

Potential presence of trihalomethanes in water intended for human consumption

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Abstract

Since the 1970s it is well known that, though water for human consumption must generally be disinfected before being distributed along the network, the use of chemicals results in the formation of many different Disinfection By-Products (DBPs). In the case of chlorine-based disinfectants, trihalomethanes (THMs) are the most widely studied: the present work first compares some national and international regulations on this subject, then, in the experimental part, compares the results of a test carried out by disinfecting water of different origin collected in three different Italian regions with different amounts of chlorine. Samples were stored at ambient temperature for seven days, then the determination of THMs was carried out by Purge and Trap extraction coupled with gas chromatography with Electron Capture Detection (ECD). The results obtained are finally compared and discussed.

Introduction

Drinking water is normally obtained from raw water through more or less complex treatment processes involving several chemicals (coagulants, disinfectants, chemicals used for removing specific pollutants, etc.) and by using them more impurities are added to or formed within treated water [3, 4]. In 1974 Rook [5] discovered the presence of trihalomethanes (THMs, mainly chloroform, dichlorobromomethane, dibromochloromethane and bromoform) in water disinfected with chlorine or its derivatives as a consequence of their reaction with natural organic matter present in the water itself, such as humic and fulvic acids. Some of these derivatives, normally indicated as Disinfection By-Products (DBPs), have either been recognised as carcinogenic [6] or may cause adverse effects during pregnancy or on descendants [7-10].

THMs started to be taken into consideration by the European regulation [11] already in the '80s, even though by that time they were not considered by themselves, but within a wider class named "Other organochlorine compounds not covered by parameter No 55 (Pesticides and related compounds)", for which only a Guide Level of 1 µg/L was fixed. Later on the next European directive [1] fixed a stringent limit (the so called PV, Parameter Value) for THMs alone of 100 µg/L. Nevertheless as a consequence of the subsidiarity principle the single 27 Member states can fix even more stringent limits, which indeed some of them did, Italy being one of those, having fixed a PV of 30 µg/L [2]. Only Denmark and the Netherlands have adopted more stringent national limits, in both cases establishing a PV of 25 µg/L [12].

The European regulation on THMs can be compared to the US regulation [13], which fixes a maximum value of 80 µg/L, but also to the WHO guidelines, which do not foresee a limit but only a reference value. In detail, they fix a guideline value for each THM: 300 µg/L for chloroform, 60 µg/L for dichlorobromomethane, 100 µg/L for dibromochloromethane and 100 µg/L for bromoform, for a total of 560 µg/L.

Finally the European directive gives no prescription concerning the amount of disinfectant to add, while the Italian regulation recommends a value of 0.2 mg/L of residual disinfectant [2].

Materials and methods

The experimental part of the present work aimed at verifying what concentration of THMs might result as a consequence of chlorination of raw water of different origin (that is, surface water or groundwater) collected in different Italian regions, specifically Liguria, Tuscany and Piedmont. Eight different samples were collected from each region and were disinfected with different amounts of chlorine, added as sodium hypochlorite. One concentration (0.5 mg/L) would reproduce the typical amount of disinfectant that might give the value of 0.2 mg/L of residual chlorine recommended by the Italian regulation [2], while the other two concentrations (1.0 and 2.0 mg/L) might be added in the case of an emergency due to microbiological pollution. The samples of raw water were collected, before any treatment, in 1-litre glass bottles

and carried to the laboratory under refrigeration. In each case, and 30' after disinfection had been carried out, the presence of residual chlorine was assessed and quantified with a portable HACH spectrophotometer (HACH Pocket Colorimeter™). The colorimetric reaction is based on the formation of a pink colour, which is obtained by adding DPD (N,N-diethyl-p-phenylenediamine). Samples were finally stored in glass vials, at room temperature and in the dark, for seven days, then the presence of residual chlorine was assessed again in order to verify if the formation of THMs might have been partially hindered by lack of disinfectant. The average value of residual chlorine obtained in each session (that is, adding 0.5, 1.0 and 2.0 mg/L of chlorine) for samples coming from a same region are shown in Tab. 1.

Sample	Residual chlorine after 7 days (0.5 mg/L added)	Residual chlorine after 7 days (1.0 mg/L added)	Residual chlorine after 7 days (2.0 mg/L added)
Liguria	0.11	0.47	1.25
Tuscany	0.22	0.51	1.32
Piedmont	0.13	0.50	1.37

Table 1. Residual chlorine after 7 days

At the end of the 7-day period the process of THMs formation was stopped by adding an excess of sodium thiosulphate to each sample, and a portion of each sample was then transferred to a specific vial in order to determine THMs by Purge and Trap extraction followed by ECD (Electron Capture Detector) gas chromatography. The reference analytical method was ISS.CAA.036 [14], with the following operating conditions:

Column: Factor Four CP Select 624 30m, 0.53 mm ID; Column temperature: 35°C for 7 min, then 7 °C/min heating up to 160 °C, to be kept for 1min; Injector temperature: 250 °C; Detector (ECD) temperature: 300°C; Carrier gas flow (helium): 5 ml/min; Makeup gas flow (nitrogen): 57 ml/min.

Results

The average results obtained in each session for samples coming from a same region are shown in Tab. 2.

Region	THMs (µg/L) after 7 days (0.5 mg/L chlorine added)	THMs (µg/L) after 7 days (1.0 mg/L chlorine added)	THMs (µg/L) after 7 days (2.0 mg/L chlorine added)
Liguria	20.0	55.7	89.8
Tuscany	25.9	51.5	72.3
Piedmont	20.4	27.3	43.0

Table 2. Average concentration of THMs in different test conditions.

Discussion

The data obtained in the three sessions have been interpreted with reference to two possible limits for THMs, that is the PV of 30 µg/L foreseen by the Italian regulation [2] and the PV of 100 µg/L fixed by the European Directive [1]. The guideline value of 560 µg/L issued by WHO is also considered, though it has to be calculated from the specific value for each THM [8].

The values obtained are summarized in Tab. 3, making reference to the percentage of samples within three different ranges and considering each region separately. The chosen ranges are:

THMs < 30 µg/L, that is below the current Italian PV; 30 µg/L < THMs < 100 µg/L, that is higher than the Italian limit, but still below the PV foreseen by the European Directive;

THMs > 100 µg/L, that is higher than the PV foreseen by the European Directive.

Liguria			
Cl ₂ mg/L	THMs < 30 µg/L	30 < THMs < 100 µg/L	THMs > 100 µg/L
0.5	87.5	12.5	0
1.0	25	75	0
2.0	12.5	62.5	25
Piedmont			
Cl ₂ mg/L	THMs < 30 µg/L	30 < THMs < 100 µg/L	THMs > 100 µg/L
0.5	87.5	12.5	0
1.0	50	50	0
2.0	75	25	0
Tuscany			
Cl ₂ mg/L	THMs < 30 µg/L	30 < THMs < 100 µg/L	THMs > 100 µg/L
0.5	75	25	0
1.0	25	75	0
2.0	25	75	0

Tab. 3. Percentage of samples within the chosen ranges

Data clearly show that even in the case of a relatively high amount of added chlorine (2.0 mg/L), the number of samples exceeding the European PV is limited; as such addition should be practised in Italy only in the case of severe microbiological risk, we can reasonably think that the consequent chemical risk due to a relatively high concentration of THMs can be considered very low. Besides, as the specific values obtained for the two non compliances have been 141.0 µg/L and 212.3 µg/L respectively, this should cause no concern as they are by far below the WHO guideline value of 560 µg/L.

Let us conclude with these final words from the WHO guidelines [8]:

"It is emphasized that adequate disinfection should never be compromised in attempting to meet guidelines for THMs. Nevertheless, in view of the potential link between

adverse reproductive outcomes and THMs, particularly brominated THMs, it is recommended that THM levels in drinking water be kept as low as practicable”.

References

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