Chemical and sensory analysis of chlorine dioxide in drinking water

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Abstract

Water utilities have traditionally focused their efforts on providing a product with health guarantees, a safe and clean water. Disinfection has been the main purpose of the water treatment. A broad range of disinfectants and technologies are available. Chlorine dioxide has been increasingly used because of its ability to avoid the formation of trihalomethanes (THMs), the most common and well known disinfection by-products.

An odour event in the water supply network in Barcelona was attributed to the use of chlorine dioxide as disinfectant. The study had two main objectives: first, develop an analytical method to analyze low levels of chlorine dioxide in presence of chlorine; and second, estimate the organoleptic properties of chlorine dioxide in order to know if they were in accordance with the effects reported by consumers (odour complaints).

The chemical study showed that two of the most common classical colorimetric methods indicated in the literature for the analysis of chlorine dioxide, DPD (N,N´-diethyl-p-phenylendiamine) and Lissamine Green B (LGB), are no selective enough to obtain reliable results when free chlorine is present. The addition of glycine as masking agent in the DPD method inhibits the response of free chlorine but also decreases the signal

of chlorine dioxide. On the other hand, the discolouration of LGB in presence of chlorine dioxide is significantly interfered by residual chlorine depending on the relative concentrations between the two agents.

The intensity of the chlorine dioxide odour was not significantly different from chlorine, the agent used traditionally in the network. But the difference tests performed showed that the smell is qualitatively different. Therefore, these results permit the episode to be explained: the change of disinfectant was detected by sensitive consumers.

INTRODUCTION

Drinking water supply companies have traditionally focused their efforts on providing a product with health guarantees, a safe and clean water. Disinfection has been the main purpose of the water treatment. A broad range of disinfectants and technologies are available. Chlorine dioxide has been increasingly used because of its ability to avoid the formation of trihalomethans (THMs), the most common and well known disinfection by-products.

The origin of the present work was a flavour and (mainly) odour episode which occurred in the water supply system of the city of Barcelona and was attributed to the use of chlorine dioxide for final disinfection in one of the sources. This agent had not been used until the moment to treat tap water in the area.

Taste and odour events in tap water deserves a brief comment. Although avoiding such events one hundred percent is certainly impossible, water supply companies must make an effort to prevent them or, when they occur, to find out their origin and deal with them as quickly as possible. The consumer mistrusts water that suddenly smells bad or tastes different than usual; the change is associated with a health risk.

These episodes can be due to a number of causes, of natural or anthropogenic character, and can come from the water resource, the treatment process, or the distribution system (Suffet et al., 1995) (Khiari et al., 1999). The way the water supply companies handle these episodes is of vital importance (Mc Guire et al., 2005) and must include effective communication with the stakeholders. Resolving an episode uses to be difficult because they are sporadic and transitory phenomena that, in most cases, appear unexpectedly and without previous warning.

Objetive

In order to know the origin of the problem and decide the actions to be taken to solve it, a study was implemented with two main purposes from different approaches:

- First, chemical analysis. Implementation of an analytical method to determine chlorine dioxide in presence of free chlorine. The literature suggests that the performance of some in used methods is not good enough, in special with respect to selectivity against free chlorine and other species. It is necessary to underline that in our case the method had to be applied to a high mineralization water (600 – 1000 mg/L). DPD and LGB methods have been evaluated.

- Second, sensory analysis. The odorous properties of chlorine dioxide in tap water had to be characterized due to that the available literature data was scarce.

LITERATURE BACKGROUND

Chlorine dioxide analysis

Traditionally, the most common methods for chlorine dioxide analysis used by utilities have been colorimetric. Different agents have been proposed: chlorophenol red, amaranth, K violet, lissamine green B (LGB) and DPD (Masschelein, 2001) (Tzanavaras, 2007). An instrumental determination by ionic chromatography previous conversion to chlorite has also been proposed (Pepich, 2007).

Among the colorimetric agents, DPD and LGB are the most used (APHA, 2002) (Chiswell and O'Halloran, 1991). DPD is a classical visible spectrotrophotometry, a "direct" colorimetry where a coloured product forms. On the contrary, LGB and the rest of the compounds work on a "reverse" basis, that is, the discolouration of the dye because of its oxidation is measured. Calibration curves for direct methods have positive slope from the axis origin (approximately), while in the second case the reference solution (dye with oxidant) is prepared to give a big absorbance and the slope is negative. In addition, linear range is much bigger for direct measurement. Therefore, the quality of the reverse methods are clearly lower and are used when there is no an easier alternative.

DPD**.** This method is without any doubt the most common one for the analysis of free and also combined chlorine (chloramines) (APHA, 2012). This compound reacts with oxidants to yield a violet product. The calibration curve is usually constructed with potassium permanganate and a specific stoichiometric factor is used for each oxidant. It has been also widely used for chlorine dioxide in commercial kits. When chlorine and chlorine dioxide are both present, glycine has to be added as masking agent: chlorine reacts to form chloroaminoacetic acid, which does not react with DPD. Some authors have pointed out a certain lack of accuracy and robustness for chlorine dioxide analysis.

Lissamine Green. In this case the method is based on a partial discolouration of the dye produced by the oxidant which is analysed. Its selectivity can be improved against free chlorine by using an ammonia buffer to bind it as chloramine (Chiswell and O'Halloran, 1991).

Sensory properties of chlorine dioxide

The information that can be found in literature about the sensory properties of chlorine dioxide is scarce. The reported results of odour and taste thresholds are about 0.2 mg/L (Piriou et al., 2004) (Suffet et al., 1995). Some works in the 1990s suggested a relationship between odours inside houses being supplied with dioxichlorinated tap water and carpeting (Dietrich et al., 1992), but no definitive conclusion was reached.

EXPERIMENTAL

DPD analysis

Free chlorine was analyzed following the conventional procedure from Standard Methods (APHA, 2012). For chlorine dioxide analysis, glycine was added to water sample and was allowed to react for 5 minutes. Then, the phosphate buffer and the DPD reactive were added.

LGB analysis

Concentrate chlorine dioxide solutions of about 0.5 g/L were prepared from reaction between sodium chlorite and acetic anhydride. They were standardized by iodometric potentiometric titration with sodium thiosulfate.

The standard curves were prepared daily with tap water (disinfected in the treatment plant by chlorination) purged with helium for ten minutes. In a 100 mL volumetric flask containing 50 mL aprox. of purged water different volumes of chlorine dioxide intermediate solution (about 35 mg/L) were poured. Next, 10 mL of ammonia/ ammonium chloride buffer pH=9 and 2 mL of LGB solution (400 mg/L) were added, and diluted to mark with purged water. The absorbance at 614 nm was spectrophotometrically read. Real water samples were analyzed using the same procedure without purge.

Odour characterization

Odour assessments were performed by an untrained panel, staff volunteers without any education in sensory analysis. Encoded water samples (200 mL) contained in Erlenmeyer flasks (500 mL) with ground-glass stoppers were heated to 45 ºC in a water bath. Odour was evaluated by swirling the contents, removing the stopper and immediately applying the nose to the mouth of the flask. Tasting sessions were performed in a specially conditioned room free from interfering odours.

Triangle test. In this difference test three samples are presented, two of them being identical. Subjects have to find the odd sample. The order of presentation and the proportion of the two samples in the overall experiment are balanced. The test was carried out in its forced option, that is to say the tasters had to compulsorily indicate a sample as different.

3.3.2 OTC**.** Odour threshold was determined according to a three alternative forced choice (3-AFC) discriminative method (ASTM E679, 2004). A series of triangle test were presented to tasters is ascendant concentrations. One of the samples from each triangle test contained a given concentration of chlorine dioxide while the other two were just blanks.

RESULTS AND DISCUSSION

DPD method

The results showed that the DPD method worked apparently well for chlorine dioxide in absence of chlorine. A real validation was not performed because from the beginning was clear that the masking effect of glycine to avoid the interference of chlorine did not work properly. Experiments with crescent concentration of glycine showed that the signal

to free chlorine did not disappear until a high concentration of glycine was reached, about 2 % w/v, but in these circumstances the response for chlorine dioxide was also affected.

As a result, the method was considered unsuitable for our source water. In fact, although some commercial kits and field methods are based on this method, this procedure has been removed from Standard Methods after the 20th edition (2002) and since then is just maintained as “reserved” method.

Lissamine Green method

The experiments with LGB showed that the quality of the method for chlorine dioxide with the Llobregat matrix water (robustness, sensivity and quantification limit, and accuracy) were not outstanding but acceptable. On the other hand, the method was capable to determine chlorine dioxide in presence of free chlorine, with some restrictions concerning the relative concentrations of the two oxidants.

The analysis were performed at pH=9 and the experiments confirmed that the results with a ammonia/chlorine ammonium buffer are clearly better that those obtained with a phosphates buffer. As is well known, ammonia reacts with chlorine forming chloramines which react with LGB just partially and

with slower kinetics.

Figure 1 shows an example of a calibration graph for chlorine dioxide analysis with LGB in absence of

free chlorine. When chlorine was added, a moderate but significant interference was detected: the signal decrease was approximately five times less than that of chlorine, both species being expressed in mg/L. Therefore the applicability of the method depends on the relative concentration of both oxidants and the required accuracy. The table 1 shows the accuracy results obtained for several waters containing different concentration of both agents. All the samples have been always prepared by using real Llobregat water.

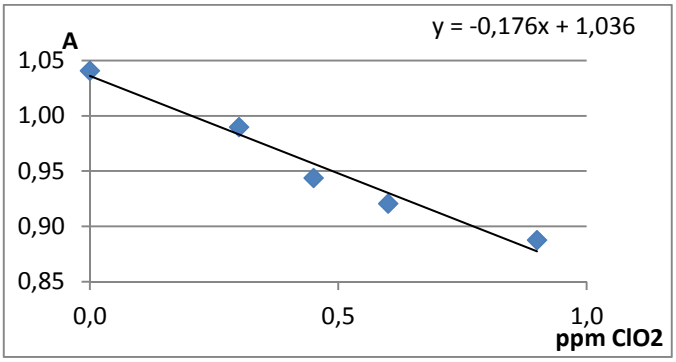

Figure 1. A typical calibration curve for chlorine dioxide analysis by LGB method.

Spiked (ppm ClO2)	Spiked (ppm Cl2)	Measurement/ Result (ppm ClO2)	Difference (ppm ClO2)	Error (%)
0,21	0,00	0,17	-0,04	-19
0,52	0,00	0,56	0,04	8
1,17	0,00	1,21	0,04	3
0,00	0,56	0,08	0,08	
0,00	1,12	0,20	0,20	
0,00	2,24	0,38	0,38	
0,54	0,51	0,62	0,08	15
0,54	1,02	0,78	0,24	44
0,54	2,04	0,90	0,36	67
0,96	0,54	1,06	0,10	10
0,96	1,08	1,11	0,15	16
0,96	2,16	1,39	0,43	45

Table 1. Interference by chlorine. Accuracy assessment on real matrix water (high TDS).

Odour threshold

The results obtained are presented in figure 2. The OTC and perception at 50 % for chlorine dioxide were around 0.1 mg/L, not significantly different from chlorine perception values, with the same method and panelists (0.09 and 0.04 mg/L). Therefore, the intensity of the odour produced by the two disinfectant agents was estimated to be similar.

Discrimination between chlorine and chlorine dioxide odours

The purpose of the experiment was to find out if chlorinated and dioxichlorinated waters could be significativiely distinguished by their odour (at the same concentration). Three levels were tested: 0.2, 0.4 and 0.8 mg/L.

Conc. (mg/L)	0,05	0,15	0,3	0,48	0,77	OTC (mg/L)
ln C	-3,00	-1,90	-1,20	-0,73	-0,26	(Geometric mean)
Subjec 1	O	O	O	O	O	0,05
Subjec 2	N	N	N	N	O	0,61
…	N	O	O	O	O	0,09
Subjec 24	N	N	O	O	O	0,21
Subjec 25	O	O	O	O	O	0,05
Subjec 26	O	O	O	O	O	0,05
Subjec 27	O	O	O	O	O	0,05
Subjec 28	Ø	N	Ø	N	O	0,61
Subjec 29	O	O	O	O	O	0,05
Subjec 30	Ø	Ø	N	O	O	0,38
Subjec 31	N	O	O	O	O	0,09
Subjec 32	N	O	O	O	O	0,09
				Global OTC		0,12

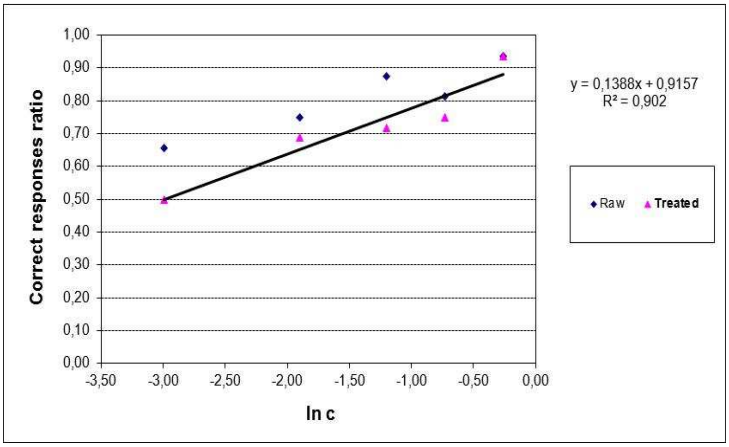

Figure 2. Top: Odour threshold concentration (OTC) for chlorine dioxide. "O" means correct answer; "N" incorrect answer; "Ø" correct answer invalidated by an incorrect answer at a higher level. Bottom: Raw results ("Ø" answers being included) and treated results (just "O" answers taken into account) vs Concentration.

The results obtained are presented in table 2. The samples were statistically different (significance level, α=0.05) at the three concentrations, that is, chlorine and chlorine dioxide odours could be actually discriminated.

Concentration (mg/L)	Triangles presented	Correct answers	Critical number	Significant difference ?
0.2	20	13	11	Yes
0.4	20	14	11	Yes
0.8	20	16	11	Yes
Global	60	43	27	Yes

Table 2. Results from triangle difference test between chlorine and chlorine dioxide treated waters.

CONCLUSIONS

-DPD. This method for chlorine dioxide analysis worked apparently well for chlorine dioxide in absence of chlorine. But the interference from free chlorine was not avoided by using glycine for a complex matrix/ high TDS (600 – 1000 mg/L) source water. In fact, although today some available commercial kits are based on this method, this procedure was removed from Standard Methods after the 22th edition (2005) and since then is has been just maintained as "reserved" method.

- LGB. Lissamine Green B method clearly improves by using the ammonia/ammonium chloride buffer instead of the phosphates one to determine chlorine dioxide in presence of free chlorine in the complex matrix water indicated above. But in any case, there are some restrictions concerning the relative concentrations of the two oxidants.

- Chlorine dioxide odour. The intensity of this disinfectant odour was not significantly different from chlorine, the agent used traditionally in the network. But the difference tests performed showed that the smell is qualitatively different. Therefore, these results permit the episode to be explained: the change of disinfectant was detected by sensitive consumers.

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