Determination of Chlorates in drinking water samples

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Introduction:

- Chlorate ions occur in drinking water as a result of chlorine products used in disinfection and have an adverse effect on the human health. The most common cause of chlorate formation is the decomposition of sodium hypochlorite (NaClO) solutions during storage, especially at high temperatures.
- Chlorate management is a challenge for European water systems, especially after the latest revision of the European legislation (EU) 2020/2184, in which a maximum concentration level for chlorate was established for the first time (0.250 mg/L and 0.700 mg/L when the applied disinfection method produces chlorate).
- Considering that an increasing number of water systems are already using or considering switching to sodium hypochlorite due to safety concerns about the use of chlorine gas, the new regulation of chlorate is a major issue for those responsible for the water supply bodies.
- Since there is no economically feasible technology to remove or reduce chlorate ions after they enter drinking water treatment systems, the key to complying with the new chlorate regulation is to prevent their formation.
- The purpose of this study is to investigate the occurrence of chlorate in drinking water as a result of using NaClO as a disinfectant.

Materials and methods:

1. Sample collection

The sampling regime covered three major categories of drinking water samples:

A. 269 samples from the Athens water supply network of which 36 concerned drinking water production facilities and 235 concerned representative and/or critical points of the water supply network, during the period 2023-2024.
B. 40 samples from a remote area with low water consumption operating secondary chlorination during the period 2023-2024.
C. 410 samples from the networks of 10 small water treatment plants outside Attica during the period 2019-2024.

2. Chemical Analysis

The water samples were analyzed for chlorate by the accredited water quality control laboratory of EYDAP with the classical method of ion chromatography with conductometric detector.
(Method 4110D, Standard Method for the Examination of Water & Wastewater, 24rth edition, 2023).

Figure 1. Ion Chromatography System

Table 1. Analytical equipment for the analysis of chlorates

ANALYTICAL EQUIPMENT	
Separation Center	Metrohm 733 Separation Center
Anion precolumn	Metrosep RP Guard 6.1011.020
Anion column	Metrosep Anion Dual 2, 6.1006.100
Detector	Metrohm 732IC
Pump	Metrohm 709 IC Pump
Eluent Solution	1,2 mmol/L Na_2CO_3/2,0 mmol/L $NaHCO_3$
Chemical signal suppression	Suppression module Metrohm
Regeneration Solution	H_2SO_4 20 mmol/L
Loop size	100 µl
Eluent flow rate	0,8 ml/min
Detector operating range	Full scale 100 µS/cm

Results - Conclusions:

A. Athens water supply network

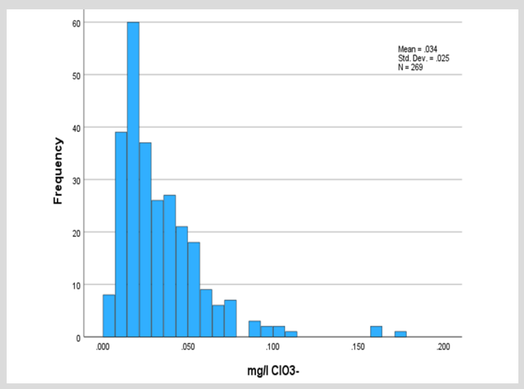

Figure 2. Frequency histogram for chlorate concentrations of Athens water supply network

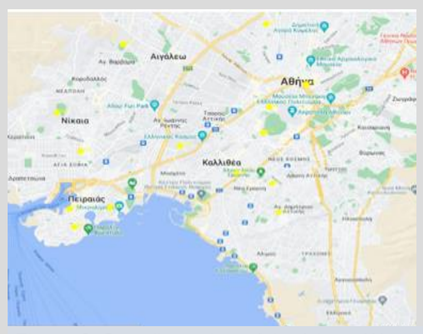

Figure 3. Sampling points of the Athens Water Supply network

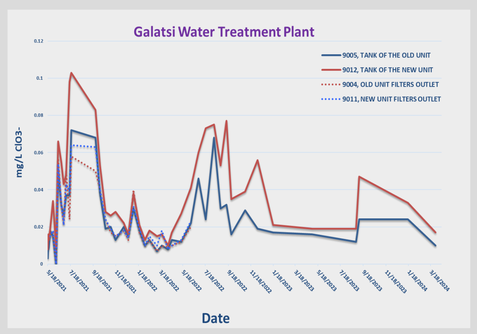

Figure 4. Chlorate measurements at Galatsi Water Treatment Plant

- The median chlorate concentration was 0.027 mg/L and the maximum concentration was 0.173 mg/L.
- There was 100% 'compliance' with the legislation's parametric values of 0.700 and 0.250 mg/L over the survey period.
- Therefore, the methods of NaClO management by the operators of the Athens water treatment plants are considered successful in terms of preventing the formation of chlorates.

B. Remote area operating meta chlorination

- The maximum chlorate concentration value was 0.229 mg/L.
- The median concentration was 0.130 mg/L, significantly higher than the corresponding 0.027 mg/L for the rest of the network, due to the additive effect from the secondary chlorination stage.

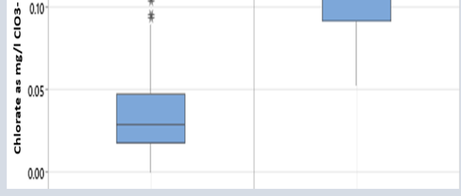

Figure 5. Comparison of chlorate measurements (mg/L) in the area where meta chlorination is applied with the measurements of the rest Athens network

C. Water supply networks of 10 small water treatment plants outside Attica

- There were no exceedances of the 0.700 mg/L parametric value. As for the value of 0.250 mg/L, the compliance concerned 69 % of the measurements. (median concentration=0.183 mg/L, max concentration=0.652 mg/L).
- A risk score was calculated for the % of measurements that exceeded the value of 0.250 mg/L at each water treatment plant.
- Proper management of hypochlorite solution is sometimes difficult, particularly in small and isolated water treatment plants due to lack of manpower, infrastructure, knowledge and awareness.
- The chlorate measurements in the tanks of the water treatment plant MEN-8 were correlated with the corresponding dates of deliveries of NaClO in order to draw useful conclusions about the optimal time to use each new batch of NaClO.

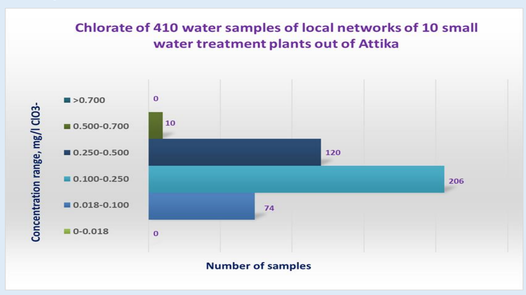

Figure 6. Classification of chlorate values of 410 samples from the networks of 10 small water treatment plants outside Attica

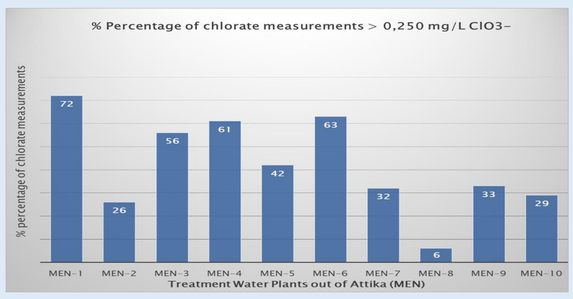

Figure 7. % Percentage of chlorate values >0.250 mg/L in the small water treatment plants out of Attica

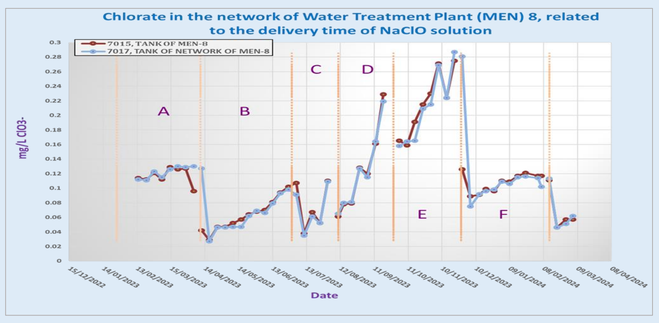

Figure 8. Chlorate measurements at the MEN-8 water network tanks

Table 2. Correlation between chlorate and other chemical parameters

Correlations

		ClO_3	Cl_2	Conductivity	TU	pH	Al
ClO_3	Pearson Correlation	1	.226**	.357*	.290**	-.239	.089
	Sig. (2-tailed)		.004	.026	<.001	.143	.260
	N	161	161	39	161	39	161
Cl2	Pearson Correlation	.226**	1	.342*	.098	-.254	.118
	Sig. (2-tailed)	.004		.033	.214	.119	.137
	N	161	161	39	161	39	161
Conductivity	Pearson Correlation	.357*	.342*	1	.078	-.021	-.074
	Sig. (2-tailed)	.026	.033		.636	.897	.655
	N	39	39	39	39	39	39
TU	Pearson Correlation	.290**	.098	.078	1	-.525**	.079
	Sig. (2-tailed)	<.001	.214	.636		<.001	.321
	N	161	161	39	161	39	161
pH	Pearson Correlation	-.239	-.254	-.021	-.525**	1	.157
	Sig. (2-tailed)	.143	.119	.897	<.001		.340
	N	39	39	39	39	39	39
Al	Pearson Correlation	.089	.118	-.074	.079	.157	1
	Sig. (2-tailed)	.260	.137	.655	.321	.340	
	N	161	161	39	161	39	161

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

D. Experimental investigation of the effect of storage time and temperature of NaClO solution on chlorate formation

In order to investigate the effect of NaClO storage time and temperature on the formation of chlorate:

- A concentrated NaClO solution was sampled upon receipt from the delivery truck at Galatsi facilities and was divided into two parts. The first sample was kept at the ambient temperature (23-25°C), while the second was kept in a water bath at 35°C. Chlorate measurements were taken during 20 days after receipt.
- The same procedure was followed but the dilutions were made in laboratory tap water. Measurements were taken during the next 10 days.

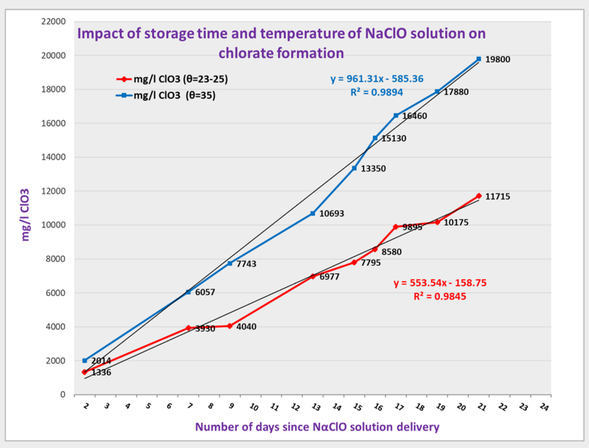

Figure 9. Plot of chlorate concentration versus storage time of NaClO solution for T=23-25ºC and T=35ºC (diluted in ultra pure water)

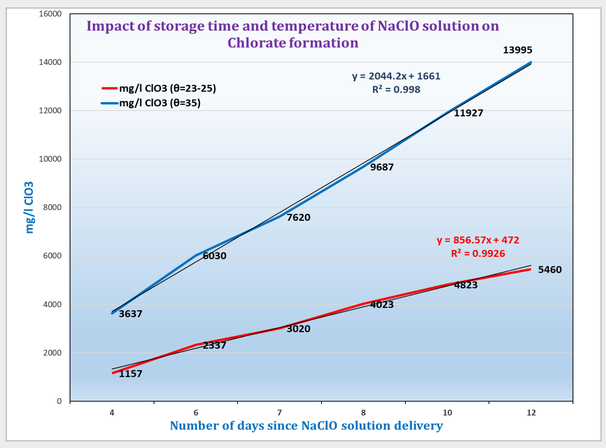

Figure 10. Plot of chlorate concentration versus storage time of NaClO solution for T=23-25ºC and T=35ºC (diluted in tap water)

- The strong positive correlation between NaClO storage time and chlorate formation was documented and the catalytic role of temperature in chlorate formation was confirmed.
- The influence of time and temperature is greater when the matrix is treated with chlorinated water.

After all, it is concluded that water companies should take action by reviewing all NaClO management practices in order to comply with the new chlorate legislation.

References

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