

Beyond DPD

A Reaction-Kinetics Architecture for Next-Generation Online Chlorine Monitoring

TECHNICAL WHITE PAPER

Introducing a kinetics-based detection paradigm
for automated chlorine monitoring enabled by
stabilized TMB chromogenic reagent platforms

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Executive Summary

Online chlorine monitoring is a critical requirement for drinking water safety, wastewater treatment, and industrial process control. For decades, most automated analyzers have relied on endpoint colorimetric chemistry derived from the N,N-diethyl-p-phenylenediamine (DPD) reaction.

While this approach has been widely adopted and standardized, endpoint measurement architectures present operational challenges in modern automated monitoring environments. These challenges include reagent instability, optical interference caused by turbidity and background coloration, and relatively slow measurement cycles.

Recent advances in reaction-kinetics detection offer an alternative analytical architecture. Rather than determining analyte concentration from the final optical absorbance of a chromogenic reaction, kinetics-based detection extracts concentration information from the early-stage reaction rate.

This white paper introduces a reaction-kinetics detection paradigm for chlorine monitoring and discusses how this architecture can enable faster measurement cycles, improved robustness in complex water matrices, and reduced maintenance requirements in automated monitoring systems.

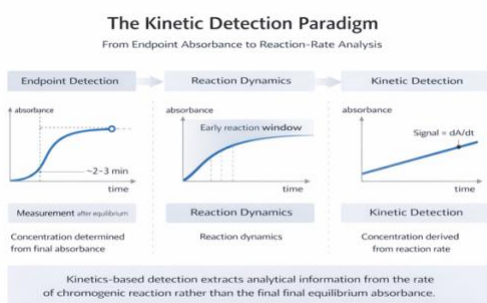


Figure 1 | Conceptual framework of kinetic chlorine detection

Conventional colorimetric assays determine chlorine concentration from the **equilibrium absorbance** measured after completion of the chromogenic reaction (left).

In the kinetic detection paradigm, analytical information is instead extracted from the **time-dependent reaction dynamics** within an early reaction window (middle).

The **initial rate of absorbance change (dA/dt)** provides the analytical signal (right), allowing chlorine concentration to be determined directly from reaction kinetics rather than from the final equilibrium state.

Key Advantages of Kinetics-Based Detection

- **Faster measurement cycles**

Early-stage slope analysis enables rapid chlorine detection without waiting for full reaction equilibrium.

- **Improved resistance to optical interference**

Rate-based signal extraction reduces sensitivity to turbidity and background color.

- **Reduced maintenance requirements**

Stabilized chromogenic reagent platforms allow extended operational lifetimes in automated analyzers.

Implications for Online Monitoring

Reaction-kinetics detection provides a promising analytical architecture for next-generation chlorine monitoring systems, particularly in applications requiring high reliability, minimal maintenance, and rapid response to changing process conditions.

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1 Introduction

Chlorine residual monitoring is a fundamental component of safe water treatment and distribution. Maintaining an appropriate chlorine concentration ensures effective microbial control while minimizing the formation of harmful disinfection by-products.

In municipal drinking water systems, continuous monitoring of disinfectant residuals is required to maintain regulatory compliance and ensure consistent water quality throughout distribution networks. Industrial processes such as cooling water treatment, wastewater disinfection, and process water management also rely on reliable chlorine monitoring.

Historically, chlorine concentration has been measured using manual grab sampling combined with laboratory analysis. As water infrastructure becomes increasingly automated, however, online analyzers capable of continuous monitoring have become essential tools for process control and regulatory compliance.

Most currently deployed online chlorine analyzers rely on automated implementations of the classical DPD colorimetric method. These instruments determine chlorine concentration by measuring the final optical absorbance generated during a chromogenic reaction.

Although endpoint colorimetric chemistry has served the water industry for decades, its implementation in automated monitoring systems presents several operational challenges, particularly in environments where water quality conditions fluctuate.

2 Endpoint Colorimetry in Online Chlorine Monitoring

Endpoint colorimetric methods determine analyte concentration by measuring the optical intensity of a chromogenic reaction after the reaction has reached equilibrium.

In the widely used DPD method, chlorine reacts with a chromogenic reagent to produce a colored compound whose absorbance can be measured spectrophotometrically. According to the Beer–Lambert relationship, the measured absorbance is proportional to analyte concentration.

Because of its simplicity and long history of regulatory acceptance, DPD colorimetry has become the dominant analytical method for chlorine monitoring in water treatment.

Automated analyzers typically replicate this chemistry by mixing a water sample with reagent, allowing the reaction to proceed for a defined reaction period, and measuring the final absorbance in an optical flow cell.

Typical online DPD analyzers complete one analytical cycle approximately every 2–4 minutes, which places an inherent limit on monitoring frequency and process responsiveness.

While effective under controlled conditions, endpoint detection introduces several operational constraints when implemented in automated monitoring systems.

3 Operational Limitations of Endpoint Detection

Reagent Stability

Traditional DPD reagents are typically formulated as aqueous solutions. These formulations are susceptible to hydrolysis, oxidation, and microbial degradation during storage and use.

As a result, many online analyzers require frequent reagent replacement and regular maintenance. In distributed monitoring systems or remote installations, these maintenance requirements can become a significant operational burden.

Optical Interference

Endpoint absorbance measurements rely on absolute optical intensity. Variations in turbidity, suspended solids, or inherent water coloration can influence measured absorbance signals.

In complex water matrices, background optical interference may reduce measurement accuracy and require additional calibration procedures.

Measurement Cycle Time

Endpoint reactions require sufficient time for full color development before the measurement can be completed. As a result, many online analyzers operate on measurement cycles of approximately 2.5 minutes per sample.

In systems where chlorine concentration fluctuates rapidly, this delay may limit the responsiveness of automated dosing control systems.

These operational constraints have motivated the exploration of alternative analytical architectures better suited for continuous and automated monitoring systems.

4 The Kinetic Detection Paradigm

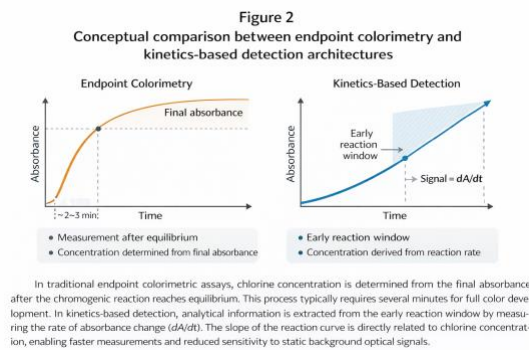


Figure 2. Conceptual comparison between endpoint colorimetry and kinetics-based detection architectures.

An alternative approach to endpoint measurement is the use of reaction kinetics to determine analyte concentration.

In chromogenic oxidation reactions used for chlorine detection, the initial rate of color formation during the early phase of the reaction is typically proportional to analyte concentration under pseudo-first-order reaction conditions.

Rather than waiting for the reaction to reach equilibrium, a kinetics-based analyzer records the time-dependent optical signal immediately after the reaction begins.

Chlorine concentration can then be determined from the slope of the absorbance curve (dA/dt) within an early reaction window.

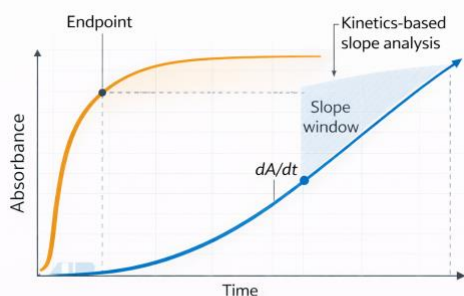


Figure 3 Reaction curve comparison illustrating endpoint detection

Figure 3. Reaction curve comparison illustrating endpoint detection versus kinetics-based slope analysis.

This approach represents a conceptual shift in analytical detection.

Endpoint detection determines concentration from the final absorbance value of the reaction.

Kinetic detection determines concentration from the reaction rate during the early phase of the reaction.

Because the analytical signal is derived from the rate of change rather than absolute optical intensity, static background signals such as turbidity or inherent water color exert significantly less influence on the measurement.

Kinetics-based detection therefore offers the potential for improved measurement robustness while enabling faster analytical cycles.

5 Stabilized Chromogenic Reagent Platforms

For kinetics-based detection to operate reliably in automated monitoring systems, the chromogenic reagent system must maintain consistent reactivity over extended operating periods.

Traditional chromogenic reagents used for chlorine detection, including classical DPD formulations, are typically prepared as aqueous solutions. While suitable for manual or short-term analytical applications, such formulations can exhibit limited long-term stability due to degradation pathways including hydrolysis, oxidation, and microbial activity.

Recent developments in reagent chemistry have introduced solvent-stabilized chromogenic reagent platforms designed specifically for automated analytical systems.

In these systems, aromatic diamine chromogens such as tetramethylbenzidine (TMB) are formulated within controlled solvent environments that significantly suppress degradation mechanisms.

By limiting exposure to hydrolysis and oxidative pathways, these stabilized reagent architectures maintain consistent chromogenic reactivity over extended storage and operating periods. Under appropriate storage conditions, stabilized reagent formulations can maintain analytical performance for up to 24 months, representing a substantial improvement over conventional aqueous reagent systems.

The improved stability of these reagent systems provides several advantages for automated chlorine monitoring:

- extended reagent shelf life
- reduced reagent replacement frequency
- improved measurement reproducibility
- simplified analyzer maintenance

Beyond operational convenience, reagent stability is also a critical enabling factor for kinetics-based analytical architectures. Because kinetic detection relies on accurate measurement of reaction rate rather than final equilibrium absorbance, the consistency of chromogenic reactivity becomes essential for reliable slope-based analysis.

Stabilized chromogenic reagent platforms therefore serve as a key enabling component in the implementation of next-generation kinetics-based chlorine monitoring technologies. Certain aspects of the stabilized chromogenic reagent technologies described in this paper are protected by issued patents and pending patent applications.

6 Experimental Performance

The kinetics-based detection concept has been evaluated through both laboratory testing and field deployments.

Analytical Range

The dynamic slope-detection approach demonstrates a linear response to chlorine concentrations across a wide range, approximately 0.01–10 ppm, covering the typical operating range required for drinking water and industrial applications.

Interference Tolerance

Testing under challenging matrix conditions shows minimal analytical deviation in the presence of elevated turbidity as well as common oxidizing metal ions such as iron and manganese.

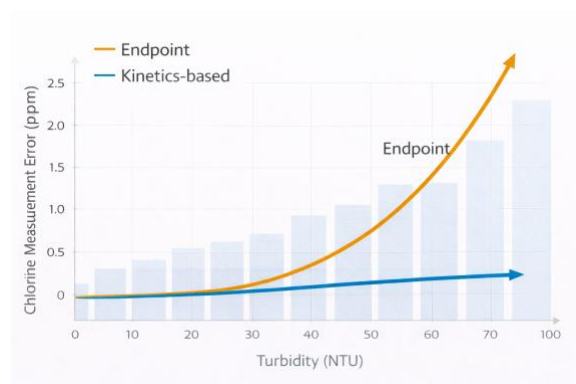


Figure 4. Comparison of measurement robustness under increasing turbidity conditions for endpoint and kinetics-based detection.

Field Deployment

Field operation in a municipal water treatment facility demonstrated stable analyzer performance over a continuous 30-day monitoring period without reagent replacement.

These results indicate that kinetics-based detection architectures can perform reliably under real-world water monitoring conditions.

7 Implications for Online Monitoring Systems

The adoption of kinetics-based detection architectures offers several potential advantages for water utilities and instrument manufacturers.

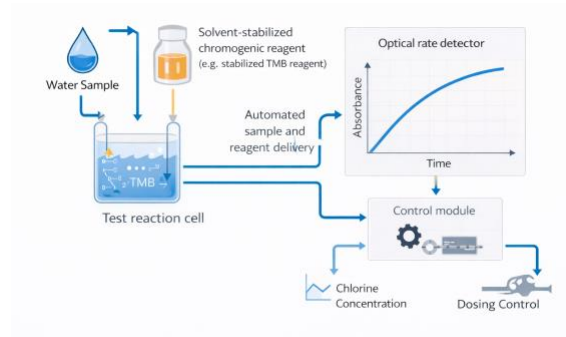


Figure 5. Conceptual architecture of a kinetics-based chlorine monitoring

Figure 5. Conceptual architecture of a kinetics-based chlorine monitoring system.

Faster Monitoring Cycles

Rapid kinetic measurements enable higher sampling frequency, allowing monitoring systems to respond more quickly to fluctuations in chlorine concentration.

Reduced Maintenance Requirements

Improved reagent stability may significantly extend service intervals and reduce the operational burden associated with reagent replacement and calibration.

Improved Measurement Robustness

Reduced sensitivity to turbidity and background coloration improves analytical reliability in complex water matrices.

Support for Distributed Monitoring

The simplified analytical architecture supports the development of compact analyzer designs suitable for distributed monitoring networks and remote installations.

8 Future Directions for Water Monitoring

As water infrastructure evolves toward automated and distributed monitoring systems, analytical technologies must adapt to new operational requirements.

Future monitoring platforms are expected to provide:

- higher sampling frequency
- reduced maintenance requirements

- improved robustness in complex environments
- integration with digital monitoring systems

Kinetics-based detection architectures represent a promising pathway toward achieving these goals.

By combining reaction-kinetics detection with stabilized chromogenic reagent platforms, next-generation analyzers may offer improved reliability and operational efficiency for water utilities and industrial users.

Conclusion

Endpoint colorimetric chemistry has served as the foundation of chlorine monitoring for many decades. However, the increasing demand for automated monitoring systems is encouraging the exploration of alternative analytical approaches.

Reaction-kinetics detection represents a conceptual shift in analytical measurement by deriving analyte concentration from reaction rate rather than equilibrium absorbance.

When combined with stabilized chromogenic reagent platforms designed for automated analyzers, this architecture offers improved robustness, faster analysis cycles, and reduced maintenance requirements.

As water monitoring infrastructure continues to evolve toward distributed and automated sensing networks, analytical architectures capable of rapid, robust, and low-maintenance operation will become increasingly important. The integration of reaction-kinetics detection with solvent-stabilized chromogenic reagents may therefore represent a new analytical framework for next-generation chlorine monitoring systems.

The concepts described in this paper are intended to stimulate further exploration of kinetics-based analytical architectures for automated water monitoring systems.