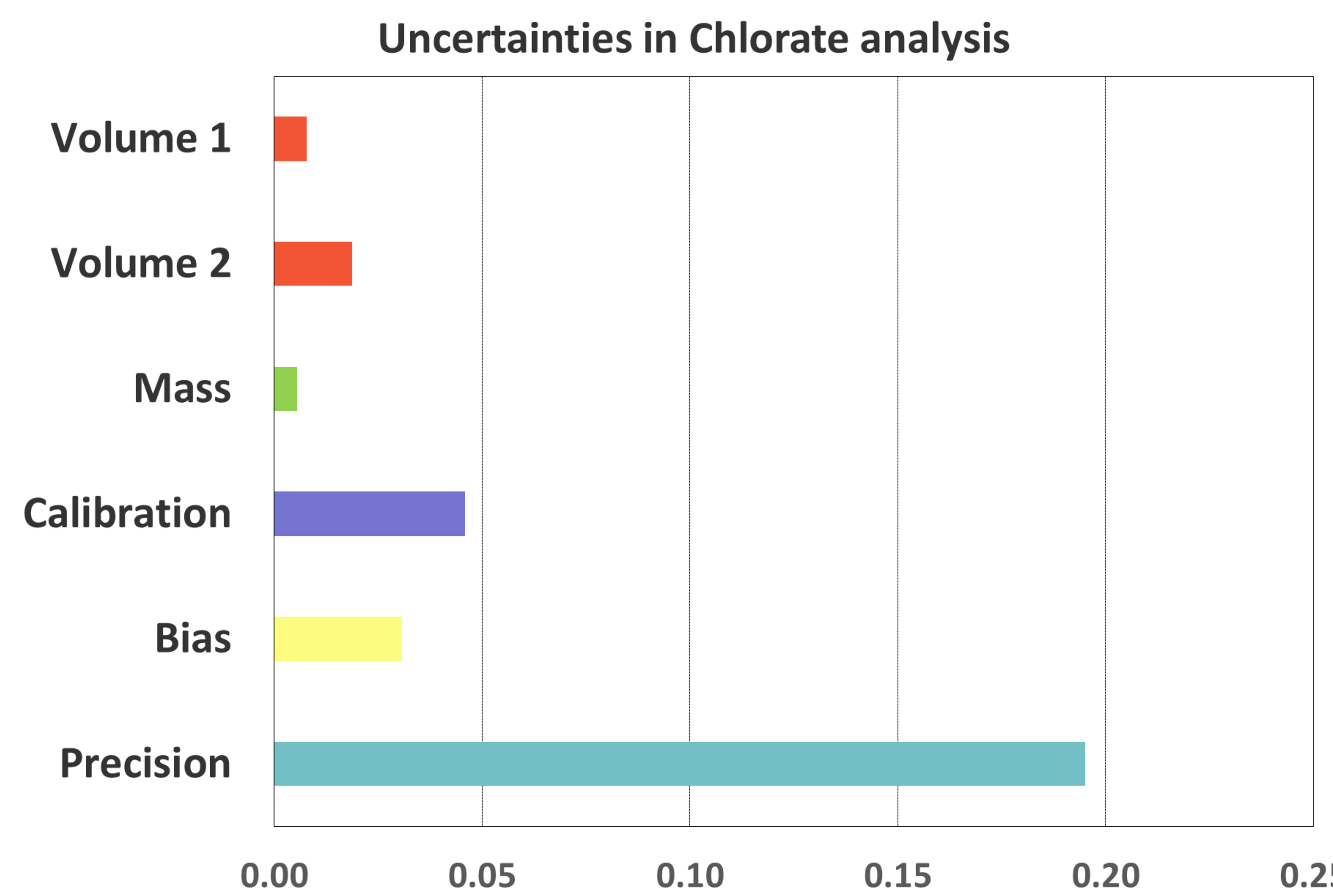


Figure 3: Component contribution in final result (mg/kg)

3a. TOTAL UNCERTAINTY (combined standard uncertainty)

The total uncertainty was calculated by combining all uncertainties associated with each component, multiplied by the measurement result ($c_{chlorate}$ = 2.7 mg/kg), as follows:

4. CONCLUSIONS

The major contribution to uncertainty arise from precision (reproducibility of recovery experiment results) and calibration (concentration calculated from calibration curve).

$$u_c(c_{chlorate}) = \sqrt{[(u_{V1}/v_1)^2 + (u_{V2}/v_2)^2 + (u_m/m)^2 + (u_{cal}/c)^2 + (u_{bias}/R_{avg})^2 + RSD_r^2]} \times c_{chlorate} = 0.20 \text{ mg/kg}$$

3b. EXPANDED UNCERTAINTY (U)

Expanded uncertainty is calculated by multiplying $u_c(c_{chlorate})$ with a coverage factor of 2, to provide a level of confidence 95%.

$U(c_{chlorate})$ = 0.40 mg/kg **Final result: (2.7 ± 0.4) mg/kg**

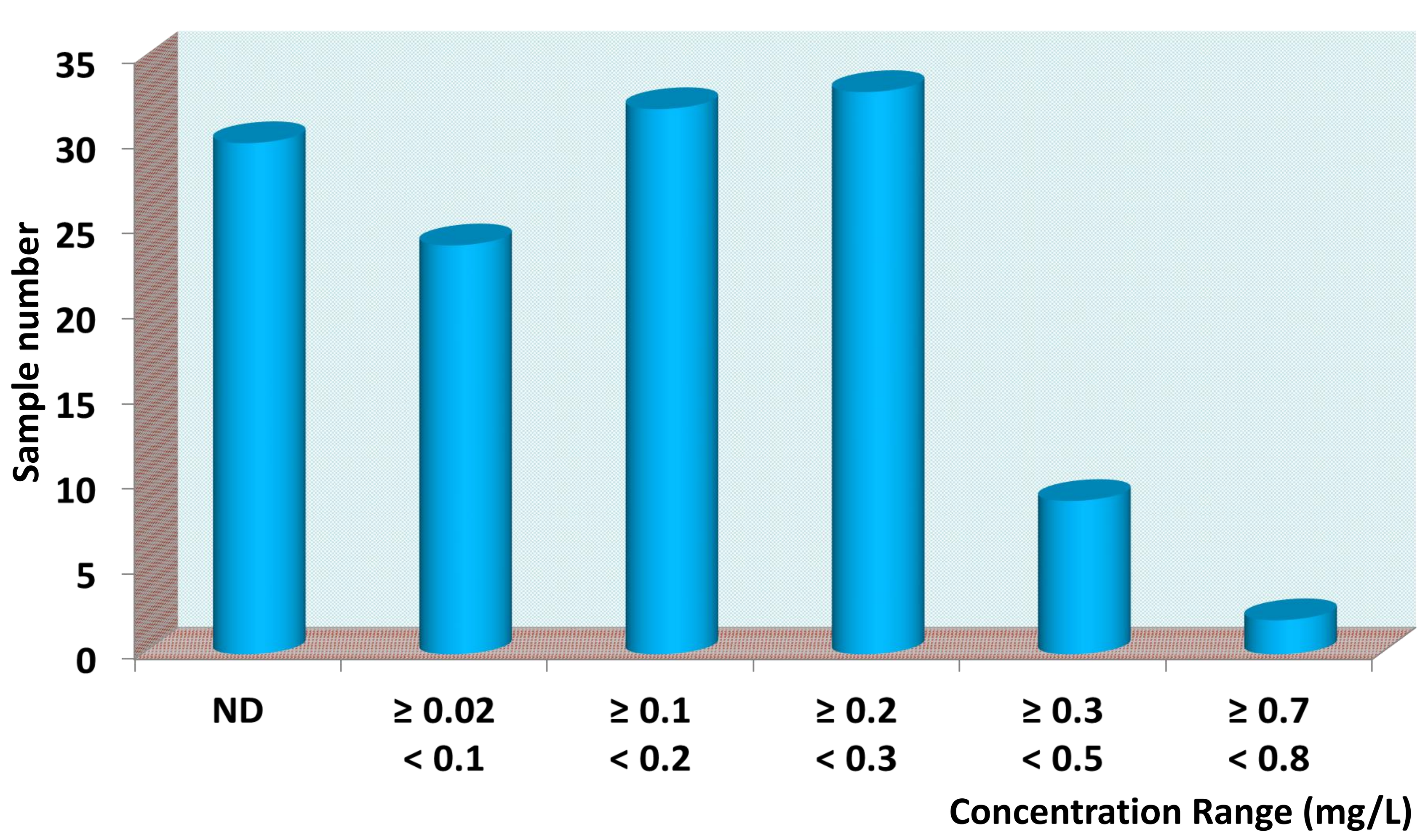


Figure 1: Results of Chlorate in 130 Cypriot water samples.

Table 1: Validation data in food – Recovery experiments

Commodity Type	Replicates	Spiking level (mg/kg)	% Recovery	% CV
Spinach	n=3	1	106.9	2.0
Strawberry	n=3	0.4	96.6	7.4
	n=6	0.2	104.2	14.0
	n=3	0.05	118.7	5.5
Grapes	n=6	0.2	95.4	6.6
	n=6	0.05	94.0	13.7
Apples	n=6	0.2	86.8	10.1
	n=5	0.05	87.7	15.7
Red Wine	n=6	0.2	97.9	5.1
	n=6	0.05	93.3	11.1
Rye	n=5	0.2	106.9	11.2
	n=5	0.05	96.3	17.0
Oranges	n=5	0.2	93.7	7.4
	n=5	0.05	101.8	14.0

Eurachem "Uncertainty in Qualitative And Quantitative Analysis"

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