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A Reaction-kinetic online determination of free chlorine using a stabilized TMB-derived chromogenic system

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Abstract

Accurate determination of free chlorine is essential for maintaining effective disinfection in drinking-water treatment and distribution systems. Conventional colorimetric methods, particularly endpoint absorbance methods such as the DPD assay, can be constrained in automated analyzers by matrix-dependent optical interference, reagent stability limitations, and relatively slow endpoint measurement cycles. Here, we report a reaction-kinetic method for online free chlorine determination based on time-resolved optical detection of chlorine-driven oxidation of a stabilized TMB-derived chromogenic reagent in a low-water solvent matrix. Instead of relying on endpoint absorbance, chlorine concentration was quantified from the initial reaction rate (dA/dt) extracted from the early absorbance-time profile. The method showed a linear response over 0.01-10 mg/L free chlorine, with a limit of detection of 0.005 mg/L and a repeatability of 2.3% RSD ($n = 6$). Comparison with a standard DPD method across 45 drinking-water and treated process-water samples showed strong agreement ($y = 0.99x + 0.02$, $R^2 = 0.996$). The reagent maintained analytical sensitivity within ±10% over 24 months under ambient storage and enabled stable operation during 30 days of continuous field deployment in a municipal drinking-water treatment facility. These results demonstrate that reaction-kinetic chromogenic detection is a practical analytical strategy for automated free chlorine determination and that stabilized TMBderived reagent chemistry can support reliable online operation under representative treated-water conditions.

Keywords

Free chlorine, online monitoring, water analysis, reaction kinetics, colorimetry, TMBderived chromogenic system, spectrophotometry

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1. Introduction

Chlorine-based disinfectants are widely used in municipal drinking water treatment to maintain microbiological safety throughout treatment and distribution. Reliable measurement of free chlorine residual is therefore important not only for process control in drinking-water treatment, but also for confirming disinfectant persistence in downstream networks and treated process-water applications.[1,4]

Among available analytical approaches, colorimetric methods remain dominant because they are sensitive, inexpensive, and readily integrated into automated analyzers. The most widely used method is based on N,N-diethyl-p-phenylenediamine (DPD), which generates a colored product that is quantified by endpoint absorbance. Although well established, endpoint measurement can be influenced by sample turbidity, apparent color, baseline drift, and reagent-aging effects, especially in instruments expected to operate continuously with limited maintenance.[2,3]

Reaction-rate methods provide an alternative quantification strategy by extracting analytical information from the rate of signal development rather than from the final absorbance value. Kinetic measurements can shorten the useful acquisition window, reduce dependence on full color development, and improve tolerance to some forms of optical and matrix variation. Despite their broad use in analytical chemistry, kinetic measurement architectures have been less systematically developed for routine online free-chlorine monitoring.[5-7]

For automated chlorine analysis, a practical kinetic method must combine three elements: a reproducible early-time optical response, a stable reagent formulation suitable for storage and field use, and an acquisition protocol that can be implemented in compact online instrumentation. These requirements are particularly relevant for distributed monitoring environments, where reagent replacement and recalibration are undesirable.[1,5,6]

In this work, we describe a reaction-kinetic analytical method for online free chlorine monitoring that combines a stabilized TMB-derived chromogenic reagent with time-resolved optical acquisition and evaluate its analytical performance and practical suitability for automated water-treatment applications. Free chlorine concentration is determined from the initial reaction rate rather than from endpoint absorbance, and analytical performance is assessed through calibration, precision, DPD comparison, interference testing, storage stability, and field deployment.

2. Experimental

2.1 Reagents and chemicals

All chemicals were of analytical grade and used as received unless otherwise stated. Unless otherwise specified, “chlorine” refers to free chlorine ($HOCl/OCl^-$) in aqueous samples. Chlorine standards were prepared from sodium hypochlorite stock solution and standardized before use.

The chromogenic reagent consisted of a stabilized TMB-derived aromatic diamine system formulated in a buffered low-water solvent matrix (nominal pH approximately 3.0). The formulation was designed to minimize background oxidation and maintain storage stability during ambient handling and long-term use. The detailed formulation is not disclosed. However, the reagent function, operating pH, measurement wavelength, acquisition protocol, kinetic signal extraction procedure, calibration approach, and analytical performance characteristics necessary for evaluation of the method are fully described.

2.2 Instrumentation and measurement setup

Time-resolved absorbance measurements were acquired using a flow-cell optical detection module with a 10 mm optical path length operating at 650 nm, corresponding to the absorption maximum of the oxidized chromogenic product. The detector was integrated into a prototype online measurement platform configured for automated reagent dosing, mixing, and short-window absorbance acquisition.

A controlled mixing and dosing module combined sample and reagent prior to optical acquisition. Data were collected at 10 Hz over a short measurement window of up to 10 s. Unless otherwise stated, each reported value represents the mean of at least three independent measurements.

2.3 Kinetic measurement procedure

A fixed volume of sample was introduced, followed by controlled injection of the chromogenic reagent. Absorbance at 650 nm was recorded continuously immediately after mixing for a short acquisition window.

The analytical signal was defined as the initial reaction rate (dA/dt) obtained by linear regression over the early linear portion of the absorbance-time trace, typically within the first few seconds after mixing. This time window was selected to maximize signal linearity while minimizing contributions from later-stage curvature and baseline drift.

2.4 Calibration and quantification

Calibration was performed using free chlorine standards spanning the concentration range relevant to drinking-water monitoring. Standards were freshly prepared from sodium hypochlorite and standardized before use. The concentration range covered 0.01-10 mg/L free chlorine.

Ordinary least-squares linear regression of dA/dt versus chlorine concentration was used to obtain the calibration function.

The limit of detection (LOD) was calculated according to:

$$\mathrm{LOD} = 3\sigma_{blank} / \mathrm{slope}$$

where σ_{blank} represents the standard deviation of ten replicate blank measurements.

2.5 Precision and agreement with the DPD reference method

Repeatability (intra-day precision) was evaluated by measuring a mid-range chlorine standard (2.0 mg/L) in six replicate measurements under identical conditions.

Intermediate precision was evaluated across three non-consecutive days using freshly prepared standards and independent reagent loading. Method agreement was assessed by comparison with a standard DPD endpoint method using 45 independent drinking-water and treated process-water samples.

2.6 Interference evaluation

Potential matrix effects commonly encountered in treated water were evaluated using representative challenge conditions including turbidity, apparent color, Fe(III), Mn(II), alkalinity, and natural organic matter (NOM). Each challenge test was compared against a chlorine-only reference under otherwise identical measurement conditions.

2.7 pH and temperature dependence

The kinetic response was measured across a pH range of 6.0-9.0 and temperatures of 15-35 °C using a fixed free chlorine concentration of 2.0 mg/L. The pH was adjusted using phosphate or borate buffer systems, and temperature was controlled using a thermostated sample compartment.

2.8 Reagent stability assessment

Reagent stability was assessed by periodically measuring the kinetic response to a fixed chlorine standard. Stability checkpoints were collected at 0, 1, 3, 6, 12, 18, and 24 months during ambient storage in sealed reagent containers protected from direct light. Analytical sensitivity at each time point was expressed relative to the initial response.

2.9 Field deployment

Field validation was conducted at a municipal drinking-water treatment facility in eastern China using a prototype online analyzer implementing the proposed kinetic method. The analyzer operated continuously for 30 days with automated measurement cycles at a 2.5-minute sampling interval. Field performance was evaluated from signal stability, operational continuity, and agreement with routine facility measurements.

3. Results and discussion

3.1 Principle of reaction-kinetic quantification

After reagent mixing, the absorbance signal increased as chromogenic oxidation proceeded. Higher free chlorine concentrations generated steeper early-time slopes. Instead of using endpoint absorbance after near-complete color development, the present method quantifies chlorine from the initial slope of the absorbance-time trace. This approach preserves the analytical information contained in the early reaction period and is well suited to short-cycle automated measurement.

3.2 Calibration performance

Calibration experiments showed a linear relationship between dA/dt and free chlorine concentration over the range of 0.01-10 mg/L with $R^2 = 0.998$. Across the eight calibration levels, relative standard deviations were below 5%, supporting good repeatability of the kinetic readout across the working range.

$dA/dt\ (\mathrm{AU\ s^{-1}}) = 0.051 \times [\mathrm{Cl}]\ (\mathrm{mg/L}) + 0.002$

The calculated limit of detection was 0.005 mg/L.

3.3 Precision and agreement with the DPD reference method

For a 2.0 mg/L chlorine standard, repeatability showed an RSD of 2.3% ($n = 6$).

Results obtained using the kinetic method were compared with those from a standard DPD endpoint method across 45 independent water samples representing drinking-water and treated process-water matrices. The two methods showed excellent agreement, with linear regression of $y = 0.99x + 0.02$ and $R^2 = 0.996$ ($n = 45$). Small residual differences observed for several samples were consistent with expected differences between endpoint and kinetic optical readout in heterogeneous matrices.

3.4 Interference tolerance

Interference studies indicated only modest signal suppression under the representative challenge conditions shown in Figure 5. Relative responses remained approximately within 89–100% of the chlorine-only reference, with the largest effect observed for apparent color, while alkalinity and NOM produced minimal response deviation. These results support the practical suitability of the kinetic method for representative treated-water conditions.

3.5 Reagent stability

The stabilized chromogenic reagent maintained analytical sensitivity within ±10% over 24 months of ambient storage, indicating resistance to background oxidation and loss of response in the low-water formulation. This level of storage stability is advantageous for online analyzers that require reduced maintenance frequency and predictable reagent replacement intervals.

3.6 Field deployment

Continuous monitoring over 30 days demonstrated stable analytical performance without routine reagent replacement or recalibration. For clarity, Figure 6 presents representative 27-day monitoring data from the full 30-day field deployment dataset. No obvious long-term signal drift was observed over the monitoring period, despite normal point-to-point fluctuations. The field study therefore supports the feasibility of applying the kinetic method in practical online chlorine-monitoring environments.

4. Conclusions

A reaction-kinetic method for online free chlorine determination was developed using a stabilized TMB-derived chromogenic reagent and time-resolved optical acquisition. Quantification based on the initial reaction rate provided a linear response over 0.01–10 mg/L, a detection limit of 0.005 mg/L, and good repeatability, while also showing excellent agreement with a conventional DPD method.

The method also showed useful tolerance to representative water-matrix interferences, retained analytical sensitivity over 24 months of ambient storage, and supported stable operation during 30 days of continuous field deployment. These results demonstrate that stabilized TMB-derived chromogenic chemistry can provide a practical reagent platform for automated online free chlorine determination in treated-water systems.

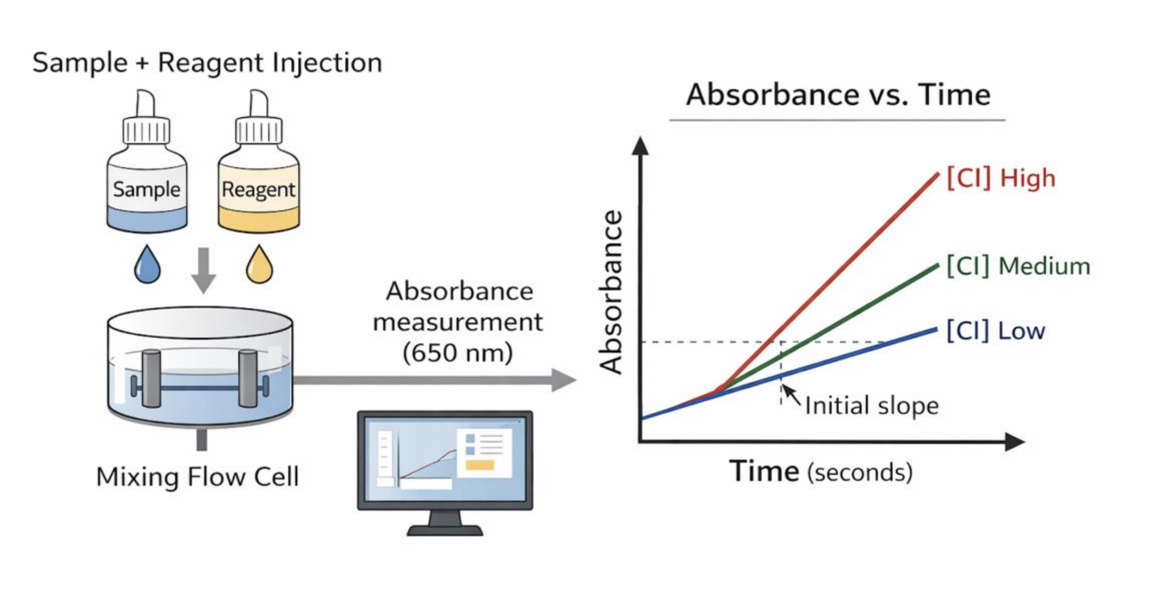
Conflicts of interest

Hao Zhang is the founder of Onestep Technologies Inc., the company that developed and holds a commercial interest in the reagent system evaluated in this study.

Author contributions

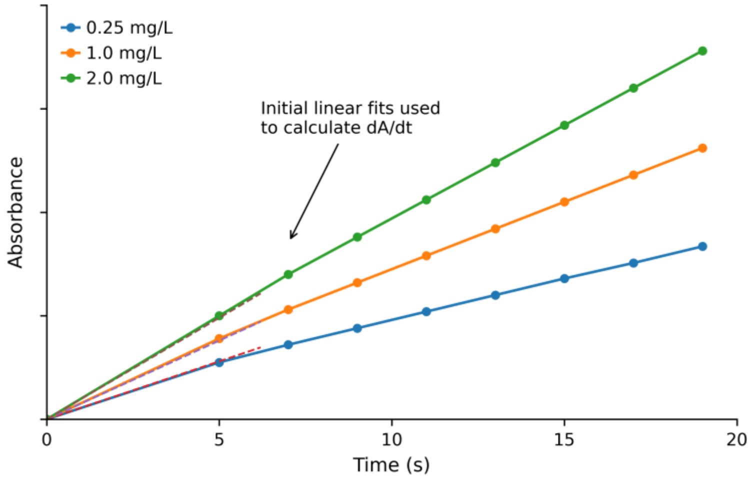
Hao Zhang: Conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing – original draft.

Figures



Chlorine concentration was quantified from the initial reaction rate (*dA/dt*).

Figure 1. Schematic illustration of the reaction-kinetic method for online free chlorine monitoring. Chlorine concentration is quantified from the initial reaction rate (dA/dt) derived from the absorbance-time profile after reagent mixing.



Higher chlorine concentrations produce steeper initial slopes (dA/dt).

Figure 2. Representative absorbance-time kinetic curves obtained for increasing free chlorine concentrations. The analytical signal is defined as the initial reaction rate (dA/dt) extracted from the early linear region of the curves.

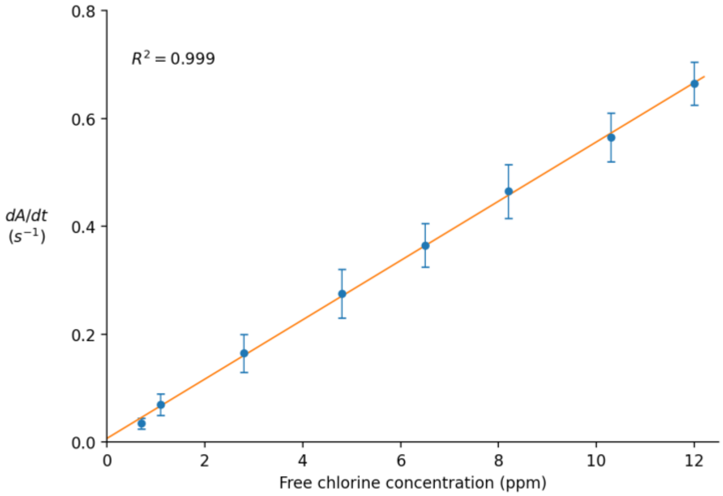


Figure 3. Calibration curve for free chlorine determination using the reaction-kinetic chromogenic method (dA/dt as the response). Error bars represent standard deviation (n = 3).

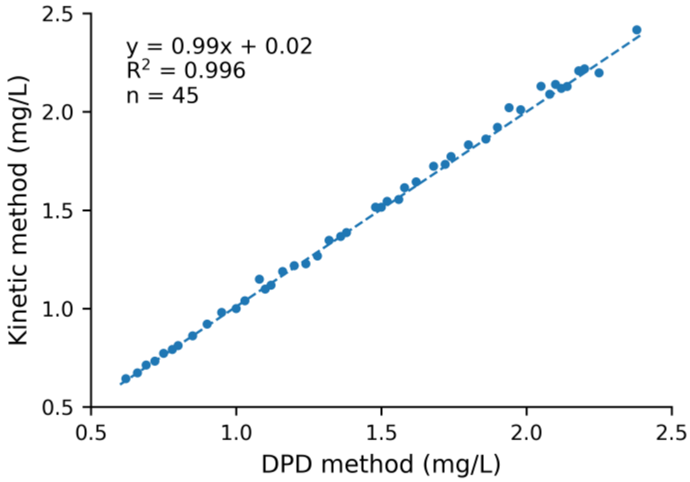


Figure 4. Correlation between free chlorine concentrations determined using the proposed kinetic method and the conventional DPD colorimetric method across 45 water samples.

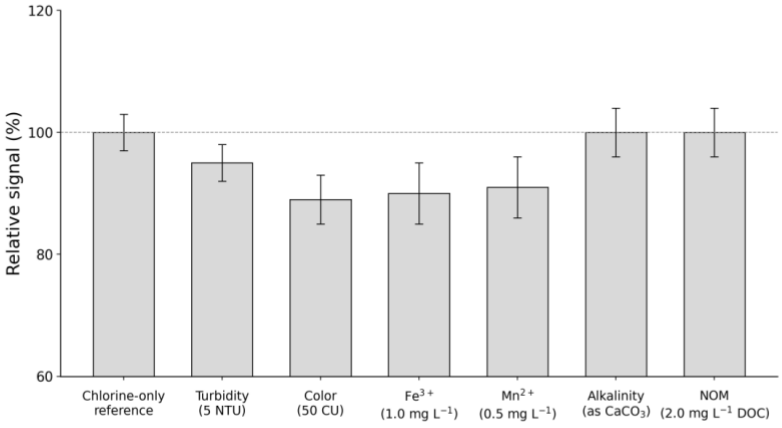


Figure 5. Interference evaluation for representative water matrix components under fixed challenge conditions. Relative signal (dA/dt) is expressed as a percentage of the chlorine-only reference response (2.0 mg/L free chlorine). Error bars represent standard deviation (n = 3). The dashed line indicates the chlorine-only reference response (100%).

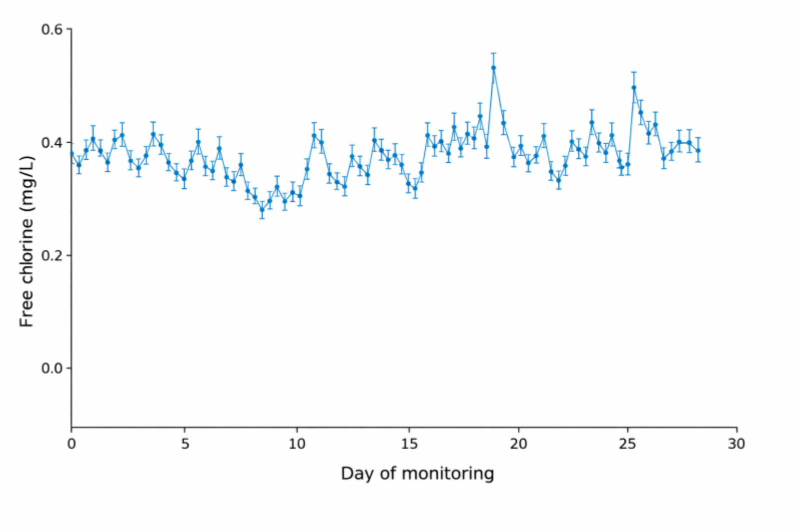


Figure 6. Representative 27-day free-chlorine monitoring data from the full 30-day field deployment in a municipal drinking-water treatment facility.

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