Technical Guidance Note

TOTAL CHLORINE MEASUREMENT AND CALIBRATION OF TOTAL CHLORINE ANALYSERS IN FREE-CHLORINATED AND CHLORAMINATED DISTRIBUTION SYSTEMS

1 Executive summary

Accurate measurement of total chlorine is fundamental to regulatory compliance, process control, and public health protection in drinking-water distribution systems. However, “total chlorine” is not a single chemical entity; rather, it is a parameter that has several meanings depending on context.

Online total chlorine analysers and sensors do not measure the same species that e.g. DPD3 based total chlorine hand-held spectrophotometers measure.

“Total chlorine” is a mix of inorganic and organic chlorine species whose composition depends strongly on the disinfectant strategy and water quality.

This guidance note provides an in-depth analysis of total chlorine measurement under both free-chlorinated and chloraminated conditions.

The document reviews the underlying disinfectant chemistry, with particular emphasis on the differences in inorganic and organic chlorine species between free-chlorine and chloramine regimes. It explains how the main analytical methods, manual DPD (free and total), monochloramine-specific indophenol, online DPD based colorimetric analysers, membrane amperometric/polarographic sensors and KI-buffered amperometric sensors, respond to these species.

The behaviour of DPD3 total-chlorine measurements at short (e.g. 60 s) and extended reaction times is examined in detail for each system type.

On this basis, the note proposes a set of best-practice calibration strategies tailored to each analyser type and disinfection regime.

Key conclusions are that:

1. Online analysers and DPD3 tests measure different species on different time scales.
2. Total-chlorine monitors of all types tend to exhibit smaller calibration errors and better internal consistency in chloraminated systems than in free-chlorinated systems; and

3. Timing is critical, all online analysers measure free chlorine and monochloramine quickly. DPD3 colour should not be left to develop long enough to react to less reactive species if it is to be used for calibrating total chlorine monitors.
4. The indophenol method provides a robust and chemically specific reference for calibrating monochloramine analysers in chloraminated networks.
5. The guidance emphasises the need for strictly timed DPD3 measurements and discourages the use of long-delay DPD3 readings for calibration purposes.

2 Introduction

Residual chlorine measurement underpins both regulatory compliance and process control in drinking-water distribution systems. A residual that is too low may compromise microbiological safety, while a residual that is too high increases taste, odour, corrosion, and disinfection by-product risks. For these reasons, water utilities rely heavily on total chlorine measurements, both as grab-sample tests and via online analysers.

Yet “total chlorine” is a deceptively simple phrase. Depending on the disinfectant strategy, water quality, and contact time, the measured “total chlorine” may consist of:

- Free chlorine ($HOCl/OCl^-$)
- Inorganic chloramines (NH_2Cl, $NHCl_2$, NCl_3)
- Organic chloramines and other N-chlorinated organics
- A variety of carbon-bound organochlorine by-products and intermediate oxidants.

Analytical methods differ in which of these species they detect, how quickly they respond, and how susceptible they are to interferences. Calibration of online instruments is therefore fundamentally a chemical problem.

This guidance note has four main objectives:

2.1 To describe the inorganic and organic chlorine species that dominate

- Free-chlorinated
- Chloraminated distribution systems.

2.2 To explain how total-chlorine measurement techniques work, including:

- DPD1 and DPD3 (manual and online),
- Membrane amperometric/polarographic free and total chlorine sensors,
- KI-buffered amperometric sensors, and
- Manual monochloramine-specific indophenol methods.

2.3 To clarify what DPD3 total chlorine measures

- On a defined 60-second time scale
- Versus when samples are left standing for extended periods.

2.4 To provide best-practice calibration guidance for each analyser type

- In free-chlorinated
- And chloraminated systems.

The intended audience includes water utility engineers, process scientists, instrument specialists, and regulators.

3 Disinfectant Chemistry in Distribution Systems

3.1 Free Chlorinated Systems

In free-chlorinated systems the residual is maintained predominantly as hypochlorous acid ($HOCl$) and its conjugate base hypochlorite (OCl^-):

The $HOCl/OCl^-$ ratio is pH-dependent, with $HOCl$ dominating under typical drinking-water conditions (pH ~7–7.5). $HOCl$ is a strong electrophilic chlorinating agent that reacts rapidly with a broad range of organic moieties, including:

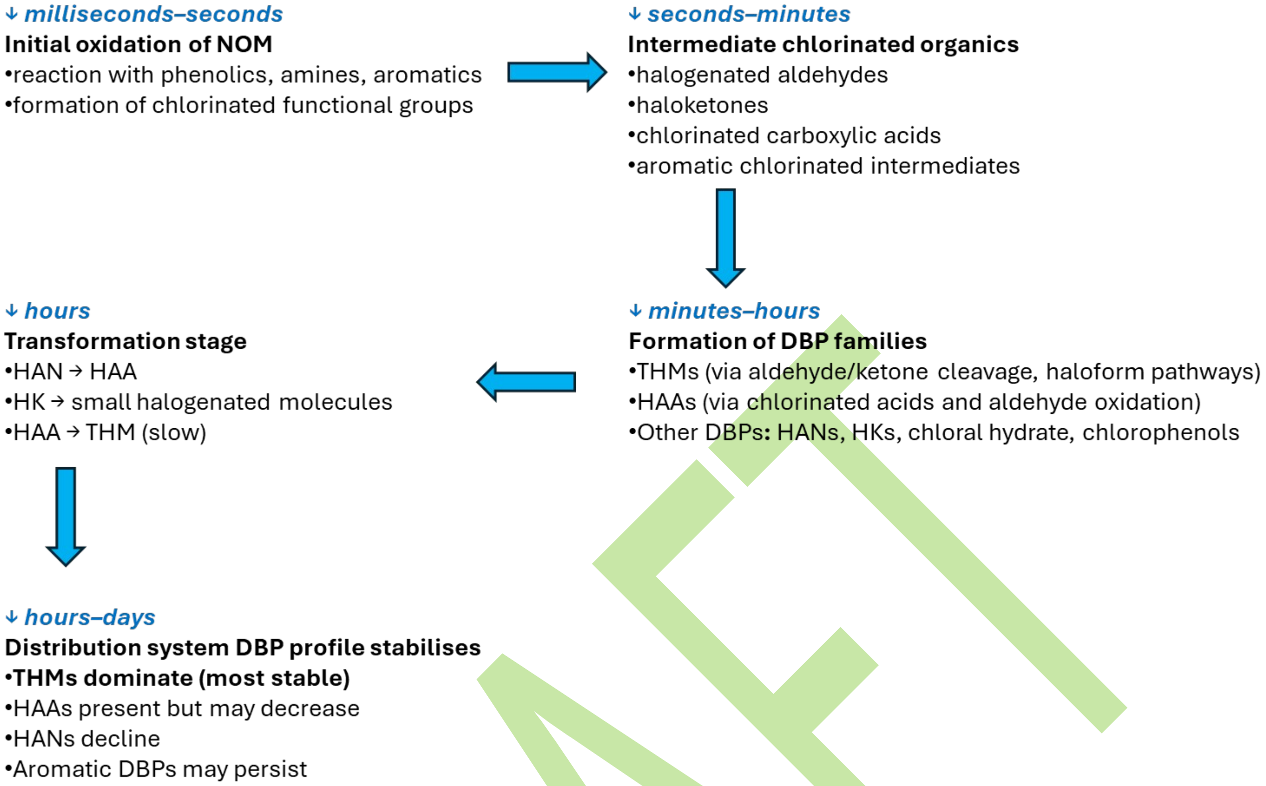
- Activated aromatic rings (e.g. phenolic groups),
- Amino groups (e.g. amino acids, peptides),
- Unsaturated carbon–carbon bonds,
- Humic and fulvic acids.

These reactions produce a diverse suite of carbon-bound organochlorine species, notably:

- Trihalomethanes (THMs),
- Haloacetic acids (HAAs),
- Haloacetonitriles (HANs),
- Chloral hydrate and haloketones,
- Chlorophenols and related aromatic chlorinated compounds,
- Other halogenated intermediates and oxidation products.

Many of these species continue to evolve as water travels through the network. Some remain relatively inert towards iodide and classical chlorine reagents; others are slow oxidants, capable of reacting with iodide or colorimetric reagents on a time scale of minutes to tens of minutes. This has direct implications for DPD-based total-chlorine measurements.

FREE-CHLORINE SPECIATION AND FORMATION OF CARBON-BOUND



↓ *milliseconds–seconds*
Initial oxidation of NOM
•reaction with phenolics, amines, aromatics
•formation of chlorinated functional groups

↓ *seconds–minutes*
Intermediate chlorinated organics
•halogenated aldehydes
•haloketones
•chlorinated carboxylic acids
•aromatic chlorinated intermediates

↓ *minutes–hours*
Formation of DBP families
•THMs (via aldehyde/ketone cleavage, haloform pathways)
•HAAs (via chlorinated acids and aldehyde oxidation)
•Other DBPs**:** HANs, HKs, chloral hydrate, chlorophenols

↓ *hours*
Transformation stage
•HAN → HAA
•HK → small halogenated molecules
•HAA → THM (slow)

↓ *hours–days*
Distribution system DBP profile stabilises
•THMs dominate (most stable)
•HAAs present but may decrease
•HANs decline
•Aromatic DBPs may persist

ORGANOCHLORINES.

3.1.1 Key implication:

In free-chlorinated systems, the measured “total chlorine” is a dynamic mixture of fast and slow oxidants. The relative contributions of these species depend on reaction time, pH, temperature, and organic load.

3.2 Chloraminated Systems

In chloraminated systems, free chlorine is dosed in the presence of ammonia, forming inorganic chloramines:

with further reactions, under less controlled conditions, potentially forming dichloramine ($NHCl_2$) and trichloramine (NCl_3). Under well-controlled water treatment conditions, the target residual is predominantly monochloramine (NH_2Cl).

Monochloramine is:

- A weaker oxidant and chlorinating agent than HOCl,
- More selective for nitrogen-containing functional groups (amines, amides, peptides),
- Substantially slower to react with carbon-based NOM.

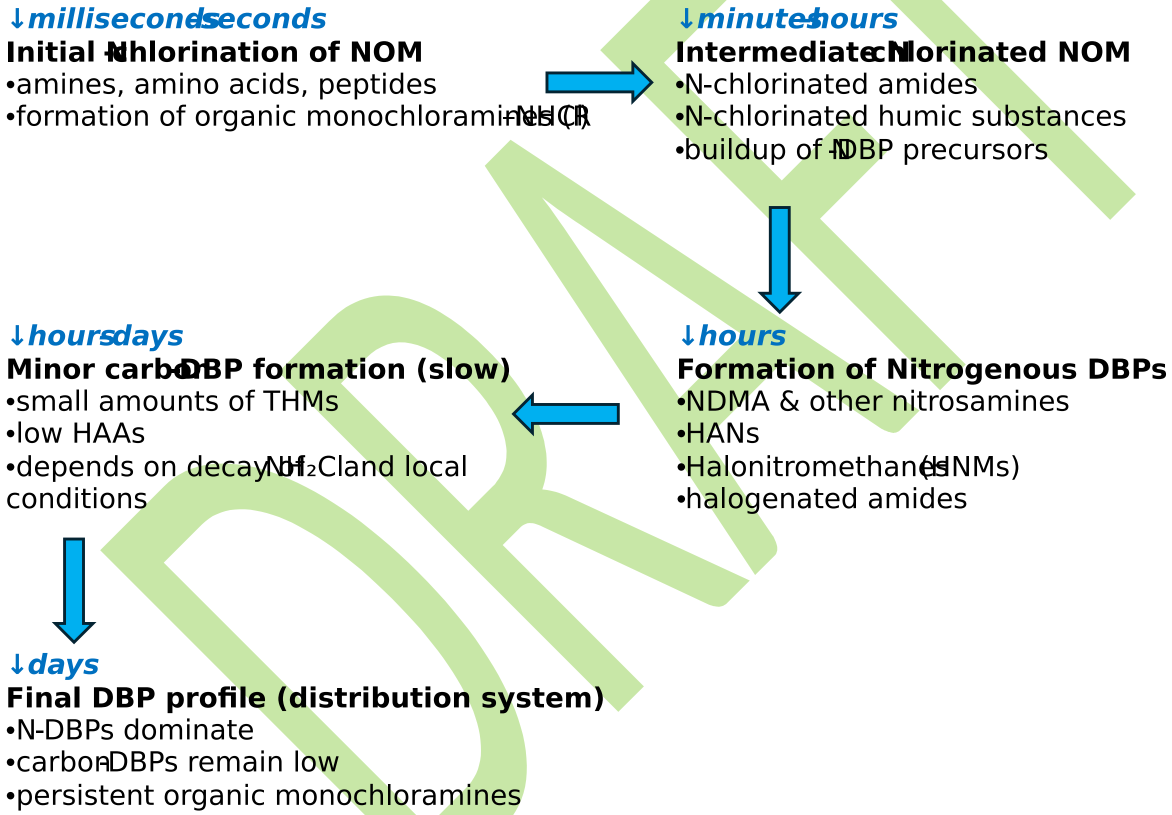
As a result, organochlorine formation in chloraminated systems is strongly biased towards N-chlorinated organic species:

- Organic chloramines (R–NHCl),
- N-chlorinated amino acids and peptides,
- N-chlorinated urea and creatinine derivatives,
- N-chlorinated NOM fractions.

These species are generally:

- Larger,
- More polar,
- Slower to diffuse through membranes, and
- Relatively unreactive towards iodide and other redox reagents on the short time scale used for chlorine analysis.

Monochloramine formation and N-chlorinated organics.



↓milliseconds–seconds

Initial N-chlorination of NOM

•amines, amino acids, peptides

•formation of organic monochloramines (R–NHCl)

↓minutes–hours

Intermediate N-chlorinated NOM

•N-chlorinated amides

•N-chlorinated humic substances

•buildup of N-DBP precursors

↓hours

Formation of Nitrogenous DBPs

•NDMA & other nitrosamines

•HANs

•Halonitromethanes (HNMs)

•halogenated amides

↓hours–days

Minor carbon-DBP formation (slow)

•small amounts of THMs

•low HAAs

•depends on decay of NH_2Cl and local conditions

↓days

Final DBP profile (distribution system)

•N-DBPs dominate

•carbon-DBPs remain low

•persistent organic monochloramines

3.2.1 Key implication

In chloraminated systems, the “total chlorine” residual is dominated by inorganic monochloramine, with a smaller contribution from other chloramines and relatively inert N-chlorinated organics. This yields a simpler and more stable analytical environment compared with free-chlorine systems.

3.3 Comparison of Organic Chlorine Profiles

A simplified comparison is useful:

Aspect	**Free-Chlorinated Systems**	**Chloraminated Systems**
Primary oxidant	$HOCl$ / OCl^-	Monochloramine (NH_2Cl)
Chlorinating strength	Strong	Moderate to weak
Main organochlorine species	THMs, HAAs, HANs, chlorophenols, haloketones, etc.	Organic chloramines, N-chlorinated amino acids/peptides
Reactivity towards iodide/DPD	Many species react slowly over minutes+	Most N-chlorinated organics are weak/slow oxidants
Analytical consequence	DPD colour drift, sensor under-response, calibration scatter	Relatively stable readings, smaller calibration errors

This underpinning chemistry explains why total chlorine measurement technologies tend to exhibit larger and more complex biases in free chlorinated systems than in chloraminated systems.

3.4 What DPD3 Does and Does Not Measure in Aged Distribution Water

As water progresses through the distribution system, the disinfectant residual decays while the DBP profile evolves toward its distribution-system equilibrium.

The DPD3 total chlorine method remains selective only for oxidising chlorine species. DPD3 quantifies any species capable of oxidising iodide ($I^- \rightarrow I_2$) within the method’s reaction time, which includes:

- Free chlorine ($HOCl/OCl^-$),
- Inorganic chloramines (NH_2Cl, $NHCl_2$; NCl_3 only partially),
- A small subset of slowly reactive N-chlorinated organic species (weak/slow oxidants).

Crucially, the major DBP families that dominate aged water, THMs, HAAs, HANs, haloketones, NDMA, and most N-DBPs, do not oxidise iodide under DPD3 conditions and therefore do not contribute to measured total chlorine.

Thus, even in well-aged water (>2 hours in the network), DPD3 measures only the remaining oxidising disinfectant species, not the DBPs that have formed. Although DBP formation and disinfectant decay occur concurrently, the DPD3 reading reflects only the oxidant chemistry, not DBP chemistry. This distinction is fundamental to correct calibration and interpretation of total-chlorine measurements.

3.5 Implications for Using DPD3 to Calibrate Online Total-Chlorine Monitors

The selective behaviour of DPD3 has direct implications for the calibration of online total-chlorine monitors. Because online instruments respond only to oxidants present on their intrinsic time scale (seconds to minutes), calibration must use a manual reference method that measures the same oxidant species pool.

3.5.1 In free-chlorinated systems

Slow-forming organochlorine intermediates accumulate as HOCl decays. Many of these species can oxidise iodide only on multi-minute timescales. Consequently:

- A timed DPD3 measurement (e.g. 60 s or 3 min) reflects mainly the fast oxidant pool (HOCl + inorganic chloramines).
- A long-delay DPD3 measurement incorporates slowly reactive organochlorines and therefore overestimates the oxidant residual relevant to online sensors.

Calibration using long-delay DPD3 therefore forces the online analyser to match a measurement that includes species it cannot detect. This leads to chronic bias: the analyser appears to “read low” even when functioning correctly.

3.5.2 In chloraminated systems

Monochloramine remains the dominant oxidant even after substantial water age. N-chlorinated organics form slowly and are poor iodide oxidants. Thus, the DPD3 reading at 60 seconds is chemically stable and closely aligned with the oxidant species that online instruments detect. For monochloramine-specific analysers, the indophenol (phenate) method provides an even more chemically specific calibration reference.

3.5.3 The operational principle is therefore:

- To calibrate online total-chlorine monitors, utilities must use strictly timed DPD3 or the indophenol method (for monochloramine) and must never use long-delay DPD3 readings.
- Alignment of measurement time scale and oxidant chemistry is critical for obtaining accurate, reliable, and consistent calibrations in both free-chlorinated and chloraminated networks

4 Analytical Methods for Total Chlorine

This section describes the main measurement methods and clarifies which species each method effectively “sees”.

1. DPD manual
2. Indophenol manual (monochloramine)
3. Online DPD colorimetyers
4. Amperometric membrane sensors

5. Bare electrode amperometric sensors
6. Buffer + KI amperometric sensors

4.1 DPD Free and Total Chlorine (Manual Methods)

The **DPD** (N, N-diethyl-p-phenylenediamine) method is the classical colorimetric approach.

4.1.1 DPD1 (free chlorine):

Measures free chlorine ($HOCl/OCl^-$). Free chlorine oxidises DPD to form a pink/red radical cation.

4.1.2 DPD3 (total chlorine):

A second reagent containing potassium iodide (KI) and often an additional buffer is added. Combined chlorine (chloramines) and other oxidants oxidise iodide (I^-) to iodine (I_2), and the iodine in turn oxidises additional DPD. The difference between DPD1 and DPD1+DPD3 readings is reported as combined chlorine.

In the total-chlorine step, the reagents and conditions are designed such that, within the specified reaction time, the method responds to:

- Free chlorine (if any remains),
- Inorganic chloramines (NH_2Cl, $NHCl_2$; NCl_3 more slowly),
- Other oxidants that can oxidise iodide under the test conditions.

4.1.3 DPD3 at ~60 Seconds

In many practical settings, particularly in process control, a 60-second reading after addition of the DPD3 (or total-chlorine) reagent is used, even though some standard methods specify 3 minutes. On this shorter time scale:

4.1.3.1 In chloraminated systems:

- Monochloramine reacts essentially to completion.
- Contribution from N-chlorinated organics is negligible.
- The reading predominantly reflects NH_2Cl (plus any minor free chlorine).

4.1.3.2 In free-chlorinated systems:

- HOCl reacts essentially instantly.
- Early-forming inorganic chloramines (if present) are captured.
- Slowly reacting carbon-bound organochlorines contribute only minimally at 60 s.

Thus, a 60-second DPD3 reading provides a snapshot of the fast oxidant pool: free chlorine plus inorganic chloramines and any other relatively fast oxidants.

4.1.4 DPD3 Long-Delay Behaviour

If the sample is left standing significantly longer than e.g. 60 seconds, for example some hand-held spectrophotometers recommend 3-10 minutes depending on temperature.

4.1.4.1 In free-chlorinated systems:

- Some organochlorine species that are slow oxidants towards iodide begin to react.

- Ongoing reactions between HOCl and NOM continue to generate new intermediate oxidants.
- The DPD colour can climb up, producing a higher apparent “total chlorine” than exists in terms of fast disinfectant species.

4.1.4.2 In chloraminated systems:

- There are fewer carbon-bound organochlorines.
- N-chlorinated organics are comparatively inert.
- Colour drift is much smaller; the reading remains close to the 60-second value.

4.1.5 Key point:

Long-delay DPD3 readings do not represent the same measurand as an online analyser. They are not suitable as a calibration reference for any type of online total-chlorine instrument. They are useful to improve understanding of the mix of chlorine species, the difference between “fast DOD3” and slow DPD3 is an indicator of how much organically bound is present.

4.2 Indophenol (Phenate) Method for Monochloramine

The indophenol (phenate) method is widely used for the determination of ammonia and, by extension, monochloramine. The chemistry is a variant of the Berthelot reaction:

- Monochloramine reacts with a phenolic reagent in the presence of a catalyst (commonly sodium nitroprusside) under alkaline conditions.
- An indophenol blue dye forms.
- The colour intensity is proportional to the concentration of monochloramine (or ammonia after appropriate conversion).

4.2.1 Key characteristics:

- The method is highly selective for inorganic monochloramine when used in chloraminated drinking water.
- Dichloramine, trichloramine, and most organic chloramines do not contribute significantly.
- Some monochloramine-specific online colorimetric analysers use an internal variant of indophenol chemistry.

4.2.2 Calibration implication:

Where an online analyser is designed to measure monochloramine specifically, the indophenol method provides a chemically equivalent and selective reference and is preferred over DPD3, which measures all combined-chlorine oxidants.

4.3 Online DPD Colorimetric Analysers

Online DPD colorimetric analysers automate the DPD chemistry in a flow cell. The key features are:

- Automated dosing of DPD1 and DPD3 (or a combined total-chlorine reagent).
- A defined **reaction time** (typically 2–3 minutes) controlled by:

- Stopping flow,
- Mixing,
- Reading absorbance at a fixed delay.
- Automated flushing and repetition on a regular cycle.

An online DPD analyser is an automated spectrophotometer

- It implements something very close to the manual standard method for free or total chlorine.
- It only measures colour after the defined reaction time, i.e. it behaves like a strictly timed manual test.
- It does not allow the colour to drift indefinitely; once measured, the sample is discarded.

Consequently, a correct calibration standard for an online DPD analyser is a manual DPD measurement performed with the same reaction time (e.g. 2–3 minutes), not a long-delay DPD sample.

4.4 Membrane Amperometric / Polarographic Total-Chlorine Sensors

Membrane amperometric or polarographic sensors comprise:

- A selective membrane (e.g. PTFE, FEP),
- An internal electrolyte (often buffered and possibly containing iodide),
- A noble metal working electrode (e.g. gold, platinum),
- A reference/counter electrode (e.g. Ag/AgCl).

Chlorine species diffuse through the membrane into the electrolyte, where they are converted to a single electroactive oxidant (e.g. HOCl, Cl_2, or I_2 depending on design), and the resulting current is proportional to concentration.

For total-chlorine versions, the design and electrolyte chemistry are adjusted so that:

- HOCl and NH_2Cl (and often $NHCl_2$) are both converted to the same electroactive species.
- The sensor is calibrated against total-chlorine DPD (as Cl_2).

4.4.1 Limitations:

- Only species that can cross the membrane and react rapidly in the electrolyte are measured.
- Large, hydrophobic, or slowly reacting organochlorines contribute little or nothing.
- Sensitivity to NH_2Cl is generally slightly lower than to HOCl, but internal chemistry is tuned to minimise this difference over the normal operating range.

4.4.2 Analytical consequence:

Membrane total-chlorine sensors tend to respond strongly to HOCl and NH_2Cl, but they do not measure all organochlorine species that might eventually react with iodide in a long-delay DPD test.

4.5 Open electrode Amperometric Total-Chlorine Sensors

Amperometric total chlorine sensors comprise:

- A noble metal working electrode (e.g. gold, platinum),
- A reference/counter electrode (e.g. Ag/AgCl).
- Some systems have two working electrodes for selectivity for free chlorine and monochloramine

The oxidant is electrochemically reduced generating a current proportional to concentration.

For total-chlorine versions, the design and electrolyte chemistry is adjusted so that HOCl and NH_2Cl are both measured. The sensor electronics apply different scaling factors to the signals for free chlorine and monochloramine and then sum them to calculate “total chlorine”.

- The sensor is calibrated against total-chlorine DPD (as Cl_2).

4.5.1 *Limitations:*

- There is no selectivity on species measured
- Flow, pressure, elcrode fouling and ionic strength of the water can affect signals.

4.5.2 *Analytical consequence:*

Open electrode amperometric total-chlorine sensors need automatic cleaning and an algorithm that compensates for ph, conductivity and temperature. They measure predominantly free and monochloramine and thus do not measure all organochlorine species that might eventually react with iodide in a long-delay DPD test.

4.6 KI-Buffered Amperometric Total-Chlorine Sensors

KI-buffered amperometric total-chlorine sensors introduce iodide (usually in an acetate or phosphate buffer) to the sample or internal electrolyte. The chemistry is similar in concept to DPD3:

1. Free chlorine and chloramines oxidise $I^- \rightarrow I_2$.
2. The sensor measures the resulting I_2 amperometrically.

4.6.1 *Advantages:*

- Provides a robust measure of total oxidising chlorine species (free + combined) within the sensor’s time scale.
- Less sensitive to pH than a pure free chlorine amperometric sensor.

4.6.2 *Limitations:*

- Slow-reacting organochlorine species may not oxidise iodide completely during the sensor’s response time.
- Like membrane sensors, KI-buffered sensors emphasise the fast oxidant pool rather than the entire set of slow organochlorines detectable by long-delay DPD.

5 What DPD3 Measures in Free Chlorinated and Chloraminated Systems

This section focuses specifically on DPD3 total chlorine and its different behaviour in the two system types.

5.1 Timing sensitivity

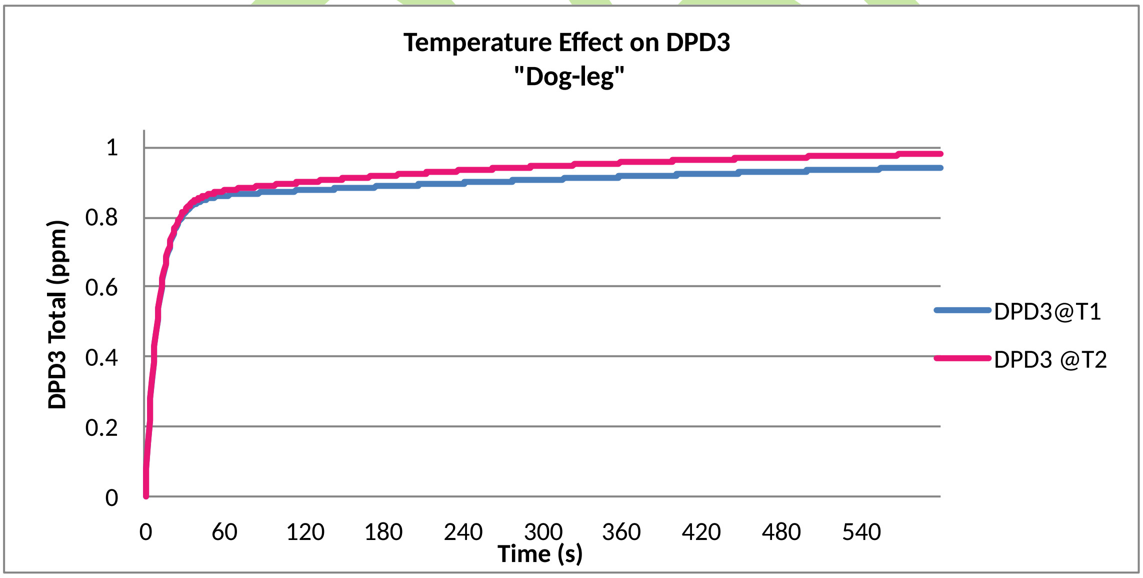
Regardless of which type of water is analysed, DPD3 total chlorine colour continues to develop after the first minute.

- Standard Methods assume an e.g 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.

5.1.1 Graphical example

Using some reasonable rate constants for the reaction of NOM based organochlorine species it is possible to calculate how the DPD3 total reading changes with time and how water temperature changes the response.

For water in a free chlorinated system with 0.85ppm free and 0.15 ppm organochlorine this is how the DPD3 readings could change with time. The total chlorine content is 1.0ppm. The DPD3 reacts almost instantaneously, within a minute, to the free fraction but reacts slowly with the organo-chlorine. Even after 10 minutes not all the organic species have reacted. Here T1 is 5 degrees C and T2 is 15 degrees C.



5.2 Free-Chlorinated Systems

5.2.1 In free-chlorinated systems:

- The fast oxidant pool includes $HOCl/OCl^-$, any inorganic chloramines formed, some early intermediate chlorinated species.
- DPD3 at **60 seconds** captures most of these fast species.

- However, as time progresses additional organochlorine species form,some slow oxidants begin to react with iodide and DPD colour continues to develop.

5.2.2 Therefore:

- A timed DPD3 reading (60 s or method-specified 3 min) reflects mainly the fast disinfectant pool.

- A long-delay DPD3 reading (5–10+ min) drifts towards a more inclusive oxidant-demand test, incorporating some slowly reacting organochlorines.

5.2.3 Critical implication:

For free-chlorinated systems, long-delay DPD3 readings can substantially overestimate the oxidant residual relevant to disinfection and online sensor readings. They are not appropriate for calibrating online total-chlorine sensors.

5.3 Chloraminated Systems

5.3.1 In chloraminated distribution systems:

- The dominant reactive species is monochloramine.
- DPD3 at ~60 seconds captures practically all the inorganic chloramine present.
- Contributions from N-chlorinated organics are negligible on this time scale.
- Leaving the sample longer yields only minor drift, if any.

5.3.2 Thus, for chloraminated systems:

- DPD3 (timed) is a more robust operational measure of “inorganic monochloramine + minor chloramines”.
- The method aligns well with membrane total-chlorine sensors and indophenol monochloramine analyses, especially when properly timed.

6 Analyser Behaviour in Free Chlorinated vs Chloraminated Systems

Bringing the chemistry and methods together, we can now summarise how the various analysers behave in each system type.

6.1 Free-Chlorinated Systems

6.1.1 DPD3 (timed):

- Responds to $HOCl/OCl^-$ and fast-forming chloramines.
- Limited inclusion of slow organochlorines at 60 s; more at 3 min.
- Good for operational residual control if timing is strictly controlled.

6.1.2 DPD3 (long delay):

- Progressive inclusion of slow organochlorines.
- Overestimation relative to fast oxidant pool.
- Poor agreement with online sensors of any type.

6.1.3 Online DPD:

- Effectively a **timed DPD test** with fixed reaction time.
- Coherent with manual DPD when timing is matched.
- Still subject to interferences if water quality is complex, but not to long-delay drift.

6.1.4 Membrane total-chlorine sensors:

- Respond strongly to $HOCl/OCl^-$; less so to slow organochlorines.
- Calibration against timed DPD is possible but may show systematic bias if significant organochlorine formation occurs.
- Changes in free to combined ratio can slightly shift sensor response.

6.1.5 Open electrode amperometric total-chlorine sensors:

- Respond strongly to $HOCl/OCl^-$; less so to slow organochlorines.
- Calibration against timed DPD3 is possible but may show systematic bias if significant organochlorine formation occurs.
- Changes in free to combined ratio can slightly shift sensor response unless the sensor uses two pairs of electrodes tuned for detection of free and monochloramine independantly

6.1.6 KI-buffered amperometric sensors:

- Respond to HOCl + chloramines that readily oxidise iodide.
- Slow organochlorines may be under-represented.
- Better than pure free-chlorine amperometric cells for total residual, but still focused on the fast oxidant pool.

6.1.7 Summary

In free-chlorinated systems, all total-chlorine methods are more vulnerable to errors caused by DPD3 measuring colour caused slow organochlorine chemistry, leading to larger calibration errors and poorer agreement between methods, especially if DPD timing is not strictly controlled.

6.2 Chloraminated Systems

6.2.1 DPD3 (timed):

- Effectively measures **monochloramine residual** with minor contributions from other chloramines.
- Minimal drift between 60 s and longer times.
- Good agreement with monochloramine-targeted online methods.

6.2.2 DPD3 (long delay):

- Progressive inclusion of slow nitrogen organochlorines.
- Overestimation relative to fast oxidant pool.
- Effects smaller than for free chlorine systems

6.2.3 Online DPD:

- Behaves like a strictly timed total-chlorine DPD test in a monochloramine system.

- Provides stable and reliable measurements if the manual DPDP timing is matched to the reaction time of the on-line analyser

6.2.4 *Membrane total-chlorine sensors:*

- Respond primarily to NH_2Cl and any free chlorine present.
- Organics are less problematic; N-chlorinated organics are largely “invisible” to the sensor but also contribute very little to DPD.
- Calibration against timed DPD3 is stable and reproducible if a short reaction time for DPD3 is used.

6.2.5 *Open electrode amperometric total-chlorine sensors:*

- Respond strongly to $HOCl/OCl^-$ and NH_2Cl; less so to slow organochlorines.
- Calibration against timed DPD3 is possible but may show systematic bias if significant organochlorine formation occurs.
- Changes in free to combined ratio can slightly shift sensor response unless the sensor uses two pairs of electrodes tuned for detection of free and monochloramine independently.

6.2.6 *KI-buffered total amperometric sensors:*

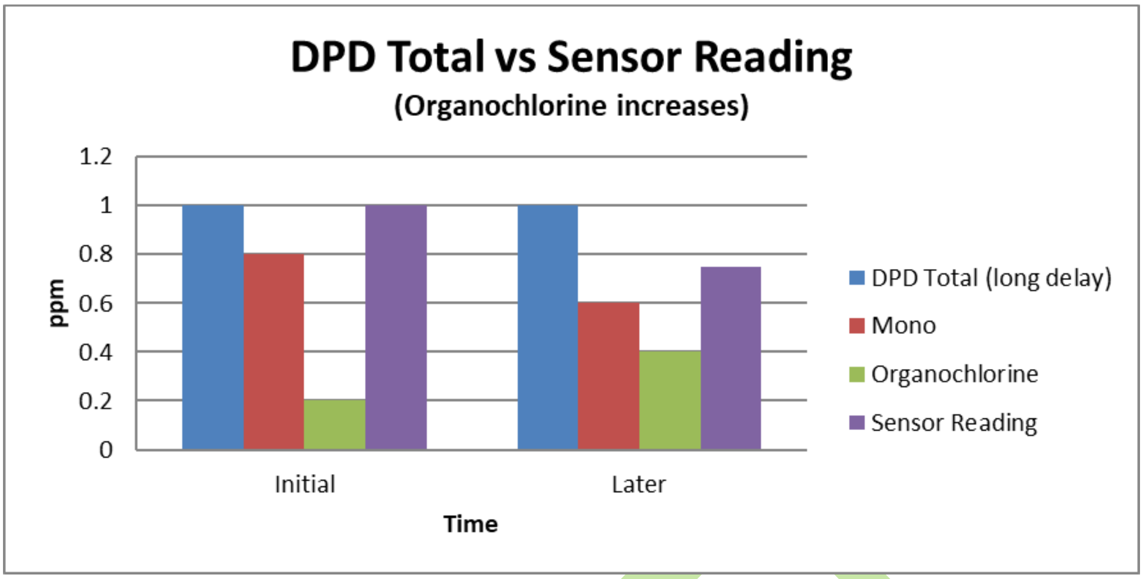
- Respond robustly to NH_2Cl.
- Minimal influence from organochlorines.
- Good agreement with timed DPD3.

6.2.7 *Summary*

In chloraminated systems, the residual chemistry is simpler, leading to smaller calibration errors and better agreement among total-chlorine measurement technologies.

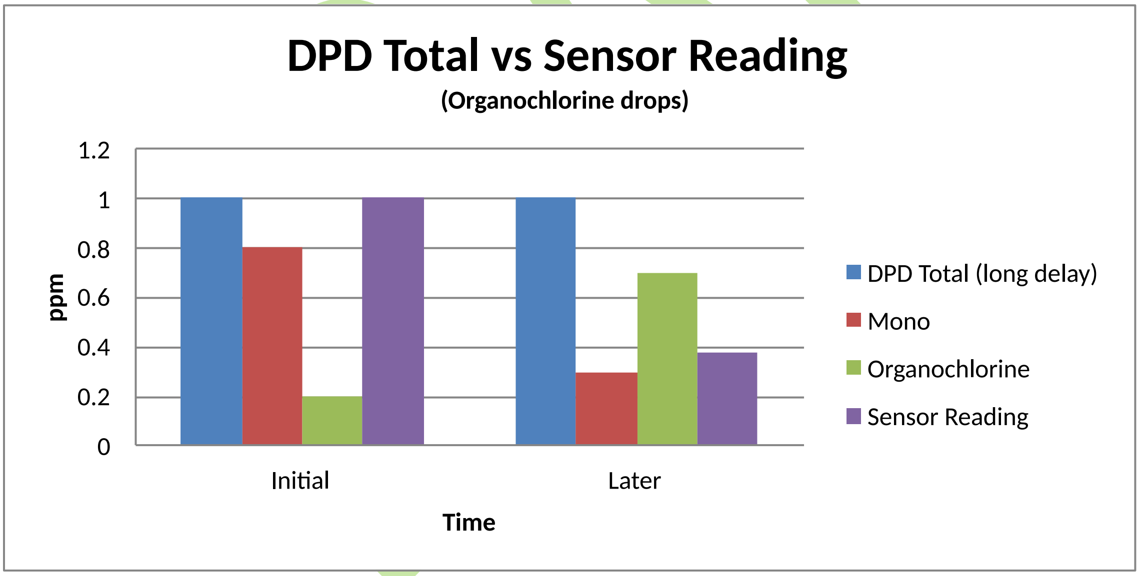
7 Graphical examples showing errors caused by leaving DPD3 too long

Consider a total chlorine monitor in a monochloraminated system 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.



Time	DPD Total (long delay)	Mono	Organochlorine	Sensor Reading
Initial	1	0.8	0.2	1
Later	1	0.6	0.4	0.75

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



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

8 Best Practice Calibration Guidance

This section summarises recommended calibration strategies by analyser type and system type, with explicit emphasis on DPD timing and the role of indophenol.

8.1 General Principles

- Use timed methods: Always calibrate against a timed DPD3, or if the analyser measures predominantly monochloramine, indophenol measurement; never use long-delay DPD3.
- Match chemistries: Where possible, calibrate against a reference method that measures the same chemical species as the analyser (e.g. indophenol for monochloramine).
- Control pH, flow, and temperature: Ensure the sensor is operating within manufacturer-specified ranges.
- Document timing and procedures: Include DPD3 reaction time, mixing, and sample handling explicitly in SOPs.

8.2 Calibration of Online DPD Colorimetric Analysers

8.2.1 For free-chlorinated and chloraminated systems.

- Calibrate against manual DPD3 using the same reaction time as the analyser. This minimises the risk of the DPD3 measuring species that the analyser does not.

8.2.2 Ensure that manual samples are:

- Taken from the same sampling point,
- Analysed immediately,
- Shielded from strong light if required.
- Do not calibrate against samples that have been left standing beyond the method-specified reaction time.

In chloraminated systems, online DPD analysers typically show excellent agreement with timed manual DPD. In free-chlorinated systems, some scatter may still occur due to organochlorine formation, but this is minimised by consistent timing.

8.3 Calibration of Membrane Amperometric/Polarographic Total-Chlorine Sensors and Open electrode amperometric sensors

8.3.1 Free-Chlorinated Systems

- Use timed DPD3 (e.g. 60 s for operational control, or 3 min if strictly following standard methods) as the calibration reference.
- Expect some systematic differences due to the sensor measuring primarily $HOCl/OCl^-$ and DPD3 including some contribution from slow intermediates.
- Avoid attempting to make the sensor match long-delay DPD3 values.

8.3.2 Chloraminated Systems

- Timed DPD3 provides a good calibration reference, as both methods largely measure NH_2Cl.
- For analysers designed to report monochloramine specifically, use indophenol as the primary calibration method:
- Calibrate the analyser to the indophenol result and use DPD3 only as a secondary check for total chlorine.

8.4 Calibration of KI-Buffered Amperometric Total-Chlorine Sensors

8.4.1 Free-Chlorinated Systems

- Use timed DPD3 as the reference.
- Ensure consistent DPD timing; differences between 60 s and 3 min must be understood and standardised.
- Recognise that the KI sensor may not fully respond to slow organochlorines; the measured value is best interpreted as the **fast oxidant residual**.

8.4.2 Chloraminated Systems

- Use timed DPD3; good agreement is usually obtained.
- For tight control of chloramination, combine:
  - ❖ Timed DPD3 (total) for regulatory perspective, and
  - ❖ Indophenol (monochloramine) for specific monochloramine control where appropriate.

8.5 Calibration of Monochloramine-Specific Analysers (Indophenol-Type)

8.5.1 Chloraminated systems

For analysers that are explicitly designed to measure monochloramine, typically using some version of the indophenol reaction internally:

- Use the indophenol monochloramine method as the primary calibration reference.
- Use DPD3 only
  - ❖ To track total chlorine (free + combined),
  - ❖ As a secondary cross-check, not as the primary calibration standard.
- In chloraminated systems, indophenol provides a true NH_2Cl concentration, allowing the analyser to be calibrated on a chemically meaningful basis.

9 Summary and Conclusions

This guidance note has explored the complex relationship between disinfectant chemistry, analytical method behaviour, and calibration practice in free-chlorinated and chloraminated distribution systems.

Key conclusions are:

9.1 System chemistry matters:

- Free-chlorinated systems generate a broad range of carbon-bound organochlorines, causing DPD colour drift and incomplete response in membrane and KI-buffered sensors.
- Chloraminated systems are dominated by monochloramine and relatively inert N-chlorinated organics, leading to simpler and more stable analytical behaviour.

9.2 DPD3 timing is critical:

- At ~60 seconds (or the method-specified time), DPD3 measures the **fast oxidant pool** (free chlorine + inorganic chloramines).

- Long delays allow slow organochlorines to contribute, particularly in free-chlorinated systems, and should not be used for calibration.

9.3 Total-chlorine monitors behave better in chloraminated systems:

- Across DPD, membrane, and KI-buffered technologies, calibration errors and disagreement between methods are generally **smaller** in chloraminated networks than in free-chlorine networks.

9.4 Indophenol is the preferred reference for monochloramine:

- For monochloramine-specific analysers, indophenol provides a direct, selective measure of NH_2Cl and is therefore the most appropriate calibration standard.

9.5 Best practice requires matching chemistry and time scale:

- Online DPD analysers must be calibrated against timed manual DPD.
- Membrane and KI-buffered sensors should be calibrated against timed DPD3, not long-delay DPD.
- Monochloramine analysers should be calibrated against indophenol.

10 The good news

By aligning calibration practice with the underlying chemistry and time scales of both the water system and the measurement method, utilities can significantly improve the reliability of total chlorine monitoring, reduce apparent discrepancies between instruments, and better manage disinfection in both free-chlorinated and chloraminated distribution networks.

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