Review of analytical methods for the determination of chlorine dioxide

Paraskevas D. Tzanavaras¹*, Demetrius G. Themelis²†, Fotini S. Kika²

¹ Quality Control Department, Cosmopharm Ltd, 20100 Korinthos, Greece
² Laboratory of Analytical Chemistry, Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

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Abstract: The present study reviews more than twenty years (1985-present) of published research on the development and application of analytical procedures for the determination of chlorine dioxide, a widely used disinfectant and bleaching agent. The review covers a variety of techniques including batch and automated spectrophotometry and fluorimetry, electroanalysis and chromatography. The analytical figures of merit to the methods are presented, while critical discussion regarding their advantages and disadvantages is addressed.

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1 Introduction

Since the beginning of the 20th century, when it was first used in Belgium, chlorine dioxide (ClO₂) has been known as a powerful disinfectant of water. The use of chlorine dioxide in drinking water treatment was extended during the 1950s, since it provided less organoleptic hindrance than chlorine. Currently, apart from water disinfection, its major uses include: pulp bleaching, control of taste and odor, control of iron and manganese and control of hydrogen sulfide and phenolic compounds [1].

Chlorine dioxide is a neutral compound of chlorine in the +IV oxidation state. It is a small, volatile and highly energetic molecule, and exists as a free radical even in

* E-mail: paristzanavaras@gmail.com
† E-mail: themelis@chem.auth.gr
dilute aqueous solutions. At high concentrations, it reacts violently with reducing agents. However, aqueous solutions of chlorine dioxide are stable in closed containers in the absence of light \[2\]. Due to a unique, one-electron transfer mechanism, it acts as a highly selective oxidant \[3\]. Water solubility — even at low temperatures — is one of the most important properties of chlorine dioxide. Compared to chlorine it is ca. 10 times more soluble and it does not hydrolyze significantly. For this reason, it can be removed easily from water by simple de-aeration.

The major advantages of using chlorine dioxide as a disinfection method for drinking water treatment include \[4–6\]:

1. It is more effective than chlorine and chloramines against certain viruses.
2. It oxidizes iron, manganese and sulfides, enhancing the clarification process.
3. It can control taste and odor phenomena resulting from algae.
4. Under proper conditions, no harmful by-products are generated.
5. Its disinfection ability is not influenced by pH.

Disadvantages include:

1. It must be produced \textit{in situ}, using suitable generators.
2. It decomposes in sun-light.
3. The cost of the equipment and sodium chlorite (as raw material) are high.

Typically, chlorine dioxide is used at a mass concentration level between 0.1 and 5.0 mg L\(^{-1}\) for water treatment. In some cases, chlorine dioxide is added to finished water thereby maintaining a residual in the distribution system to control microbes. This procedure is more common in Europe than in the United States. The European Union (EU) and the United States Environmental Protection Agency (EPA) recommend that the Maximum Residual Disinfectant Level (MRDL) and the Maximum Residual Disinfectant Level Goal (MRDLG) of ClO\(_2\) is 0.8 mg L\(^{-1}\). The MRDL represents the highest level of a disinfectant allowed in drinking water. Convincing evidence exists that addition of a disinfectant is necessary for control of microbial contaminants. The MRDLG represents the level of a drinking water disinfectant below which there is no known or expected risk to health \[1, 7\].

The aim of this review is to present published work on the development and application of analytical procedures for the determination of chlorine dioxide, covering an extended period of more than twenty years (1985-2006). The methods are categorized as spectrophotometric (section 2), fluorimetric (section 3), electroanalytical (section 4) and chromatographic (section 5). Other less common applications such as chemiluminometric and enzymatic are summarized in section 6 of this review. The procedures are reviewed in terms of analytical methodology, figures of merit and analyses of actual samples. Valuable information on sampling strategies and stability of solutions is also included.

## 2 Spectrophotometric methods

Spectrophotometry is the most widely applied technique for the determination of chlorine dioxide. Spectrophotometry offers simplicity, cost-effective instrumentation readily
available in all laboratories and the potential for automation. The variety of existing suitable reagents for spectrophotometric analyses has led to the publication of a considerable number of analytical procedures [8–27], which are presented in Table 1.

Direct UV methods are based on measurement of the absorbance of chlorine dioxide at either 359 [26] or 360 nm [12], or in the range 320-400 nm by high resolution scanning [14]. However, most of the published assays are based on color-fading oxidation reactions of dyes with chlorine dioxide. Typical examples of such dyes are chlorophenol red [15, 20, 27], amaranth [13], rhodamine B [21], lissamine green B [24], neutral red [17], naphthol green [9], bromocresol purple [11] and scarlet red K-2BP [16]. Alternative approaches include reaction of chlorine dioxide with iodide to form iodine and subsequent photometric detection [25] and reaction with the 4-aminoantipyrine-phenol system [8, 19].

In terms of the mode of operation, spectrophotometric methods for the determination of chlorine dioxide can be grouped into batch [9, 11, 13, 14, 16-18, 20-24, 27] or flow injection (FI) procedures [8, 10, 12, 13, 15, 19, 25, 26]. FI is a low-pressure, continuous flow technique capable of automating many chemical processes (e.g. liquid-liquid and solid-phase extraction, enzymatic and chemical reactions, preconcentration and dilution steps, etc.). FI is based on controlled dispersion of a well-defined sample zone injected into a continuously moving carrier stream. All necessary steps for analyte detection are performed as the sample zone flows from the injection valve towards the flow-through detection system. Compared to batch methods, FI offers increased analyses rates, improved precision and automated handling of samples and reagents. This latter feature is of great importance for the analysis of chlorine dioxide, since loss of the volatile analyte is minimized within the “closed” FI system. A significant advantage of FI in the development of methods for the determination of chlorine dioxide is the possibility of the incorporation of a gas-diffusion step in the flow manifold [8, 12, 13, 15, 26], increasing significantly the selectivity for chlorine dioxide as compared to volatile species. However, a sacrifice in sensitivity must be considered, since transportation of the analyte through the membrane of the gas-diffusion unit is not quantitative. A typical example is the amaranth-based assay proposed by Emmert et al. [13]. The detection limit of the batch approach was 6 µg L⁻¹; however, automation using FI resulted in a detection limit of 140 µg L⁻¹.

The two most critical features governing the efficiency and applicability of spectrophotometric assays for the determination of chlorine dioxide are the detection limit and selectivity against potential interferents commonly found in actual samples, primarily chlorine-species and metal ions. The reaction of chlorine dioxide with 4-aminoantipyrine and phenol is promising in terms of the limit of detection. Watanabe et al. [19] reported a flow injection assay based on this reaction that was capable of determining chlorine dioxide in the range of 5-1500 µg L⁻¹. Selectivity against metals, chlorate and chlorite was enhanced by using an off-line purge-trap system. The interference of hypochlorite was suppressed up to 1.5 mg L⁻¹ at pH=9. However, no data on chlorine interference and applications in actual samples were reported. Based on the same reaction, Jin et al. [8] developed an FI-preconcentration procedure for the determination of the analyte. The limit of detection was ten times lower (0.5 µg L⁻¹) as compared to that reported by
Watanabe et al. [19]. The product of the reaction formed off-line was subsequently pre-
concentrated on-line in the FI system by passage through a PTFE fiber and elution with ethanol. Using a gas-diffusion system for selectivity enhancement, the presence of cations, chlorate, chlorite and hypochlorite were adequately tolerated. No data on chlorine interfer-
ence were included. Emmert et al. [13] reported a detailed study on the selectivity of a method based on decoloration of amaranth by chlorine dioxide in both batch and FI modes. The authors determined that minimal interferences from chlorite, chlorate
and iron(III) existed while selectivity against MnO$_x$ can be achieved using an on-line gas-
diffusion step. Chlorine is kinetically discriminated by the method as it reacts slower than
chlorine dioxide; its interference is further minimized by using an ammonia-ammonium
chloride buffer at pH=9.2 (chlorine is converted to the non-reacting chloramine). Concen-
trations of chlorine up to 10 mg L$^{-1}$ were tolerated in the batch mode, while selectivity
was enhanced using flow injection (up to 400 mg L$^{-1}$ of chlorine). However, as already
mentioned previously, the detection limit of the batch procedure was much lower (6 µg L$^{-1}$
versus 140 µg L$^{-1}$). Additional data on detection limits, ranges of determination, strate-
gies for selectivity enhancement and applications of spectrophotometric methods for the
determination of chlorine dioxide are included in Table 1.

3 Fluorimetric methods

Fluorimetric assays are generally more selective than UV-Vis spectrophotometric assays
due to the combined use of excitation and emission wavelengths, and the use of photo-
multiplier tubes that enable the development of very sensitive analytical methods. All
fluorescence-based assays reporting the determination of chlorine dioxide are indirect as-
says based on the quenching effect of chlorine dioxide on the native fluorescence of organic
compounds.

Watanabe et al. [28] reported a simple and sensitive assay using chromotropic acid as
the fluorescent reagent. Dynamic fluorescence quenching was achieved rapidly in citrate
buffer medium. The reported limit of detection (LOD) was extremely low (0.55 µg L$^{-1}$)
and chlorine dioxide could be determined up to 1.4 mg L$^{-1}$. Cations commonly found in
water samples did not interfere with the analyses. The method was applied to synthetic
samples with satisfactory results.

Based on the promising work of Watanabe et al. [28], Themelis and Kika [29] recently
reported the automation of the reaction of chlorine dioxide with chromotropic acid using
flow injection analysis. In order to enhance the selectivity of the procedure, a gas-diffusion
unit was incorporated in the flow manifold. The sampling rate was 30 h$^{-1}$, while the re-
ported detection limit was 30 µg L$^{-1}$. Compared to that reported by Watanabe et al.
[28], the higher LOD can be justified by considering the kinetic nature of flow injection
analysis and the fact that only part of the chlorine dioxide present in the sample diffuses
from the donor to the acceptor stream of the gas-diffusion unit. The gas-diffusion step had
a marked effect on the selectivity of the method. Some characteristic examples include
increased tolerance against chlorine (20-fold), against hypochlorite (13-fold), against bo-
rate (15000-fold) and against copper (20-fold). The method was applied to spiked water and beverage samples.

The research group of Jiang [30, 31] reported that chlorine dioxide exhibited a similar quenching effect on the native fluorescence of fluorescein and rhodamine S. In both cases, NH$_4$Cl-NH$_4$OH buffer was used. The LOD of the fluorescein method was 28 µg L$^{-1}$, while the rhodamine S assay was determined to be more sensitive (LOD = 6 µg L$^{-1}$) and rapid (5 min reaction time) compared to reagents having similar chemical structures (rhodamine G, rhodamine B and butyl-rhodamine B) [31]. Interference studies confirmed the selectivity of the rhodamine S method. Chlorine-species were tolerated at mass concentration ratios of 94 for chlorine, 417 for chlorate, 281 for chlorite and 63 for hypochlorite. The applicability of the developed assay was examined by analyzing synthetic samples. The mechanism of the quenching reaction was briefly discussed [31].

4 Electroanalytical methods

Electroanalytical methods applied to the determination of chlorine dioxide include amperometry [32], differential pulse voltammetry [33, 34], and chlorine dioxide selective electrodes [35]. Ivaska et al. [32] studied the application of an amperometric sensor for in-line monitoring of chlorine dioxide at a pulp-bleaching facility. Comparison of platinum and glassy carbon rotating working electrodes exhibited similar behavior at pH = 4. However, at higher and lower pH values (pH = 2-8) the glassy carbon electrode performed better than the platinum electrode because the glassy carbon electrode proved to be fairly insensitive to pH changes. For this reason, the use of the glassy carbon electrode was recommended by the authors rather than the platinum electrode. The concentrations determined using the proposed method were in good agreement with a standard titrimetric method.

Oikawa et al. [35] proposed a simple approach for the determination of the analyte using a chlorine dioxide selective electrode. The working electrode was composed of gold, while a silver counter electrode was used. The electrode responded rapidly (90% response within 20 s) over a wide range of chlorine dioxide concentrations (20 µg L$^{-1}$ – 100 mg L$^{-1}$). The limit of detection was 2 µg L$^{-1}$. The accuracy of the procedure was tested by comparison to UV spectrophotometry. Chloride and chlorate showed no response to the electrode, whereas chlorite was adequately tolerated. The only interfering compound to which the electrode responded considerably was chlorine. In addition to sensitivity and a wide range of determination, other advantages of the proposed method included simple operation, potential for automation and field application due to its portability.

Two sensitive voltammetric methods were developed by Quentel et al. [33, 34] for the determination of chlorine dioxide in tap water samples. Both are indirect procedures, based on the oxidation by the analyte of Alizarin Red S [34] and Indigo-Carmine [33]. The authors demonstrated that the decrease of the stripping peaks of the dyes measured at a hanging mercury electrode were proportional to chlorine dioxide concentration. Each of the methods were very sensitive, having detection limits of 2 µg L$^{-1}$ [34] and 1 µg L$^{-1}$
Ozone was determined to interfere in both methods. The interfering effects of Cu(II), Al(III) and Mn(II) in the Alizarin method were eliminated by using EDTA as a masking agent. Chlorite, hypochlorite and chlorate were adequately tolerated in both cases, whereas no data on the potential effect of chlorine were included.

5 Chromatographic methods

Separation assays reporting the determination of chlorine dioxide involve ion chromatography (IC) with conductivity [36, 37], spectrophotometric [38] or combined UV-conductivity [39] detection systems. A common characteristic of most IC procedures is the conversion of chlorine dioxide to chlorite prior to injection onto the analytical column [36, 37, 39]. Other separation techniques applied to the determination of chlorine dioxide include gas chromatography coupled to mass spectrometric detection (GC-MS) [40].

Bjorkholm et al. [37] used IC to determine chlorine dioxide in the workplace air of a pulp bleaching plant. Sampling was performed with the use of 30 ml midget impingers filled with 15 ml of a neutrally buffered KI solution (10 mM), to convert chlorine dioxide to chlorite ions. In order to remove excess I⁻ from the sample prior to injection in the chromatographic system, the authors adopted a column-switching approach using a suitable precolumn for sample clean-up. Employing a 250 × 4 mm i.d. anion exchange column and 0.75 mM sodium bicarbonate as eluent, the retention time of the analyte was ca. 10 min. Suppressed conductivity detection enabled the determination of chlorine dioxide at 22 µg L⁻¹ levels. The authors suggested that special attention should be given to cleaning glassware in order to avoid external contamination. Best stability of the samples was achieved when they remained refrigerated and protected from light.

The IC procedure using non-suppressed conductivity detection proposed by Poovey and Rando [36] is more simplistic instrumentally, but less sensitive compared to the aforementioned method because the reported limit of detection is 130 µg L⁻¹. Conversion of chlorine dioxide to chlorite was achieved using the same method as above (neutrally buffered KI). The effect of excess iodide on the separation was eliminated by pretreating the analytical column (250 × 4.6 mm i.d.) with 500 ml of a 1 % solution of KI (pH = 4.5). 1-hexane sulfonic acid (3.5 mM, pH = 4.4) was determined to produce optimal separation at a flow rate of 2.0 ml min⁻¹. Under these conditions, the retention time of chlorine dioxide was ca. 7.5 min. The IC method developed was applied to assess personal exposure to chlorine dioxide at four pulp/paper mills. The results demonstrated that 3.9 % of 336 samples had detectable levels of chlorine dioxide.

Sullivan and Douek [39] applied IC for the determination of chlorine dioxide in bleach effluents from a craft mill. In the proposed method, they used a combination of UV (at 205 nm) and suppressed conductivity detection. A different approach was adopted in order to quantitatively convert chlorine dioxide to chlorite by using H₂O₂ under alkaline conditions as a reductant. The primary advantage of using H₂O₂ is that its excess and reaction by-products do not interfere with the IC procedure. Compared to conductivity, UV detection offers the possibility of measuring chlorine dioxide in the presence of large
amounts of formate. Using a boric acid-tetraborate eluent at a flow rate of 1 ml min\(^{-1}\), chlorite (corresponding to chlorine dioxide) was eluted in ca. 4 min. The method allowed determination of chlorine dioxide in the range of 0.1-10 mg L\(^{-1}\).

An alternative IC approach was proposed by Watanabe et al. [38]. The authors determined that it was not necessary to convert chlorine dioxide to chlorite prior to injection into the chromatographic system. Using a home-made PTFE tube column (130 x 1 mm i.d.) packed with an anion exchange resin (particle size 35 – 55 µm) and at a flow rate of 0.5 ml min\(^{-1}\), chlorine dioxide was eluted rapidly at ca. 1.5 min. A mixture of NaHCO\(_3\)-Na\(_2\)CO\(_3\) was used as the eluent and detection was conducted at 503 nm after post-column reaction based on the 4-aminoantipyrine/phenol system. The method developed enabled the determination of chlorine dioxide in the range of 1-20 mg L\(^{-1}\), with a detection limit of 0.2 mg L\(^{-1}\).

A recently published work [40] takes advantage of the sensitivity of gas chromatography with mass spectrometric detection to develop a method capable of determining chlorine dioxide in water samples at the low ppb level. However, despite the low detection limit (1 ng mL\(^{-1}\)), the proposed GC-MS method suffers from three main drawbacks: a) CG-MS instrumentation is complicated and expensive compared to photometric, fluorimetric and even IC techniques, and therefore, it is still not available to many laboratories; b) the method is unattractive to routine analysis since it is based on a two-step derivatization reaction followed by liquid-liquid extraction prior to final measurement; and, c) hypochlorite interferes seriously even at concentration levels equal to chlorine dioxide.

6 Other applications

Less common approaches for the determination of chlorine dioxide include chemiluminescence [41] and enzymatic-based techniques [42]. Hollowell et al. took advantage of the chemiluminescence produced by the reaction of chlorine dioxide with luminol in high pH medium to develop a highly sensitive and selective assay for its determination [41]. The reaction was automated using FI analysis. A gas-diffusion approach was employed in order to enhance the selectivity of the method primarily against chlorine. The authors found that the highest sensitivity was achieved by adding H\(_2\)O\(_2\) in the reaction system (at pH = 9). However, the selectivity against chlorine was low (selectivity factor of 10). The experiments showed that at a pH of 13 and without using H\(_2\)O\(_2\), the selectivity was increased impressively with an acceptable sacrifice in sensitivity. The incorporation of the gas-diffusion step in the flow manifold resulted in a selectivity factor of 1500 against chlorine, while monochloramine was determined not to interfere. The detection limit was 5 µg L\(^{-1}\), and the range of linear determination was extended to 2000 µg L\(^{-1}\). Despite the enhanced selectivity of the method, positive errors were observed when chlorine was present in large excess (> 250:1). In such cases, the authors recommended the use of oxalic acid in the donor stream of the manifold, as a masking agent for chlorine.

An alternative approach for the determination of chlorine dioxide was proposed by Tinoco et al. [42]. The assay is based on the de-coloration of the dye, reactive yellow
FGRL, by the enzyme horseradish peroxidase in the presence of chlorine dioxide. The rate of the enzymatic reaction was monitored photometrically at 410 nm. Under the optimized pH and enzyme concentration values and using a reaction time of 15 min, as little as 0.2 mg L\(^{-1}\) of the analyte could be determined. Selectivity studies at high concentrations of several compounds, including organic solvents, detergents, ions etc, showed that only hypochlorite interfered seriously.

7 Conclusions

The viability of an analytical method dedicated to the determination of chlorine dioxide is dependent on a variety of parameters including sensitivity, selectivity, cost effectiveness, availability of instrumentation, simplicity, rapidity, etc. The ideal method of choice, however, depends on additional demands of the analytical chemist, e.g. FI analysis is not more advantageous than batch techniques if only a couple of samples must be analyzed. However, multiple methods exist in the literature that can fulfill almost all possible demands.

Spectrophotometry and fluorimetry are advantageous in terms of simplicity, low-cost, and widely-available instrumentation. A variety of reagents such as amaranth (LOD = 6 µg L\(^{-1}\)), chromotropic acid (LOD = 0.55 µg L\(^{-1}\)), rhodamine S (LOD = 6 µg L\(^{-1}\)), lissamine green B (LOD = 30 µg L\(^{-1}\)) etc., offer adequate sensitivity for most routine applications. Selectivity in the presence of other chlorine species and oxidizing agents is also a key feature. In order to avoid the use of masking agents, FI analysis coupled to gas-diffusion separation seems a promising and advantageous solution. FI with chemiluminescence detection is a powerful combination for the determination of chlorine dioxide in terms of selectivity, sensitivity and automation. IC may be generally less sensitive and more time consuming and complicated, but it offers enhanced selectivity and the very important potential for multi-analyte determination (e.g. chlorine dioxide, chlorate, chlorite etc).

An interesting electroanalytical approach based on the use of a chlorine dioxide selective electrode offers a low detection limit (LOD = 2 µg L\(^{-1}\)) and a wide determination range (0.02 – 100 mg L\(^{-1}\)). The incorporation of such an electrode in a FI system with gas-diffusion separation could result in an advantageous assay in terms of automation, sensitivity and selectivity and seems worthy of investigation.

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| Mode               | Reagent                        | LOD \((\mu g \text{ L}^{-1})\) | Upper limit \((\mu g \text{ L}^{-1})\) | Selectivity / Masking agents | Application          | Ref |
|-------------------|--------------------------------|-------------------------------|------------------------------------|-------------------------------|----------------------|-----|
| FI-preconcentration | 4-Aminoantipyrine + Phenol     | 0.5                           | 250                                | Gas-diffusion                 | Tap water            | [8] |
| Batch             | Naphthol Green                 | 100                           | 13000                              | \(\text{NH}_4\)-sulfamate     | Water                | [9] |
| Reverse-FI        | Leuco-methylene Blue           | 20                            | 1910                               | Oxalic acid                   | Spiked tap water     | [10]|
| Batch             | Bromocresol Purple             | 10                            | 2800                               | EDTA & \(\text{NH}_4\)-sulfamate | Water                | [11]|
| Continuous flow   | Direct UV at 360 nm            | 52                            | 11810                              | Gas-diffusion                 | Water                | [12]|
| Batch / FI        | Amaranth                       | 6 / 140                       | 1300 / 2000                        | Gas-diffusion                 | Synthetic samples    | [13]|
| Batch             | UV spectrum at 320-400 nm      | 1000                          | –                                  | –                             | Brine liquors        | [14]|
| FI                | Chlorophenol Red               | 20                            | 500                                | Gas-diffusion                 | Water                | [15]|
| Batch             | Scarlet Red K-2BP              | 172                           | 6720                               | –                             | –                    | [16]|
| Batch             | Neutral Red                    | 10                            | 30000                              | DMSO                           | Water                | [17]|
| Batch extraction  | Leuco-methylene Blue           | 20                            | 950                                | Oxalic acid                   | Synthetic samples    | [18]|
| FI                | 4-Aminoantipyrine + Phenol     | 5                             | 1500                               | Purge-Trap                     | –                    | [19]|
| Batch             | Chlorophenol Red               | 120                           | 1940                               | Oxalic acid, Selective        | Synthetic samples    | [20]|
| Batch             | Rhodamine B                    | 40                            | 1500                               | Selective                     | Water                | [21]|
| Batch             | m-Aminobenzyl Alcohol          | 100                           | 2000                               | EDTA                           | Water                | [22]|
| Batch             | Cresol Red                     | 4                             | 1360                               | –                              | Water                | [23]|
| Batch             | Lissamine Green B              | 30                            | 500                                | Selective                     | Water                | [24]|
| FI                | Potassium Iodide               | –                             | 10000                              | Oxalic acid                   | –                    | [25]|
| FI                | Direct UV at 359 nm            | 450                           | 142000                             | Gas-diffusion & Oxalic acid   | –                    | [26]|
| Batch             | Chlorophenol Red               | –                             | 400                                | Sodium cyclamate & thioacetamide | –                    | [27]|

**Table 1** Determination of chlorine dioxide by UV-Vis spectrophotometric methods.