

# **An Improved Accurate Method for The Automated Determination of Residual Chlorine in Saline Water**

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## **Abstract**

The determination of residual chlorine with o-tolidine in saline water has been studied. The method proposed is based on the use of reverse flow injection analysis for the monitoring of chlorine in saline samples with low cost and reduction of waste production. The linearity of the method (up to  $1.8 \text{ mg L}^{-1}$ ) covers the chlorine concentrations used in most water treatment processes. The precision of the method was 0.93 % (RSD) for  $1.4 \text{ mg L}^{-1}$  chlorine. The method is also applicable to non-saline water and the limits of detection were  $0.11 \text{ mg L}^{-1}$  and  $0.04 \text{ mg L}^{-1}$  for saline and non-saline matrices, respectively. The method has been successfully applied to the analysis of residual chlorine in both synthetic and real samples. The sample throughput was  $60 \text{ h}^{-1}$ .

**Keywords:** Residual chlorine, o-tolidine, r-FIA, saline water, desalination

## **1. Introduction**

The disinfecting properties of chlorine are frequently used in water treatment processes, such as drinking water production, sewage treatment or saline water desalination. Although several approaches may be used, chlorination is commonly done by addition of either chlorine gas or hypochlorite solutions [1-2]. To ensure the correction of disinfection, treated water must content about  $0.4\text{-}1 \text{ mg L}^{-1}$  of residual chlorine [1-4].

There are several analytical methods to quantify residual chlorine in water, based on different techniques such as spectrophotometry, chemiluminescence, potentiometry or other electrochemical approaches [5-10]. Nevertheless the most commonly used are two colorimetric

methods based on addition of o-tolidine or N,N'-diethyl-p-phenylenediamine (DPD) reagents, respectively [9-12].

To overcome the difficulty of calibration caused by the instability of chlorine, these methods use calibration lines obtained from chromate-dichromate (o-tolidine method) and permanganate (DPD method), which present similar colors to those obtained from the reaction of chlorine and the respective reagent. These calibration strategies allow for an approximate estimation of residual chlorine in most cases, especially for non-saline water, but give more inaccurate results for saline water. This effect may be of particular importance in, for example, seawater desalination plants, where an excess of chlorine may be added to feed seawater, with the corresponding economical and environmental problems caused by this excess [4,13].

In this paper, we have studied the influence of salinity in the o-tolidine method, and we have developed a reverse flow injection analysis (rFIA) methodology that permits the accurate on-line determination of residual chlorine in saline water in, for example, power and desalination plants.

## **2. Experimental section**

### **2.1. Apparatus**

Spectrophotometric measurements were carried out by using a Novaspec II VIS spectrophotometer (Pharmacia, Sweden) and a quartz cell with 10 mm pathlength (Starna, UK).

The FIA manifold (see Figure 1) consisted of a four-path peristaltic pump Minipuls 3 (Gilson, France) equipped with Tygon tubing, which was used to control the flows of reagent and sample solutions. A Model 1106 injection valve (Omnifit, UK) completed the manifold. Transport lines and reaction coils were made of 0.8-mm i.d. PTFE tubing (Omnifit, UK), and connections were made of polypropylene (Omnifit, UK).

Acidity was measured with a Model 2001 pH-meter provided with a model 52-02 combined glass-Ag/AgCl electrode (Crison, Spain).

### **2.2. Reagents and solutions**

Chlorine solutions were prepared from a sodium hypochlorite 10-13% solution (Aldrich, USA). This solution was standardized by iodometric titration before use, to determine chlorine concentration. When needed, salinity of solutions was varied by adding sodium chloride (Merck, Germany). o-Tolidine (Aldrich, USA) solutions were prepared in 1.6 mol L<sup>-1</sup> HCl (Merck, Germany).

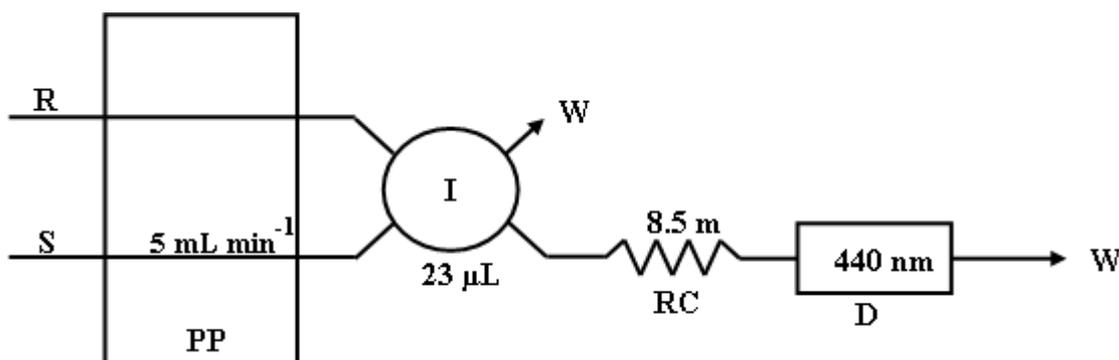
The chromate-dichromate standard solutions were prepared by dilution of a stock solution containing  $2.4 \times 10^{-3} \text{ mol L}^{-1}$  potassium chromate and  $5.3 \times 10^{-5} \text{ mol L}^{-1}$  potassium dichromate (Panreac, Spain), in a  $0.1 \text{ mol L}^{-1}$  phosphate buffer solution at pH 6.45.

All reagents except sodium hypochlorite (pure) were of analytical grade. Water was deionised to a resistivity above  $18 \text{ M}\Omega \text{ cm}^{-1}$  with a MilliQ system (Millipore, USA).

### 2.3. Procedure

Batch experiments were performed to study the effect of salinity in the o-tolidine method and to estimate the inaccuracy of the chromate-dichromate calibration method in saline samples.

To minimize waste production, a rFIA manifold was assembled to determine residual chlorine in saline samples (see Fig. 1). The colorimetric reagent was injected into a sample stream, and the absorbance obtained was measured. During optimization, all samples were analyzed in triplicate, and absorbance of corresponding blank solution was subtracted.



**Figure 1.** Reverse flow injection manifold for the determination of chlorine in saline water. R: reagent; S: sample; PP: peristaltic pump; I: injection valve; RC: reaction coil; D: detector; W: waste. Optimum conditions as indicated.

## 3. Results and discussion

### 3.1. Effect of salinity on the o-tolidine-chlorine reaction

To evaluate the effect of salinity on the determination method, we constructed calibration lines within the range  $0\text{-}2.0 \text{ mg L}^{-1}$  chlorine with different salinity. The results obtained are shown in Table 1. As observed, salinity produced an increasing loss of analytical parameters, including sensitivity. In this table, we included also the results of standard chromate-dichromate method ( $0\text{-}1.0 \text{ mg L}^{-1}$ ). This method gave results similar to those obtained for non-saline water,

but produced inaccurate results if used for the analysis of saline samples. Thus, the analysis of 7 samples containing between 0.1-1.0 mg L<sup>-1</sup> chlorine in 30 g L<sup>-1</sup> NaCl with the chromate/dichromate method gave relative errors between 28-53%, with an averaged relative error of 42%.

**Table 1.** Characteristics of batch o-tolidine methodology for different saline concentration.

| NaCl / g L <sup>-1</sup> | Slope | y-Intercept | R <sup>2</sup> | LOD / mg L <sup>-1</sup> |
|--------------------------|-------|-------------|----------------|--------------------------|
| 0                        | 0.800 | -0.010      | 0.9999         | 0.011                    |
| 10                       | 0.757 | -0.027      | 0.998          | 0.041                    |
| 20                       | 0.740 | -0.038      | 0.997          | 0.044                    |
| 30                       | 0.719 | -0.053      | 0.99           | 0.086                    |
| Chromate/Dichromate      | 0.854 | 0.001       | 0.9999         | 0.016                    |

### 3.2. Optimization of rFIA method

A rFIA manifold (see Fig.1) was used to minimize the consume of reagent, because of both economical and environmental considerations. To optimize the performance of the manifold, the absorbance of the chlorine–o-tolidine complex was measured as a function of reagent concentration (0.01-0.20%), reaction coil length (4.5-11.5 m), injection volume (23-73 µL), and sample flow rate (2.5-6.5 mL min<sup>-1</sup>). To reach the best operational conditions, we used an univariate method, where one variable is varied by maintaining constant the rest. In all optimization experiments, carrier solution was 1 mg L<sup>-1</sup> chlorine in 30 g L<sup>-1</sup> NaCl.

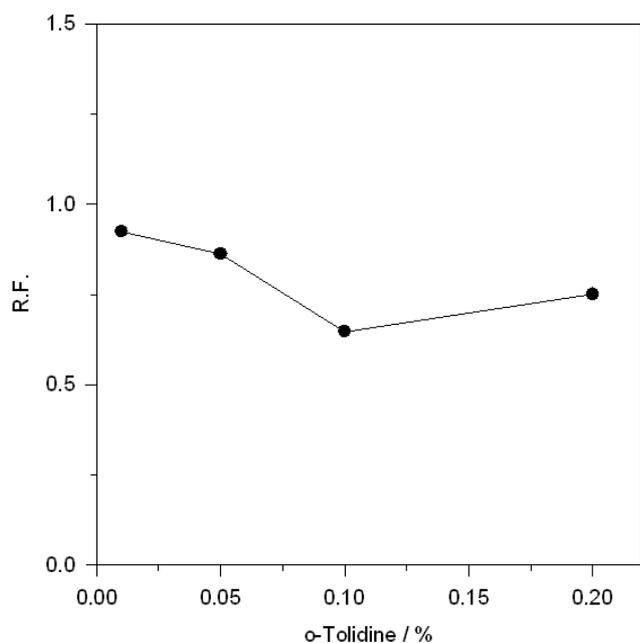
While sensitivity is not a problem within the normal chlorine concentration ranges used in the water plants using chlorination, precision is more conflictive, due to chlorine instability. For this reason, for the study of the analytical performance of the rFIA system, both the absorbance of the obtained complex and the precision of its measurement were used as the experimental variables to be maximized. Thus, a response function, *R.F.*, was calculated for each experiment as:

$$R.F.=0.8 \cdot A + 0.2 \cdot \frac{1}{RSD}$$

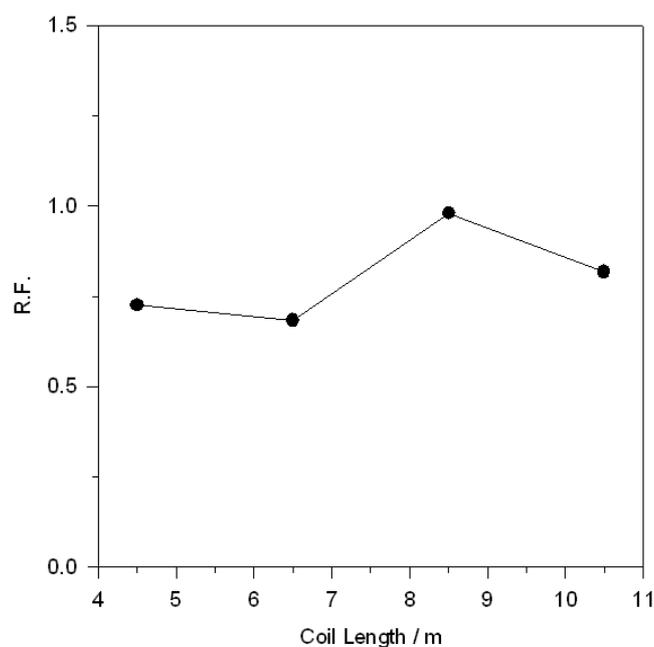
where  $A$  is the absorbance of the complex (with a weight of 80% in  $R.F.$ ) and  $RSD$  is the relative standard deviation of the measurement (with a weight of 20% in  $R.F.$ ).

Figure 2 shows the variation of  $RF$  with reagent concentration. Other conditions were: reaction coil length: 4.5 m, injection volume: 52  $\mu\text{L}$ , sample flow rate: 2.5  $\text{mL min}^{-1}$ . As optimum reagent concentration, 0.01% was selected, because it was the maximum value of response function, and permits lower reagent consumption.

The effect of reaction coil length in  $RF$  is shown in Fig. 3. Normal behavior is observed in the curve, with an initial increase caused by the better mixing of the injected reagent and flowing sample, a maximum reached at 8.5 m, and a decrease caused by the dispersion observed for longer reaction coils. Other conditions were: 0.01 % *o*-tolidine, injection volume: 52  $\mu\text{L}$ , and sample flow rate: 2.5  $\text{mL min}^{-1}$ .



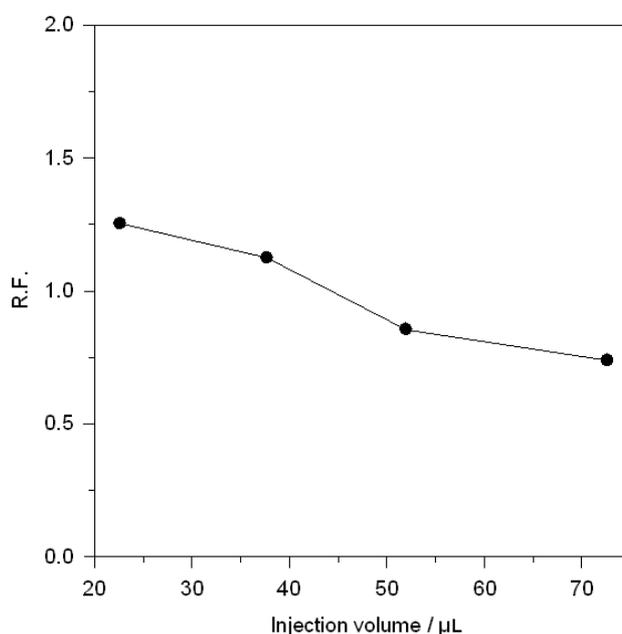
**Figure 2.** Dependence of response function,  $RF$ , on reagent concentration. Reaction coil: 4.5 m; injection volume: 52  $\mu\text{L}$ ; flow rate: 2.5  $\text{mL min}^{-1}$ .



**Figure 3.** Dependence of response function,  $RF$ , on reaction coil length. Reagent concentration: 0.01 %; injection volume: 52  $\mu\text{L}$ ; flow rate: 2.5  $\text{mL min}^{-1}$ .

Figure 4 shows the variation of  $RF$  with different reagent injection volumes. The value of  $RF$  decreased with injection volume, mainly due to the higher  $RSD$  obtained when increasing the reagent volume introduced into sample stream. The highest value of  $RF$  was

obtained for 23  $\mu\text{L}$ . Other conditions were: 0.01 % o-tolidine, reaction coil length: 8.5 m, and sample flow rate: 2.5  $\text{mL min}^{-1}$ .



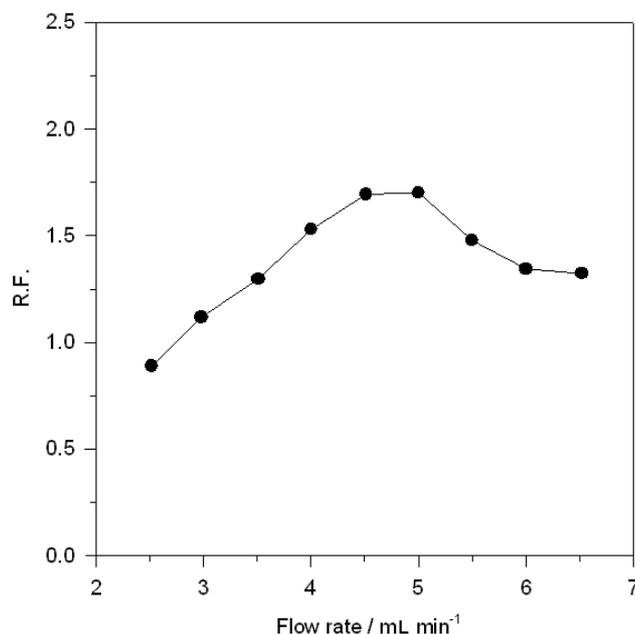
**Figure 4.** Dependence of response function, RF, on reagent injection volume. Reagent concentration: 0.01 %; reaction coil: 8.5 m; flow rate: 2.5  $\text{mL min}^{-1}$ .

The last variable studied was the sample flow rate. The results obtained are shown in Fig. 5. The initial increase was attributed to the increase in absorbance, then, a maximum is reached at 5  $\text{mL min}^{-1}$ . For higher rates, the precision of the measurements decreased, and then, RF decreased as well.

The best performance of the rFIA system used for the determination of chlorine was achieved in the following conditions: o-tolidine concentration: 0.01%, reaction coil length: 8.5 m, injection volume: 23  $\mu\text{L}$ , sample flow rate: 5  $\text{mL min}^{-1}$ . At these conditions, up to 60 samples per hour may be analyzed.

The calibration curve (0-2.0  $\text{mg L}^{-1}$ ) was constructed to determine the features of the method. The curve was linear up to 1.8  $\text{mg L}^{-1}$ , giving the equation  $y=0.654(\pm 0.064)x + 0.038(\pm 0.068)$  ( $r^2=0.995$ ). The confident intervals for slope and y-intercept were calculated as  $ts_a$  and  $ts_b$ , where  $s_a$  and  $s_b$  are the standard deviations of slope and y-intercept, respectively, and  $t$  is the Student-t ( $p=0.05$ ,  $n-2$ ). The precision of the method, estimated as RSD, was 0.93%, evaluated by analyzing eleven samples containing 1.4  $\text{mg L}^{-1}$  chlorine. The limit of

detection (LOD) of the method, calculated as  $3s_b/m$ , where  $s_b$  is again the standard deviation of the y-intercept and  $m$  is the slope of the straight line, was  $0.11 \text{ mg L}^{-1}$ .



**Figure 5.** Dependence of response function, RF, on sample flow rate. Reagent concentration: 0.01 %; reaction coil: 8.5 m; injection volume: 23  $\mu\text{L}$ .

At the same conditions, a second calibration set was prepared with non-saline solutions, to study the applicability of the new system to the determination of chlorine in non-saline samples. The calibration curve was linear between 0.1 and 1  $\text{mg L}^{-1}$ , with an equation  $y=0.702(\pm 0.042)x + 0.068(\pm 0.025)$  ( $r^2=0.996$ ), and a LOD of 0.04  $\text{mg L}^{-1}$ .

### 3.3 Validation of rFIA method

The method was validated by determination of chlorine in several samples. As the instability of chlorine prevents the use of certified samples, we analyzed both synthetic and real samples previously spiked with a known chlorine concentration. When using real samples, chlorine concentrations may vary as a consequence of reactions with the components of the sample. Thus, after 15 minutes, they were analyzed by two different batch methodologies (o-tolidine and DPD [9,10]), and the average of the two results was used as reference value. The data generated by the present method were obtained from the average of five successive injections. Table 2 shows the results obtained. Samples 1-3 were synthetic

saline water ( $30 \text{ g L}^{-1} \text{ NaCl}$ ) spiked with different chlorine amounts. Sample 4 was real seawater spiked with  $0.8 \text{ mg L}^{-1}$  chlorine. Sample 5 was tap water directed analyzed without chlorine addition.

As observed, the concentrations obtained by the proposed method were in good agreement with those used as reference. The accuracy of the results was confirmed using a t-test. Experimental values of  $t$  (see Table 2) were always less than the critical value  $t=2.78$  ( $p=0.05$ ,  $n=5$ ). Thus, the retention of the null hypothesis indicates that there were no significant differences between reference and calculated chlorine concentrations.

**Table 2.** Results of chlorine analysis.

| Sample | $\text{Cl}_2 / \text{mg L}^{-1}$ |                 |                 | $\varepsilon_r^{(a)}$ | $t_{\text{exp}}^{(b)}$ |
|--------|----------------------------------|-----------------|-----------------|-----------------------|------------------------|
|        | Added                            | Reference       | This method     |                       |                        |
| 1      | 0.4                              | $0.43 \pm 0.01$ | $0.41 \pm 0.02$ | -4.6                  | 2.24                   |
| 2      | 0.8                              | $0.82 \pm 0.06$ | $0.83 \pm 0.02$ | +1.2                  | 1.12                   |
| 3      | 1.4                              | $1.41 \pm 0.02$ | $1.43 \pm 0.02$ | +1.4                  | 2.24                   |
| 4      | 0.8                              | $0.56 \pm 0.16$ | $0.55 \pm 0.04$ | -1.8                  | 0.56                   |
| 5      | -                                | $0.35 \pm 0.03$ | $0.33 \pm 0.02$ | -5.7                  | 2.24                   |

Samples 1-3: synthetic saline samples ( $30 \text{ g L}^{-1}$ )

Sample 4: real seawater

Sample 5: tap water

<sup>(a)</sup>  $\varepsilon_r$ : relative error

<sup>(b)</sup>  $t_{\text{exp}}$ :  $t$ / experimental (critical value: 2.78)

#### 4. Conclusions

The proposed method avoids the negative effects caused by high concentrations of chloride ions in the analysis of residual chlorine, and allows for its accurate determination in saline water. The use of rFIA permits the continuous monitoring of chlorine, decreasing both the cost of the analysis and waste production.

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