



TECHNICAL GUIDANCE NOTE HS 11-25

CALIBRATING TOTAL CHLORINE & MONOCHLORAMINE MONITORS USING DPD BASED HANDHELD SPECTROPHOTOMETERS

1 Executive summary

Online monitoring of total chlorine or monochloramine relies fundamentally on the handheld DPD3 test for calibration, yet this widely accepted standard is fraught with inconsistencies.

- Online total chlorine monitors, sensors, analysers of all types only measure free chlorine and monochloramine.
- The result of a DPD3 test is dependent on the time the test is left to run before the colour is measured

While all online monitors provide real-time data for operational control, they respond much faster than DPD3, leading to a possible systematic calibration mismatch, where the online sensor appears "low" if the DPD3 test is allowed to develop color beyond the standard 60-second window. This discrepancy is not typically an indicator of monitors failure but a difference in chemical kinetics and species sensitivity.

Successful, reproducible calibration requires operators to adopt a strict e.g. 60-second timing protocol for total chlorine and to and recognise that perfect agreement between fast response online monitors and the slower DPD3 method is neither expected nor chemically possible.

In sort, a calibration error can be "baked in" because the DPD3 measures things that the monitors do not.

2 Introduction

This guidance is intended to help all operators understand:

- Why numbers may differ
- How to use each method responsibly
- How to calibrate correctly
- How to set realistic expectations for online sensors

Chlorine measurement remains central to water safety, treatment optimisation, and regulatory compliance. Across drinking water, industrial process water, and wastewater, operators rely on a wide variety of online total chlorine and monochloramine analysers. These include:

- Colorimetric DPD analysers
- KI/buffer-based iodometric systems
- Membrane amperometric sensors



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- Open-electrode amperometric systems
- Multi-parameter platforms that separate free chlorine and monochloramine

Although these technologies differ widely, **they all depend on handheld DPD3 tests for calibration and verification.**

This guidance note, written from an independent and technical standpoint, explains:

- How DPD3 chemistry works
- The limitations of DPD3 when used as a calibration reference
- How those limitations affect each analyser type
- Why timing differences between handheld DPD3 and online sensors matter
- How to calibrate responsibly and consistently
- Common pitfalls and how to avoid them

The goal is to provide water professionals with clear advice, enabling informed calibration practices and realistic expectations of analyser performance.

3 Understanding DPD Chemistry

3.1 Free chlorine DPD-1

DPD-1 measures:

- Hypochlorous acid (HOCl)
- Hypochlorite ion (OCl⁻)

DPD-1 reacts rapidly, producing a stable pink colour within 30–60 seconds.

3.2 Total chlorine DPD-3

DPD-3 contains **potassium iodide (KI)**. Combined chlorine species oxidise iodide to iodine, which then oxidises DPD:

Combined chlorine + I⁻ → I₂ → DPD dye

Total chlorine = free chlorine + combined chlorine

3.3 Monochloramine (sometimes called combined chlorine)

Not measured directly. Calculated as:

Monochloramine = total chlorine – free chlorine

3.4 The “operational” nature of DPD

DPD3 does **not** measure all chlorine-containing species equally. It measures **DPD-reactive chlorine**, not absolute “true total chlorine.” The results of DPD3 are dependent on how long the chemistry is left to react before the colour change is measured. There will usually be some slow reacting chlorine species that are not measured.

This distinction underpins every section of this document.



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4 Limitations of DPD3 as a Calibration Reference for total chlorine monitors

DPD3 is widely used because it is simple, well-understood, and globally standardised. However, it has intrinsic limitations that operators and regulators must recognise.

4.1 Slow-reacting combined chlorine species

DPD3 accurately measures:

- Monochloramine
- Dichloramine

However, it **reacts only partially or very slowly** with:

- Organic chloramines
- Amino-acid chloramines
- Peptide/protein-bound chloramines
- Natural Organic Matter (NOM)-bound chlorine
- Some secondary/tertiary amine chloramines

These species can take **minutes** to oxidise iodide and each species will have a different reaction time

4.2 Timing sensitivity

DPD3 total chlorine colour **continues to develop** after the first minute.

- Standard Methods assume an 1-minute reading.
- Some handheld instruments recommend **6-8 minutes**, especially in cold water. Some instruments come with look up tables that give reaction times based on water temperature.

4.3 Subtraction error if used to calculate monochloramine

Monochloramine = Total - Free

Errors in both components accumulate.

4.4 DPD does not measure “true” total chlorine

DPD3 “misses” a proportion of slow, weak, or large organic chloramines. Even a long delay DPD3 total chlorine test will be **lower than true total chlorine load**, especially in waters with:

- High NOM
- Wastewater influence
- High organic nitrogen
- Industrial contamination



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5 Why Online Total Chlorine Instruments and Handheld DPD3 might “Disagree”

Disagreement between online total chlorine instruments and DPD3 does not necessarily indicate analyser drift. It is often due to time-response mismatch, species sensitivity differences, or DPD3 timing inconsistencies.

5.1 Online monitor timing

Online systems do not “wait” 6–8 minutes.

Their typical reaction windows/response times are:

- DPD colorimeters: 45–90 seconds
- KI/buffer iodometric: 30–60 seconds (fast iodide oxidation)
- Membrane amperometric: instantaneous (milliseconds, seconds)
- Open-electrode amperometric: instantaneous (milliseconds, seconds)

These instruments measure their target species **in real time**. If handheld DPD3 is allowed to develop colour for several minutes, it will detect **more slow-reacting organic chloramines** than the online analyser ever can. This causes a **systematic calibration mismatch: DPD3 increases over minutes, online analysers do not**. This is the most common source of calibration “disagreement.”

6 Technology-by-Technology Discussion

6.1 Online Colorimetric DPD3 Analysers

- Mechanism identical to handheld DPD3.
- Best match when handheld DPD uses **1-minute total chlorine timing**.
- Cannot replicate 6–8 minute readings.

If handheld timing is long, the handheld will read higher and the analyser appears low.

6.2 KI + Buffer Iodometric Analysers

Includes systems using:

- pH 4 buffer + KI
- Air-stripping iodine detection
- Flow-cell iodometry

Strengths:

- Fast iodide oxidation
- Very good for monochloramine
- Reasonable overall agreement with DPD

Limitations:

- Still under-respond to slow organic chloramines



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- Cannot match long-wait DPD3

Calibration must be tied to **1-minute DPD3 total chlorine**.

6.3 Membrane Amperometric Total Chlorine Sensors

These measure:

- HOCl
- NH_2Cl
- Limited response to NHCl_2
- Minimal response to organic chloramines

Strengths:

- Very stable
- Fast
- Low maintenance

Limitations:

- Largest mismatch vs long-wait DPD
- Designed for operational disinfectant control, not full speciation

Never calibrate to DPD measured after >90 seconds.

6.4 Open-Electrode Amperometric Sensors (Free & Mono Channels)

Examples include advanced multiparameter platforms.

Strengths:

- Direct measurement of HOCl or NH_2Cl
- Very fast response
- No reagents or membranes

Limitations:

- Completely blind to organic chloramines
- Will always appear “low” vs long-wait DPD

Calibrate only against **DPD3 values taken at strict timing intervals**.

7 Summary Table — How Calibration Errors Occur

Factor	Effect on DPD	Effect on Online Analyser	Result
Long DPD wait time (3–8 min)	Increases value	No change	Online appears low

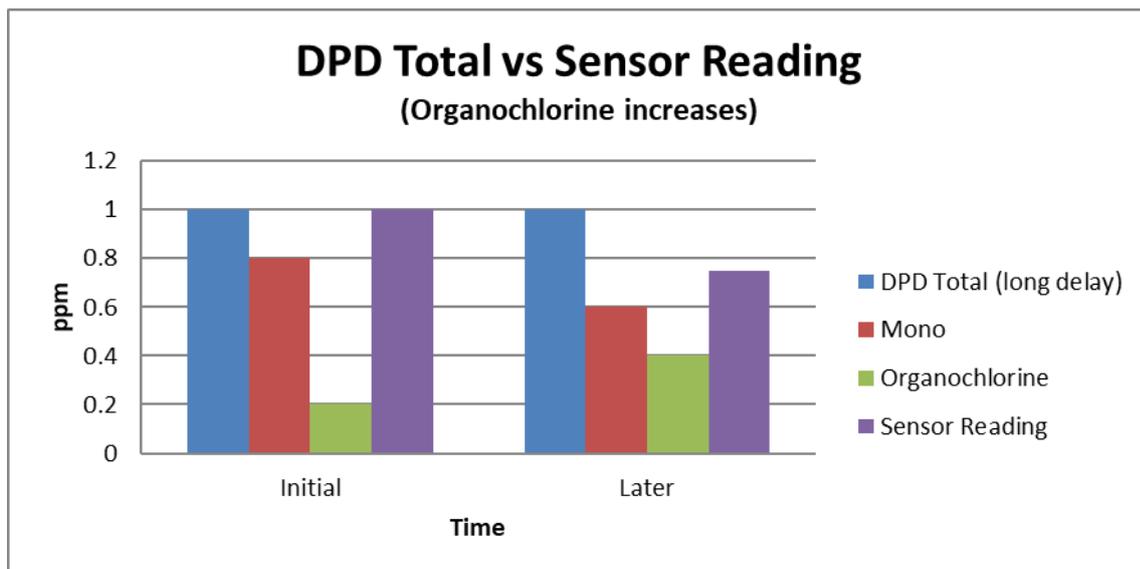


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Cold water	Slower reaction, tendency to over-wait	No change	Calibration mismatch
High NOM / organic chloramines	Partial detection only	Minimal detection	Both low vs true combined chlorine, but mismatch varies
Dichloramine present	Raises DPD-free slightly	Membrane sensor often blind	Sensor appears low
Subtraction method for monochloramine	Amplifies error especially when free is low	Mono sensor stable	DPD-monochloramine drifts while sensor stays steady

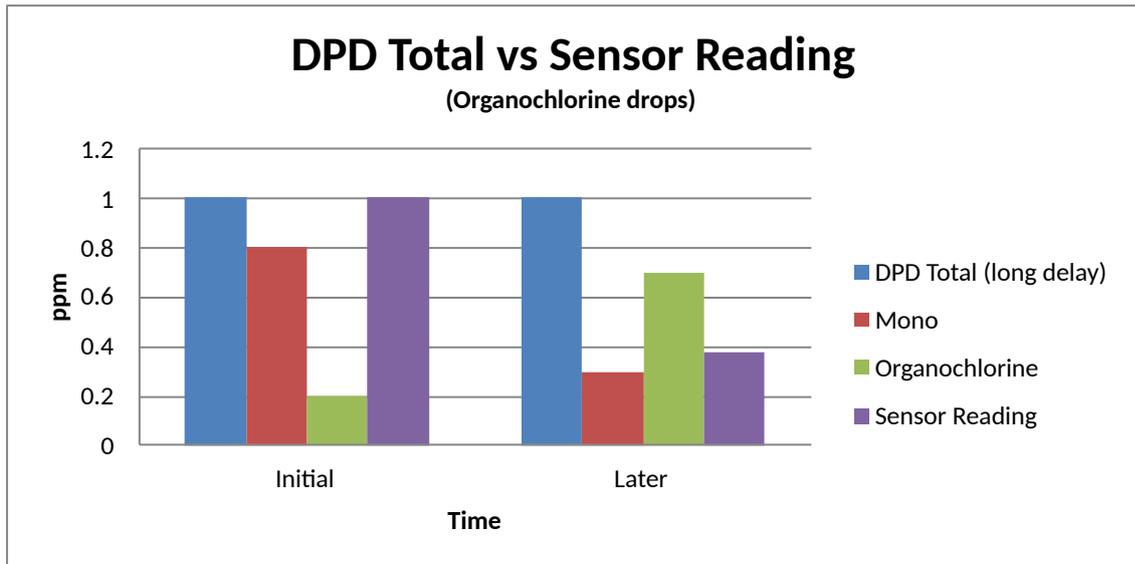
8 Graphical example

Consider a total chlorine monitor calibrated to 1ppm using long delay DPD3. Mono is 0.8 and organochlorine is 0.2ppm. At the next validation the DPD3 still shows 1.0ppm BUT critically the ratio of mono to organochlorine has changed. Mono has dropped to 0.6ppm and organochlorine has risen to 0.4ppm. The monitor will now read low as the thing it measures has decreased although the total measured by DPD3 has stayed the same.



If the ratio changes further, for example longer into a distribution system with a bigger water age the apparent errors are more pronounced.

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Time	DPD Total (long delay)	Mono	Organochlorine	Sensor Reading
Initial	1	0.8	0.2	1
Later	1	0.3	0.7	0.375

9 Practical Field SOP for Calibration

(Applies to all manufacturers & monitor/analyser types)

9.1 Step 1 — Sampling

- Sample directly from monitor/analyser outlet.
- Flush sample line for 30–60 seconds.

9.2 Step 2 — Free Chlorine (DPD-1)

- Add DPD-1.
- Read strictly at 30–60 seconds.
- Record value.

9.3 Step 3 — Total Chlorine (DPD-3)

- Add DPD-3 immediately after free chlorine reading.
- Read strictly at 60 seconds.
- Never use >90 seconds timing for calibration.
- Record value.

9.4 Step 4 — Monochloramine Calculation

Mono = Total - Free

- Record value.

9.5 Step 5 — Apply to monitor/analyser

Ensure monitor/analyser mode matches species (free, mono, total).

Enter values carefully.

Complete zero or slope adjustments as per manufacturer instructions.



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9.6 Step 6 — Verify

Take a second sample 5 minutes later.

If results differ by >0.05–0.1 mg/l, investigate sampling/chemistry issues.

9.7 Step 7 — Record conditions

- Temperature
- pH
- Residual levels
- Any unusual plant operations (booster, mixing, changeover)

10 Is new terminology needed?

All total chlorine monitors only measure free + mono. DPD3 measures different things depending on how long the test is left to run. One way to improve would be to adopt different terminology:

- Long delay DPD3 is called "DPD3 total" chlorine. Free+ Mono + "most" organochlorine
- Total chlorine as measured by all analysers is called "active total". Free + mono
- Use long delay DPD3 for investigative purposes only. The difference between 60 second DPD3 and 3-8 minutes DPD3 is an indicator of the amount of organochlorine species. It would be good practice to record the values after 1 minute and 3-8 minutes.
- Use e.g. 60 second DPD3 for regulatory purposes and for calibrating ALL total chlorine monitors

11 Final Message from “Doctor Chlorine”

- DPD3 total chlorine is a valuable and widely accepted method, but it is not perfect. It measures only DPD3-reactive chlorine and the results have a time dependence.
- Online analysers respond faster and only detect free and mono, perfect agreement is neither expected nor chemically possible.
- Consistent timing, consistent documented methods and procedures, and informed interpretation are the keys to successful calibration.
- Used correctly, DPD3 remains a powerful tool provided everyone understands its strengths and its limitations.

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