

# Chlorine Dioxide DBPs (Disinfection By-Products) in Drinking Water

C. Lasagna<sup>\*1</sup>, E. Raffo<sup>2</sup>, M. Bianchi<sup>2</sup>, L. Pocaterra<sup>2</sup>

<sup>1</sup> Iren Acqua Gas S.p.A., Via Piacenza, 54 – Genoa (Italy). \*E-mail: claudia.lasagna@irenacquagas.it

<sup>2</sup> Laboratori Iren Acqua Gas S.p.A., Via Piacenza, 54 – Genoa (Italy)

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## Abstract

**Since the 1970s it has been well known that, though water for human consumption is generally 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 dioxide, the most important and represented DBPs are chlorite and chlorate: after an introduction concerning the current Italian regulation on this subject, in the experimental part the results of a 7-year monitoring campaign, concerning water of different origin collected from taps in various Italian regions, are shown. The analytical technique used for the determination of chlorite and chlorate was Ion Chromatography. The results obtained are finally discussed.**

## Introduction

Drinking water is generally obtained from raw water through more or less complex treatment processes involving several chemicals (coagulants, disinfectants, chemicals used for removing specific pollutants, etc.). As a consequence of any treatment train in which such chemicals are used, impurities are either added to or formed within the treated water [1, 2]. With regard to disinfection, the substances obtained are all grouped in a very wide and non-homogeneous class under the common name of Disinfection By-Products (DBPs). Since the 1970s [3] the best known and most studied DBPs are trihalomethanes (THMs), which are formed as a consequence of the reaction of chlorine or its derivatives (hypochlorites, chloramines, etc.) with the natural organic matter present in the raw water itself, such as humic and fulvic acids. As in the 1980s THMs had been indicated as possible carcinogenic [4], the search for alternative

disinfectants, that wouldn't form such derivatives, began. By that time other disinfectants than chlorine and its derivatives had already been on the market for decades, but very little was known about their possible DBPs. Further studies allowed to know that chlorine dioxide mostly forms inorganic derivatives (chlorite and chlorate, [5]), and that the same occurs with ozone (bromate, [6]) and UV radiation (nitrite, [7]). Thus, from the point of view of DBPs formation, the ideal disinfectant doesn't exist. Nevertheless the main concern must be how to minimize DBPs in order to keep their concentration below a reasonable limit, without compromising the effect of disinfection.

As for chlorine dioxide, though we have said that most DBPs are of inorganic origin, also organic products are formed, such as haloacetic acids, which are already regulated in some parts of the world [8]. Nevertheless in the following we will take care only of the inorganic species.

At present the health effects of chlorite and chlorate on adults, pregnant women and children are quite well known [9]. The critical effect of chlorite appears to be oxidative damage that leads to anemia and methemoglobinemia, while the developmental effects seem to be less sensitive than the hematological effects [10]. Besides an epidemiological study found a weak association between term-SGA (Small-for-Gestational-Age) outcomes and elevated levels of chlorite [11], with risk increasing upon inhalation, though chlorite is not a volatile substance.

Chlorate clearly affects thyroid function, probably mostly by inhibition of the NIS (Natrium Iodide Symporter). Cancer development on rats has been demonstrated, while similar effects on humans have not yet been proved [12, 13].

The current European regulation on water for human consumption [14] doesn't take chlorite and chlorate into account. It is true that some Member States have at least included chlorite into their national implementation of the Directive [15], Italy being one of them [16]. Since the issue of the current Italian regulation on drinking water in 2001, chlorite has been one of the most controversial parameters. Before 25th December 2003 there was no limit for chlorite, but from that date until 25th December 2006 a limit was provisionally set at 800 µg/L, with a final Parameter Value (PV) of 200 µg/L to be reached within the latter date. Unfortunately the monitoring campaign carried out in many water distribution systems in the

interim period allowed to realise that such limit was too stringent and very hard to meet: this is why in September 2006 a new decree was issued [17] and the PV for chlorite was ultimately set at 700 µg/L, which is the current Italian reference, fully coincident with the WHO guideline value [18]. As said before, another inorganic DBP is formed when chlorine dioxide is used, either as an oxidant or as a disinfectant, that is chlorate. This by-product has not yet been taken into account by any national legislation on drinking water in Europe, even though WHO has set a guideline value of 700 µg/L for it [18].

## Materials and methods

The experimental part of the present work aimed at verifying what concentration of chlorite and chlorate might result, as a consequence of disinfection with chlorine dioxide, in real samples in different distribution systems. During a 7-year monitoring campaign, which began in January 2004 and ended in September 2011, more than 2,000 water samples were collected along the distribution systems from different water networks. The raw water treated for producing the samples collected during this study was in most cases surface water rather than groundwater.

Samples were collected in various Italian regions, predominantly Liguria and Piedmont. All of them had been treated in plants using chlorine dioxide as disinfectant. Samples had been collected in plastic bottles, no headspace left in order to minimize any change in the concentration of the analytes after sampling. In the case of chlorite the sample must be nitrogen-stripped in order to keep the concentration of this anion stable for at least 48 hours. Finally the analysis was carried out with Ion Chromatography: the anions were separated along an ion-exchange column and detected thanks to a conductometric detector, following the suppression of the electric conductivity of the eluent solution. Fig. 1 shows an example

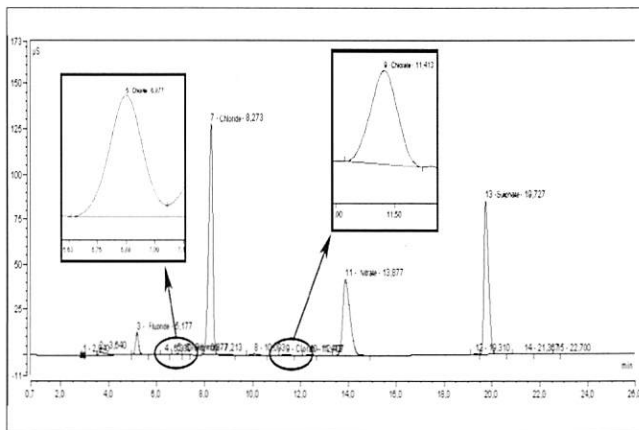


Figure 1. Chromatogram of a sample of water disinfected with chlorine dioxide.

of chromatogram. In detail a DIONEX ICS3000 ion chromatograph was used, with an analytical set specific for low concentration anions in drinking water, equipped with

an AS19 Dionex analytical column (diameter: 2 mm; length: 250 mm; stationary phase: polyvinyl benzilammonium and divinylbenzene) and an AG19 guard column with the same stationary phase. The analytical method [18] had been specifically tested and validated in the case of water for human consumption and perfectly complies with what the current Italian regulation requires [16]. In the following the analytical conditions are summarized:

Analytical column: AS19  
Guard column: AG19  
Eluent solution: 20 mM KOH  
Eluent generator: EGC KOH Cartridge  
Column flow: 0.2 ml/min  
Column temperature: 30 °C  
Suppressor: ASRS 300 2 mm  
Injection volume: 25 µl  
Pressure: 1500 psi  
Time of analysis: 30 min

## Results

The concentrations measured for chlorite were grouped in different ranges and compared with the current Italian PV of 700 µg/L, effective since late 2006 (Tab. 1 and Fig. 2).

Table 1. Data concerning chlorite.

	Chlorite	% of samples
n. samples	2428	
< 10 µg/l	978	40.3
<100 µg/l	335	13.8
>100 <200 µg/l	264	10.9
>200 < 500 µg/l	800	32.9
>500 < 700 µg/l	46	1.9
> 700 µg/l	5	0.2

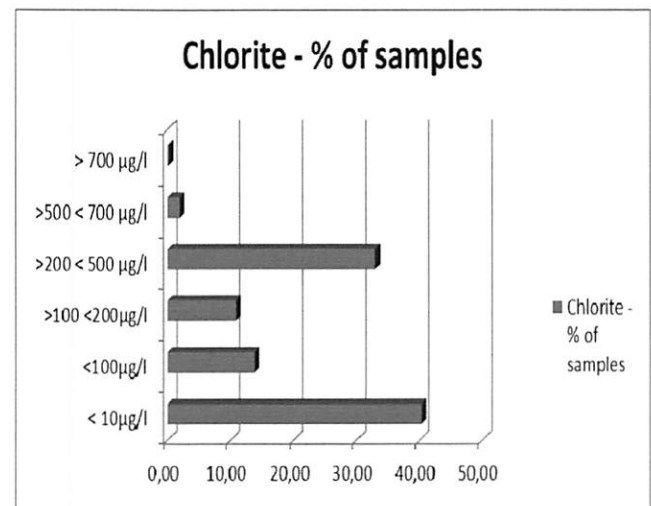


Figure 2. Distribution of chlorite concentration in samples.

As data concerning chlorate are easily obtained during the same analytical session of chlorite, they were collected, grouped in different ranges and finally compared, in absence

of any Italian regulation, just with the WHO guideline of 700 µg/L (Tab. 2 and Fig. 3).

Table 2. Data concerning chlorate.

	Chlorate	% of samples
n. samples	2428	
< 10 µg/l	721	29.7
<100 µg/l	805	33.2
>100 <200 µg/l	469	19.3
>200 < 500 µg/l	324	13.3
>500 < 700 µg/l	109	4.5
> 700 µg/l	0	0.0

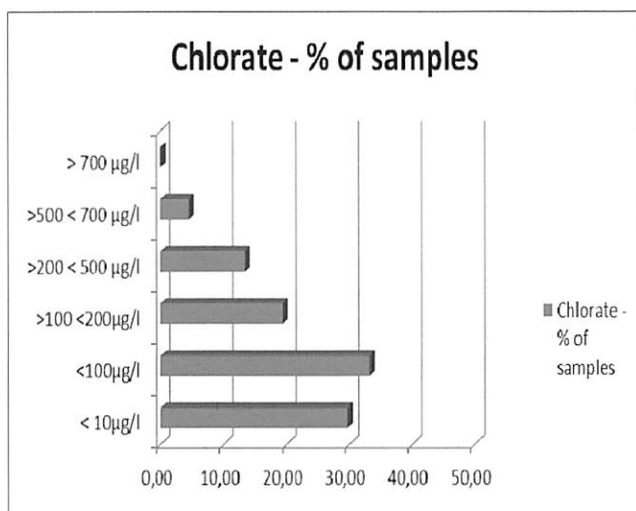


Figure 3. Distribution of chlorate concentration in samples.

## Discussion

As it can be easily seen upon the examination of the data summarized in Tab. 1 and Tab. 2, the quality of the water samples analysed during the 7-year monitoring campaign are quite comforting: should the very - and excessively - stringent limit of 200 µg/l, originally foreseen by the Italian regulation for chlorite, have been enforced, approximately 35% of the samples collected would have exceeded it. The much more realistic current Italian limit of 700 µg/l has caused only 0.2% of anomalous samples exceeding the PV, while none of them exceeded the guideline value set by WHO for chlorate. These data are extremely comforting and prove how the Italian regulation on drinking water and the subsequent correct management of drinking water treatment plants can guarantee safety for human health.

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