



IWW Water Centre – IWW Rheinisch-Westfälisches Institut
für Wasser Beratungs- und Entwicklungsgesellschaft mbH

Tintometer Chlorine comparative study

Project results corresponding to the offer 10045-3/2018

September 2018

**Client: Tintometer GmbH
(Dortmund)**



Conducted by

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für Wasser Beratungs- und Entwicklungsgesellschaft mbH

Mülheim an der Ruhr, dated

10.09.2018, Dr Wolf Merkel

p.p.

by order of

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1 Summary

The subject of this project is the performance of a comparative study of the photometric determination of free chlorine and total chlorine in water under laboratory conditions with the following reagents:

Free chlorine	Total chlorine
Tintometer Chlorine free DPD/F10	Tintometer Chlorine total DPD/F10
Tintometer Chlorine free DPD/F F25	Tintometer Chlorine total DPD/F25
HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL	HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL
HACH DPD Free Chlorine Reagent Powder Pillows, 25 mL	HACH DPD Total Chlorine Reagent Powder Pillows, 25 mL

The measurements were performed in two concentration ranges (0.02–2 mg/L chlorine and 0.1–10 mg/L chlorine) as well as in different aqueous matrices (demineralised water, swimming pool water, potable water, water with select concentrations of alkalinity, nitrate, chloride, copper and fluoride). All measurements were carried out using the Hach DR 900. The following methods were implemented regardless of the reagents used:

Concentration range	Free chlorine	Total chlorine
0.02–2 mg/L	Hach Method 8021, Programme 80 Chlorine F&T PP	Hach Method 8167, Programme 80 Chlorine F&T PP
	DOC316.53.01023	DOC316.53.01027
0.1–10 mg/L	Hach Method 10069, Programme 88 Chlorine F&T HR	Hach Method 10070, Programme 88 Chlorine F&T HR
	DOC3116.53.01025	DOC316.53.01029

The relative standard deviations of the repeat measurements (N = 3) and the recoveries were used to evaluate the measurement results.

Free chlorine	Tintometer	HACH
Average relative standard deviation ([Cl ₂] = 0.02–2 mg/L)	2.1%	2.3%
Average relative standard deviation ([Cl ₂] = 0.1–10 mg/L)	0.8%	0.5%

Total chlorine	Tintometer	HACH
Average relative standard deviation ([Cl ₂] = 0.02–2 mg/L)	0.8%	1.0%
Average relative standard deviation ([Cl ₂] = 0.1–10 mg/L)	0.4%	0.5%

The average relative standard deviations (N = 3) determined with the reagents of Tintometer GmbH / Hach Lange GmbH are at a similar level when determining the free chlorine concentration and the total chlorine concentration.

Free chlorine	Tintometer against reference	HACH against reference	Tintometer against HACH
Average recovery ([Cl ₂] = 0.02–2 mg/L)	93%	93%	100%
Average recovery ([Cl ₂] = 0.1–10 mg/L)	99%	101%	98%

Total chlorine	Tintometer against reference	HACH against reference	Tintometer against HACH
Average recovery ([Cl ₂] = 0.02–2 mg/L)	96%	97%	99%
Average recovery ([Cl ₂] = 0.1–10 mg/L)	96%	99%	97%

The differences between the average recoveries of free chlorine and total chlorine determined with the reagents of Tintometer GmbH in comparison to the Hach Lange GmbH method are coincidental and thus, not probable and not significant ($P = 99\%$).

The data regarding average relative standard deviations and recoveries relates to the concentration ranges and aqueous matrices examined within the scope of the comparative study.

2 Introduction and background

The subject of this project is the performance of a comparative study of the photometric determination of free chlorine and total chlorine in aqueous matrices under laboratory conditions with the following reagents:

Free chlorine	Total chlorine
Tintometer Chlorine free DPD/F10	Tintometer Chlorine total DPD/F10
Tintometer Chlorine free DPD/F F25	Tintometer Chlorine total DPD/F25
HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL	HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL
HACH DPD Free Chlorine Reagent Powder Pillows, 25 mL	HACH DPD Total Chlorine Reagent Powder Pillows, 25 mL

The measurement of free chlorine and total chlorine with the reagents from both manufacturers is based on the colorimetric DPD method (N,N-Diethyl-1.4-phenylendiamine).

The measurements are performed in different concentration ranges as well as in different aqueous matrices (demineralised water, swimming pool water, potable water, water with select contents).

The testing scope and the testing conditions are illustrated in Table 1 .

All measurements were carried out using the Hach DR 900. The following methods were implemented regardless of the reagents used:

Concentration range	Free chlorine	Total chlorine
0.02–2 mg/L	Hach Method 8021, Programme 80 Chlorine F&T PP DOC316.53.01023	Hach Method 8167, Programme 80 Chlorine F&T PP DOC316.53.01027
0.1–10 mg/L	Hach Method 10069, Programme 88 Chlorine F&T HR DOC3116.53.01025	Hach Method 10070, Programme 88 Chlorine F&T HR DOC316.53.01029

The recovery and precision are used to compare the measured values.

The recovery of free chlorine and total chlorine concentrations is used as a gauge of the accuracy of the measurements.

- Determination of the recovery function: linear regression of the concentrations of free chlorine and total chlorine determined with the reagents of Tintometer GmbH and Hach Lange GmbH plotted against the concentrations determined by the standardised DPD reference method according to DIN EN ISO 7393-2 (reference concentration).
- Determining the percentual recovery rates of free chlorine and total chlorine concentrations determined with the reagents of Tintometer GmbH in comparison to the Hach Lange GmbH reagents.

The recovery rate is calculated as follows:

$$\text{recovery rate [\%]} = \frac{\frac{\text{measured concentration}}{\text{reference concentration}}}{\frac{\text{reference concentration}}{\text{reference concentration}}} \times 100 [\%]$$

The standard deviation of the repeat measurement (N = 3) is used as a precision gauge (recoverability under laboratory conditions).

Table 1: Test scope and conditions (measuring device: Hach DR 900).

No.	Test	[Chlorine] [mg/L]	Method	Execution
	Measurement of free chlorine in demineralised water	0; 0.1; 0.5; 1.0; 1.5; 2.0 0; 2; 4; 6; 8; 10	Hach Method 8021, Programme 80 Chlorine F&T PP Hach Method 10069, Programme 88 Chlorine F&T HR	3 repetitions per measurement point (amount 6), each with Tintometer and HACH reagents
	Measurement of total chlorine in demineralised water	0; 0.1; 0.5; 1.0; 1.5; 2.0 0; 2; 4; 6; 8; 10	Hach Method 8167, Programme 80 Chlorine F&T PP Hach Method 10070, Programme 88 Chlorine F&T HR	3 repetitions per measurement point (amount 6), each with Tintometer and HACH reagents
	Measurement of free chlorine in potable and swimming pool water	0; 0.25; 1; 1.75; 8.0	Hach Method 8021, Programme 80 Chlorine F&T PP Hach Method 10069, Programme 88 Chlorine F&T HR	3 repetitions per measurement point (amount 5) and matrix (amount 2), each with Tintometer and HACH reagents
	Measurement of total chlorine in potable and swimming pool water	0; 0.25; 1; 1.75; 8.0	Hach Method 8167, Programme 80 Chlorine F&T PP Hach Method 10070, Programme 88 Chlorine F&T HR	3 repetitions per measurement point (amount 5) and matrix (amount 2), each with Tintometer and HACH reagents
	Measurement of free chlorine in water with selected contents: High alkalinity (100 mg/L CaCO ₃) Nitrate (10 mg/L) Chloride (1200 mg/L) Copper (1 mg/L) Fluoride (4 mg/L)	0.25	Hach Method 8021, Programme 80 Chlorine F&T PP	3 repetitions per measurement point (amount 1) and matrix (amount 5), each with Tintometer and HACH reagents
	Measurement of total chlorine in water with selected contents: High alkalinity (100 mg/L CaCO ₃) Nitrate (10 mg/L) Chloride (1200 mg/L) Copper (1 mg/L) Fluoride (4 mg/L)	0.25	Hach Method 8167, Programme 80 Chlorine F&T PP	3 repetitions per measurement point (amount 1) and matrix (amount 5), each with Tintometer and HACH reagents

3 Results and evaluation

3.1 Measurement of free chlorine

Illustration of recoveries and precision of the free chlorine concentration determined with the reagents of Tintometer GmbH and Hach Lange GmbH compared to the reference method according to DIN EN ISO 7393-2 (recovery function)

In the following Figures 1–4, the measurement results of the free chlorine concentration determined with the reagents of Tintometer GmbH and Hach Lange GmbH are plotted against the measurement values determined using the reference method according to DIN EN ISO 7393-2.

The measured values are each illustrated as average and standard deviations of triplicate measurements. The linear regression functions show the average recovery versus the reference concentration over the entire working range (recovery functions).

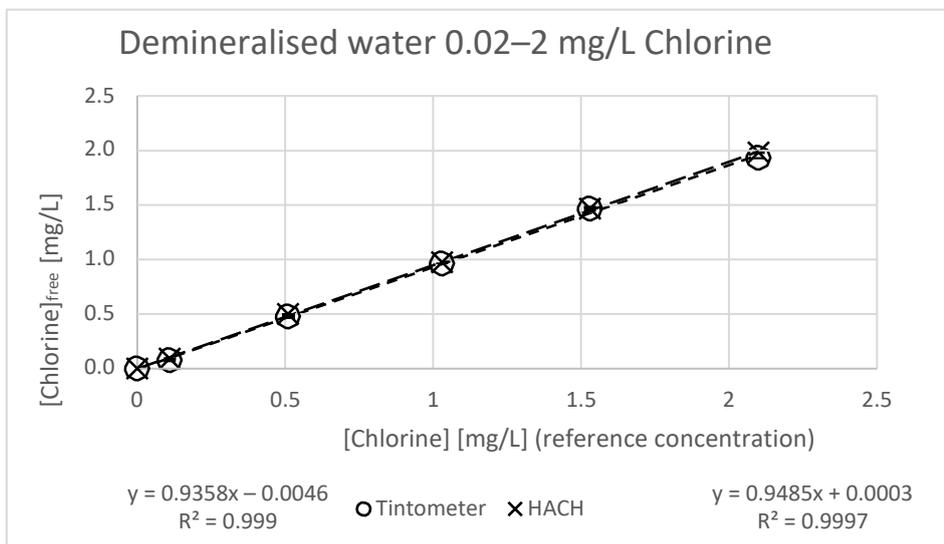


Figure 1: Recovery functions:
Free chlorine in demineralised water (0.02–2 mg/L);
Average values of the free chlorine concentration measured with “Tintometer Chlorine free DPD/F10” / “HACH DPD Free Chlorine Reagent Pillows, 10 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

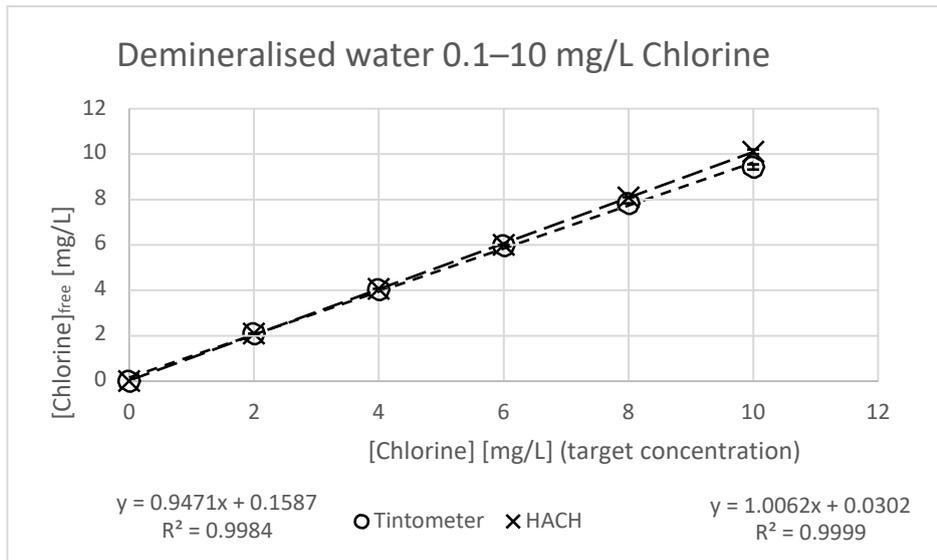


Figure 2: Recovery functions:
 Free chlorine in demineralised water (0.1–10 mg/L);
 Average values of the free chlorine concentration measured with “Tintometer Chlorine free DPD/F25” / “HACH DPD Free Chlorine Reagent Powder Pillows, 25 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

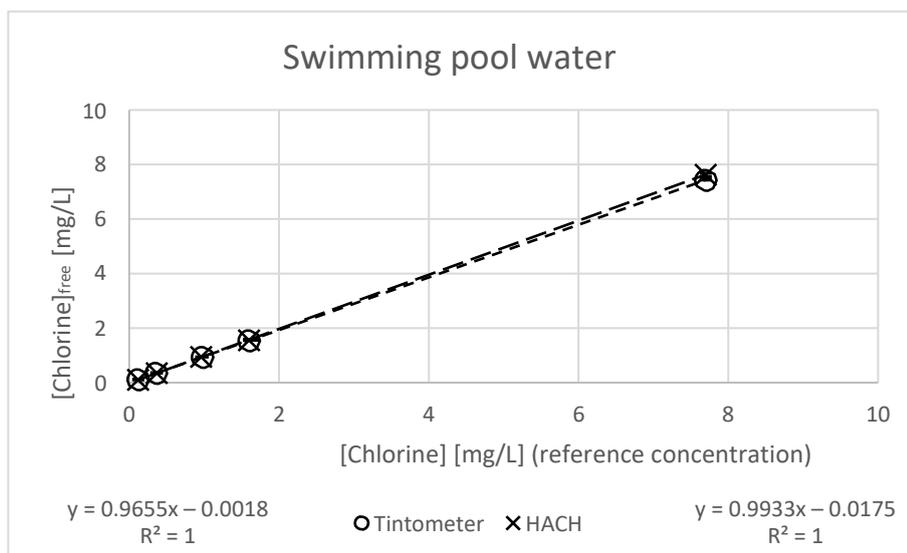


Figure 3: Recovery functions:
 Free chlorine in swimming pool water (0.25–8 mg/L);
 Average values of the free chlorine concentration measured with “Tintometer Chlorine free DPD/F10 and F25” / “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL and 25 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

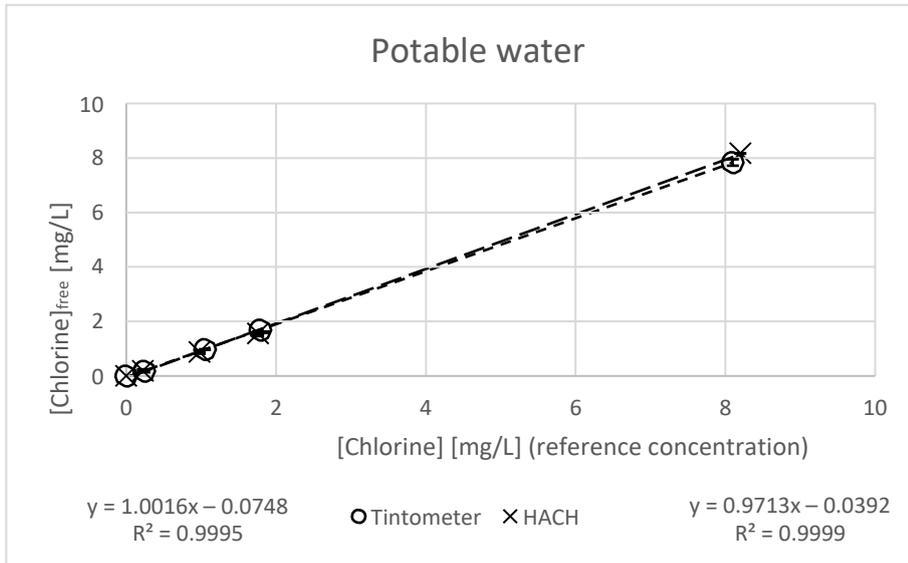


Figure 4: Recovery functions:

Free chlorine in potable water (0.25–8 mg/L);

Average values of the free chlorine concentration measured with “Tintometer Chlorine free DPD/F10 and F25” / “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL and 25 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

Figure 5 shows the average values of the free chlorine concentration measured with “Tintometer Chlorine free DPD/F10” / “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL” in water with select contents. The target concentration is 0.25 mg/l free chlorine.

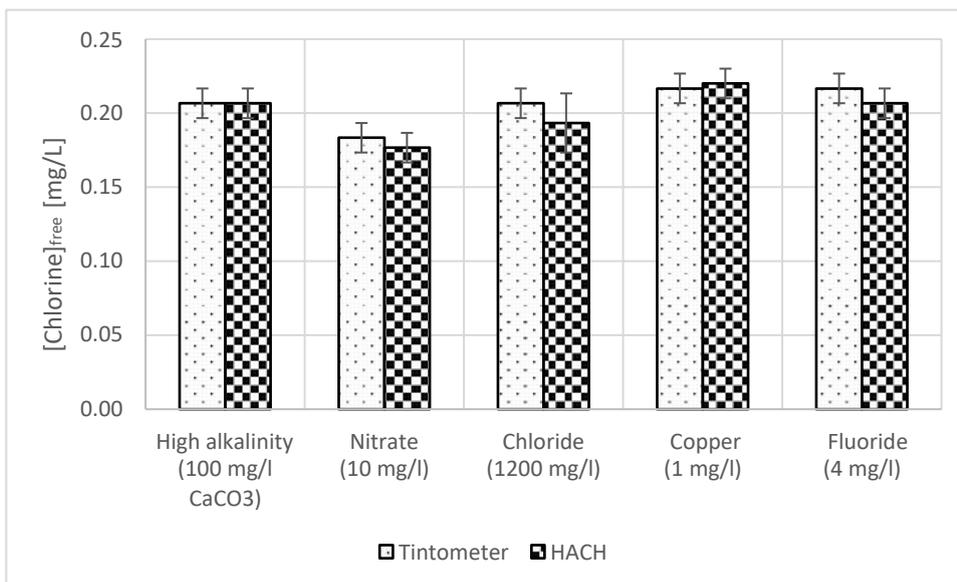


Figure 5: Average values of the free chlorine concentration in waters with select contents measured with “Tintometer Chlorine free DPD/F10” / “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL”

Illustration of recovery rates of the free chlorine concentration determined with the reagents of Tintometer GmbH in comparison to the Hach Lange GmbH reagents

The following figures show the percentual recovery rates of the free chlorine concentrations.

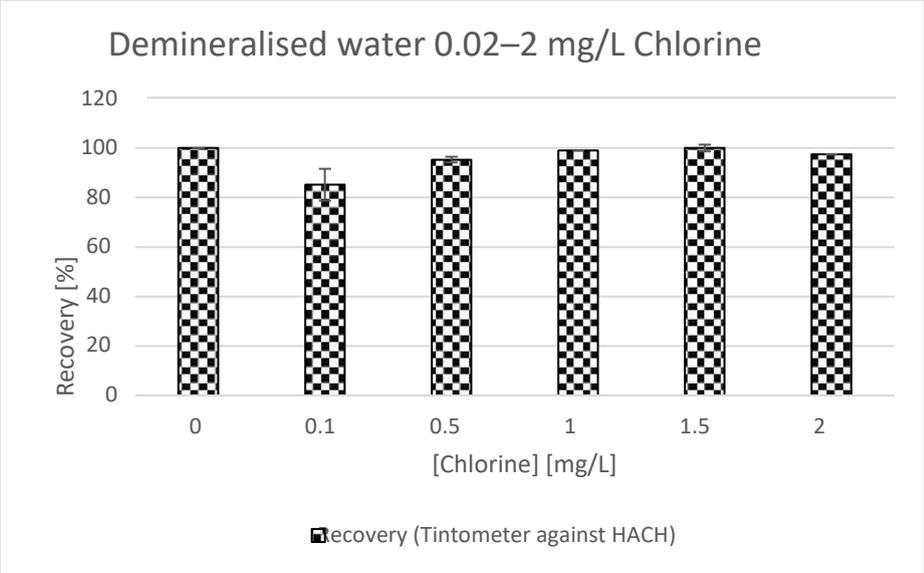


Figure 6: Recovery rates of the free chlorine in demineralised water with different chlorine concentrations measured with “Tintometer Chlorine free DPD/F10” in comparison to “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL”

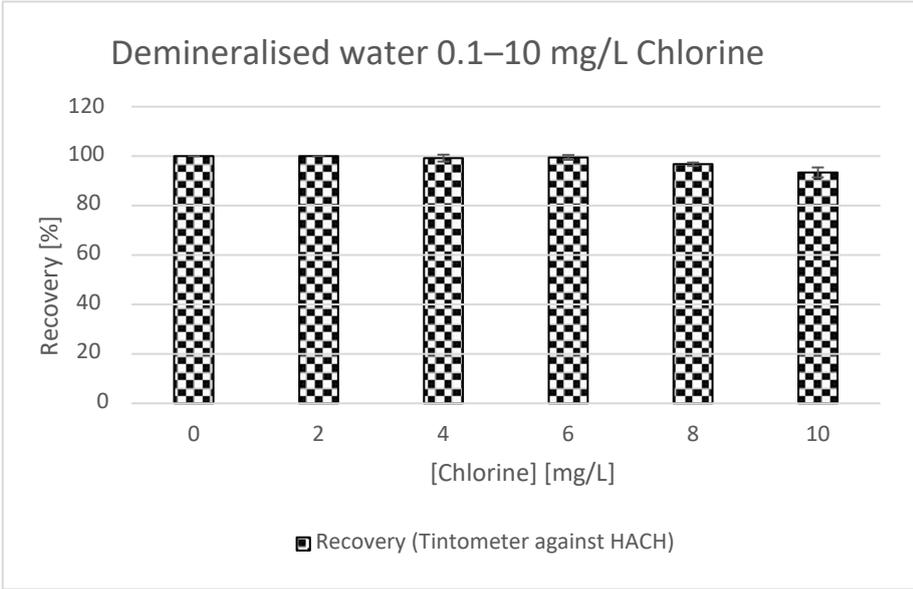


Figure 7: Recovery rates of the free chlorine in demineralised water with different chlorine concentrations measured with “Tintometer Chlorine free DPD/F25” in comparison to “HACH DPD Free Chlorine Reagent Powder Pillows, 25 mL”

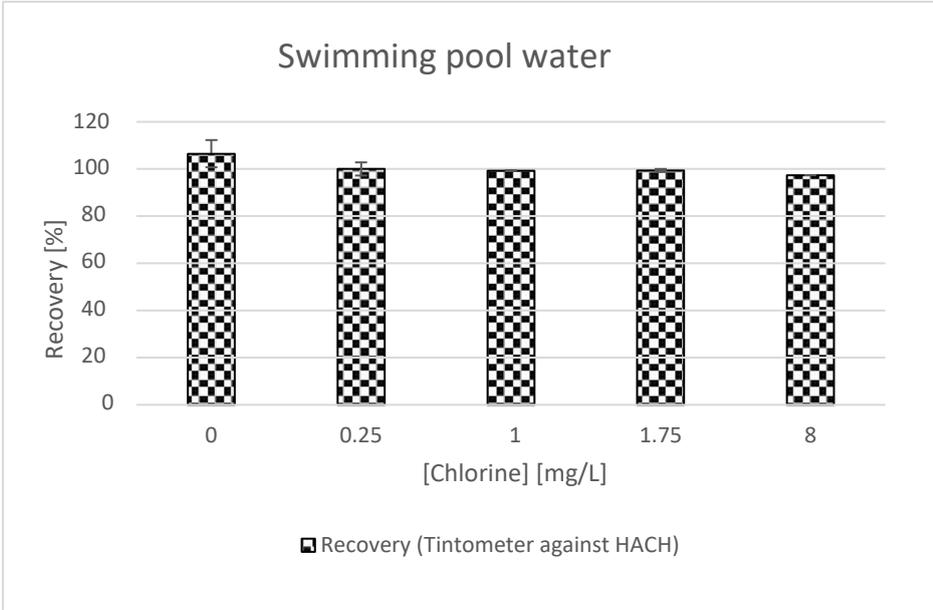


Figure 8: Recovery rates of the free chlorine in swimming pool water with different chlorine concentrations measured with “Tintometer Chlorine free DPD/F10 and F25” / “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL and 25 mL”

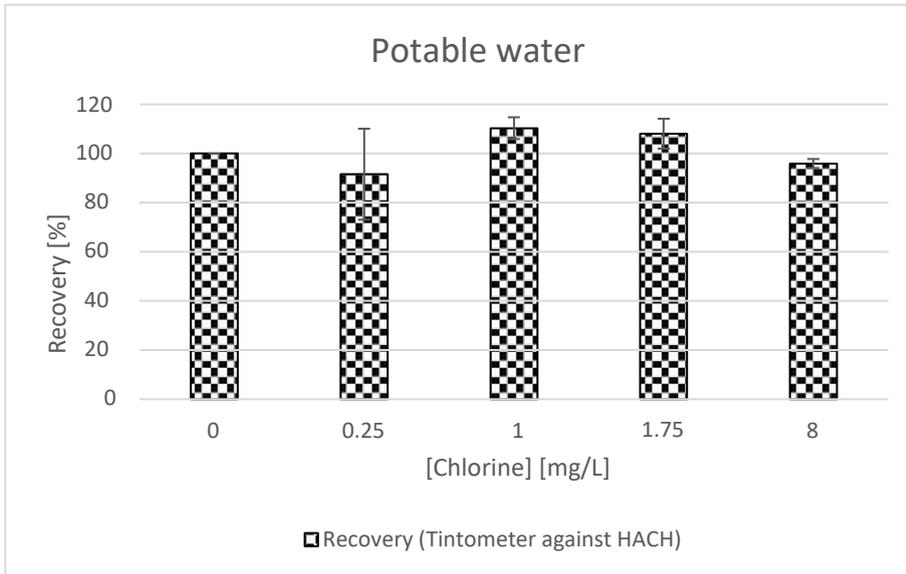


Figure 9: Recovery rates of free chlorine in potable water with different chlorine concentrations measured with “Tintometer Chlorine free DPD/F10 and F25” / “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL and 25 mL”

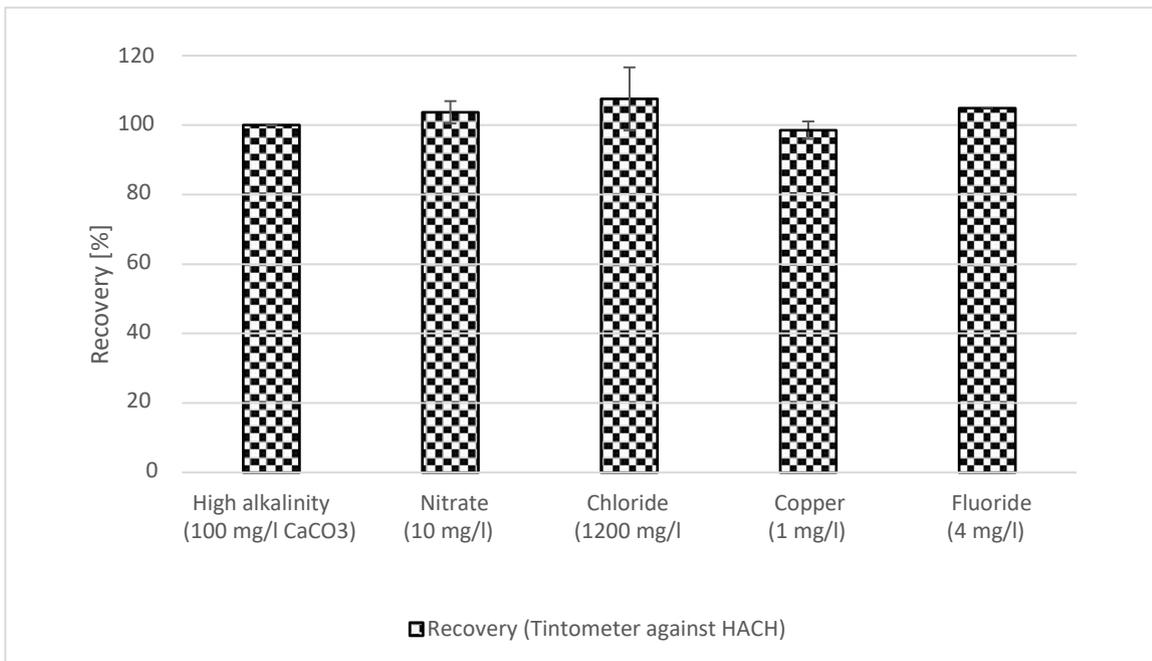


Figure 10: Recovery rates of free chlorine in waters with select contents measured with “Tintometer Chlorine free DPD/F10” in comparison to “HACH DPD Free Chlorine Reagent Powder Pillows, 10 mL” with a free chlorine concentration of 0.25 mg/L

Assessment of the standard deviation

The relative standard deviations of the free chlorine concentrations determined with the Tintometer GmbH reagents are between 0 and 13.5% for the low concentration range (0.02–2 mg/L free chlorine) and between 0 and 1.5% for the high concentration range (0.1–10 mg/L free chlorine). The relative standard deviations averaged over the respective fields of application and all examined matrices are at 2.1% for the low concentration range (0.02–2 mg/L free chlorine) and at 0.8% for the high concentration range (0.1–10 mg/L free chlorine).

The relative standard deviations of the free chlorine concentrations determined with the Hach Lange GmbH reagents are between 0 and 15.8% for the low concentration range (0.02–2 mg/L free chlorine) and between 0 and 1.4% for the high concentration range (0.1–10 mg/L free chlorine). The relative standard deviations averaged over the respective fields of application and examined matrices are at 2.3% for the low concentration range (0.02–2 mg/L free chlorine) and at 0.5% for the high concentration range (0.1–10 mg/L free chlorine).

The average relative standard deviations are illustrated in the overview in Table 2.

Table 2: Overview of the relative standard deviations (N = 3) while determining the free chlorine concentration

	Tintometer	HACH
Range of the relative standard deviations ([Cl ₂] = 0.02–2 mg/L)	0–13.5%	0–15.8%
Average relative standard deviation ([Cl ₂] = 0.02–2 mg/L)	2.1%	2.3%
Range of the relative standard deviations ([Cl ₂] = 0.1–10 mg/L)	0–1.5%	0–1.4%
Average relative standard deviation ([Cl ₂] = 0.1–10 mg/L)	0.8%	0.5%

Result

The average relative standard deviations (N = 3) determined with the reagents of Tintometer GmbH / Hach Lange GmbH are at a similar level when determining the free chlorine concentration (measurement range 0.02–2 mg/L: 2.1–2.3%; measurement range 0.1–10 mg/L: 0.5–0.8%).

The data regarding the relative standard deviations relates to the concentration ranges and aqueous matrices examined within the scope of the comparative study.

Assessment of the recovery

When **compared with the reference concentrations according to DIN EN ISO 7393-2**, the recoveries of the free chlorine concentrations determined with the **Tintometer GmbH** reagents are between 70 and 101% for the low concentration range (0.02–2 mg/L free chlorine) with standard deviations between 0 and 18%, and between 94 and 105% for the high concentration range (0.1–10 mg/L free chlorine) with standard deviations between 0 and 1.4%. Averaged over the respective fields of application, the recovery is at 93% in the low concentration range (0.02–2 mg/L free chlorine) and at 99% for the high concentration range (0.1–10 mg/L free chlorine).

When **compared with the reference concentrations according to DIN EN ISO 7393-2**, the recoveries of the free chlorine concentrations determined with the **Hach Lange GmbH** reagents are between 80 and 98% for the low concentration range (0.02–2 mg/L free chlorine) with standard deviations between 0 and 14%, and between 95 and 105% for the high concentration range (0.1–10 mg/L free chlorine) with standard deviations between 0 and 1.4%. Averaged over the respective fields of application, the recovery is at 93% in the low concentration range (0.02–2 mg/L free chlorine) and at 101% for the high concentration range (0.1–10 mg/L free chlorine).

When compared to the free chlorine concentrations determined with the **Hach Lange GmbH** reagents, the recoveries of the free chlorine concentrations determined with the **Tintometer GmbH** reagents are **between** 85 and 110% for the low concentration range (0.02–2 mg/L free chlorine) with standard deviations between 0 and 18.5%, and between 93 and 100% for the high concentration range (0.1–10 mg/L free chlorine) with standard deviations between 0 and 2.0%. Averaged over the respective fields of application, the recovery is at 100% in the low concentration range (0.02–2 mg/L free chlorine) and at 98% for the high concentration range (0.1–10 mg/L free chlorine).

The results of the recoveries are illustrated in the overview in Table 3 .

Table 3: Overview of the average recoveries while determining the free chlorine concentration

	Tintometer against reference	HACH against reference	Tintometer against HACH
Range of the recovery ([Cl ₂] = 0.02–2 mg/L)	70–101%	80–98%	85–110%
Average recovery ([Cl ₂] = 0.02–2 mg/L)	93%	93%	100%
Range of the recovery ([Cl ₂] = 0.1–10 mg/L)	94–105%	95–105%	93–100%
Average recovery ([Cl ₂] = 0.1–10 mg/L)	99%	101%	98%

Result

The differences between the average recoveries of free chlorine determined with the Tintometer GmbH reagents in comparison to the Hach Lange GmbH method are coincidental and thus not probable and not significant (P = 99%) (average recoveries 98–100%).

The data regarding the recoveries relates to the concentration ranges and aqueous matrices examined within the scope of the comparative study.

3.2 Measurement of total chlorine

Illustration of recoveries and precision of the total chlorine concentration determined with the reagents of Tintometer GmbH and Hach Lange GmbH compared to the reference method according to DIN EN ISO 7393-2 (recovery function)

In the following figures, the measurement results of the total chlorine concentration determined with the reagents of Tintometer GmbH and Hach Lange GmbH are plotted against the measurement values determined using the reference method according to DIN EN ISO 7393-2.

The measured values are each illustrated as average and standard deviations of triplicate measurements. The linear regression functions show the average recovery versus the reference concentration over the entire concentration range (recovery function).

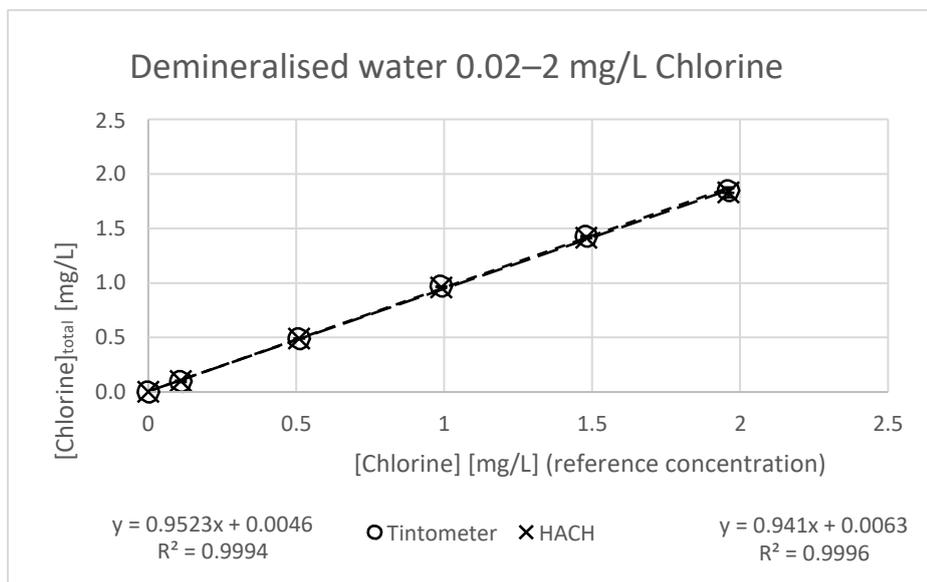


Figure 11: Recovery functions:
Total chlorine in demineralised water (0.02–2 mg/L);
Average values of the total chlorine concentration measured with “Tintometer Chlorine total DPD/F10” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

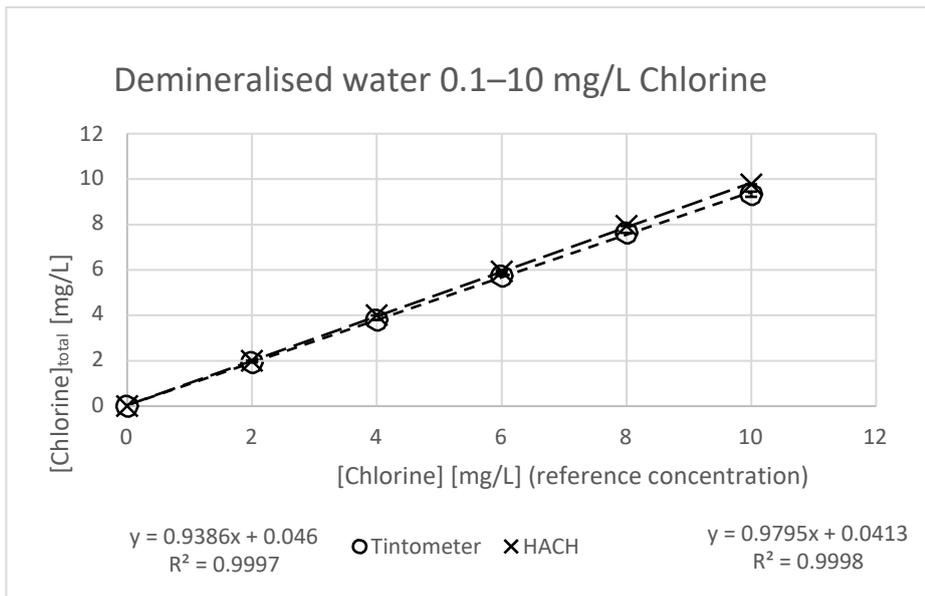


Figure 12: Recovery functions:
 Total chlorine in demineralised water (0.1–10 mg/L);
 Average values of the total chlorine concentration measured with “Tintometer Chlorine total DPD/F25” / “HACH DPD Total Chlorine Reagent Powder Pillows, 25 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

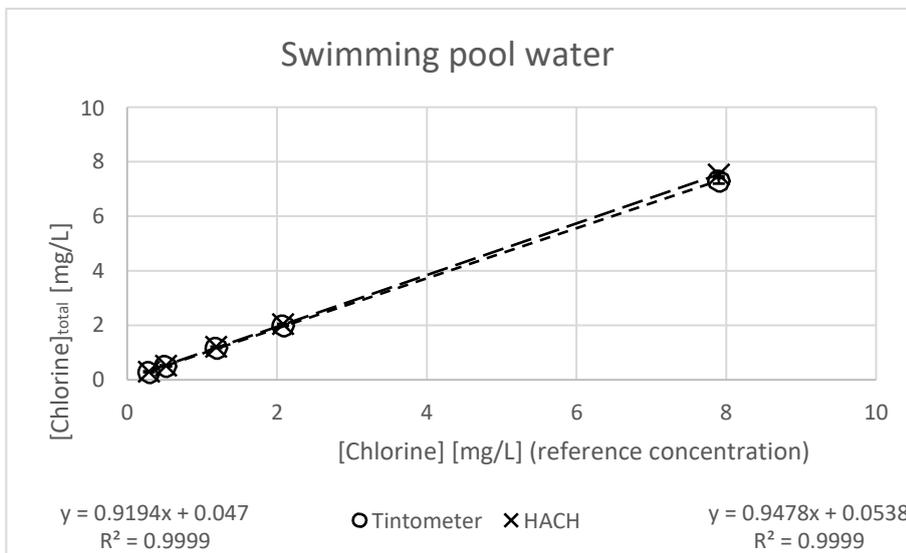


Figure 13: Recovery functions:
 Total chlorine in swimming pool water (0.25–8 mg/L);
 Average values of the total chlorine concentration measured with “Tintometer Chlorine total DPD/F10 and F25” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL and 25 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

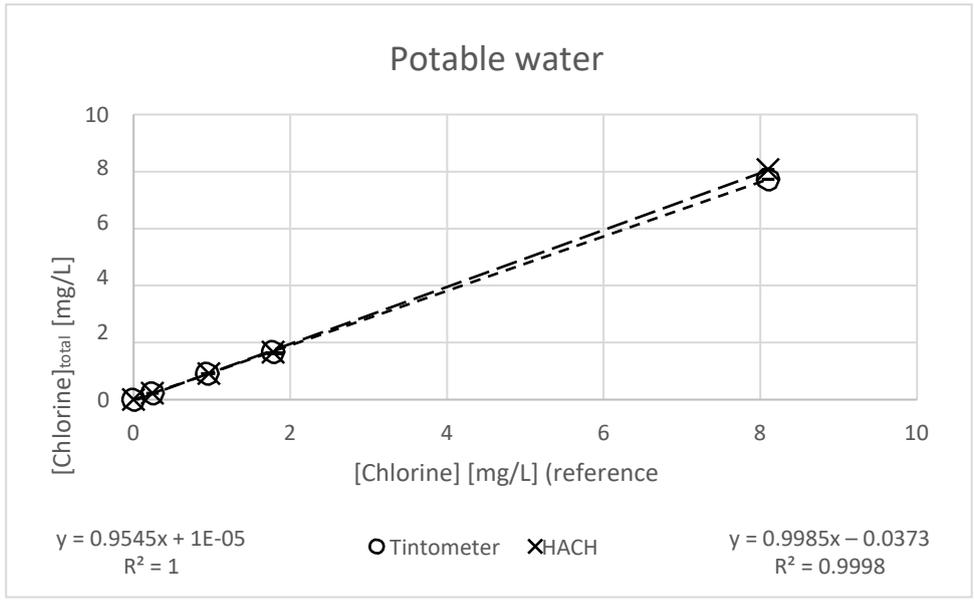


Figure 14: Recovery functions:
 Total chlorine in potable water (0.25–8 mg/L);
 Average values of the total chlorine concentration measured with “Tintometer Chlorine total DPD/F10 and F25” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL and 25 mL” plotted against the reference concentration according to DIN EN ISO 7393-2

Figure 15 shows the average values of the total chlorine concentration measured with “Tintometer Chlorine total DPD/F10” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL” in water with select contents. The target concentration is 0.25 mg/l total chlorine.

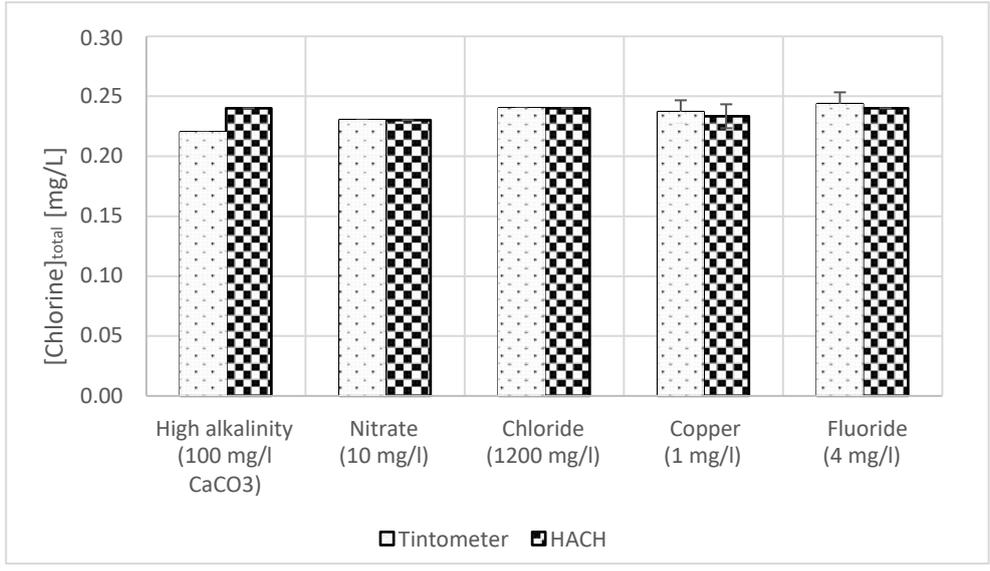


Figure 15: Average values of the total chlorine concentration in waters with select contents measured with “Tintometer Chlorine total DPD/F10” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL”

Illustration of recovery rates of the total chlorine concentration determined with the reagents of Tintometer GmbH in comparison to the Hach Lange GmbH reagents

The following figures show the percentual recovery rates of the total chlorine concentrations.

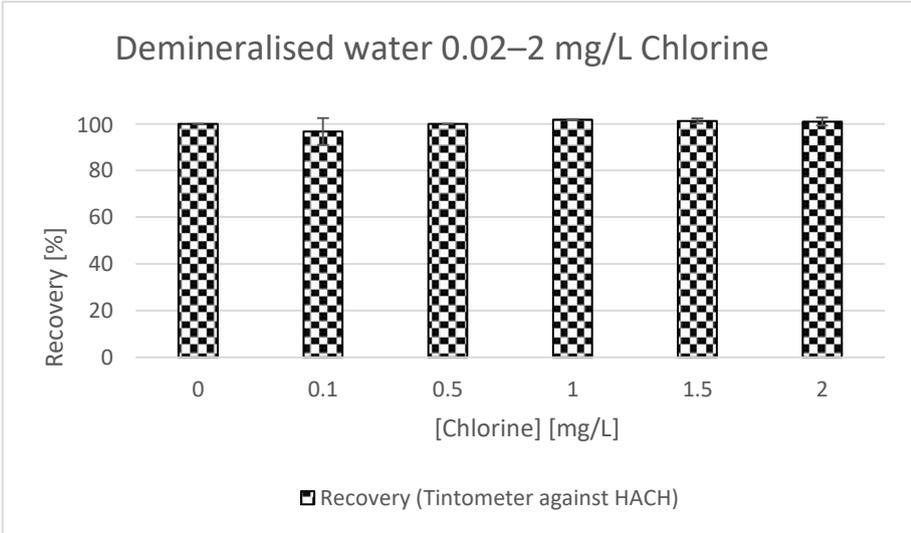


Figure 16: Recovery rates of total chlorine in demineralised water with different chlorine concentrations measured with “Tintometer total chlorine DPD/F10” in comparison to “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL”

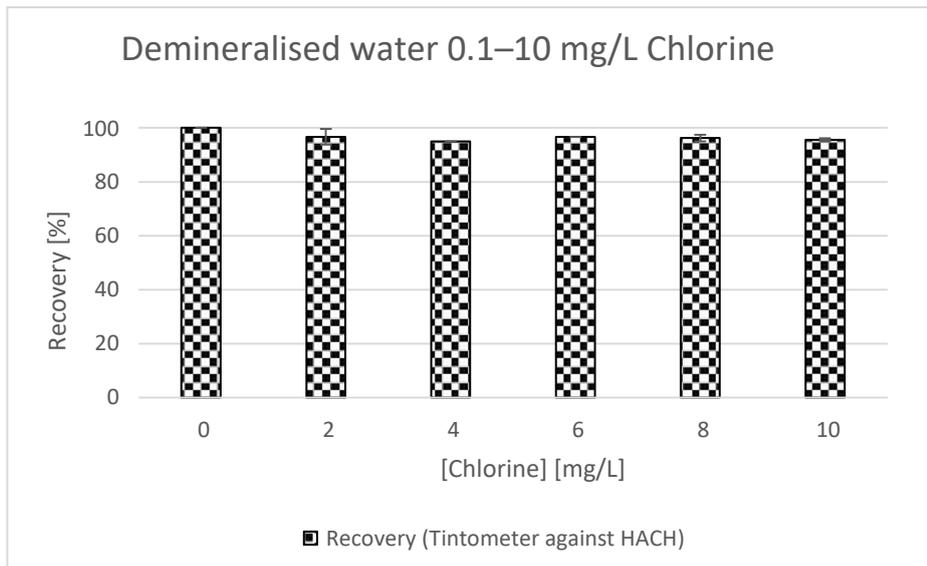


Figure 17: Recovery rates of total chlorine in demineralised water with different chlorine concentrations measured with “Tintometer total chlorine DPD/F25” in comparison to “HACH DPD Total Chlorine Reagent Powder Pillows, 25 mL”

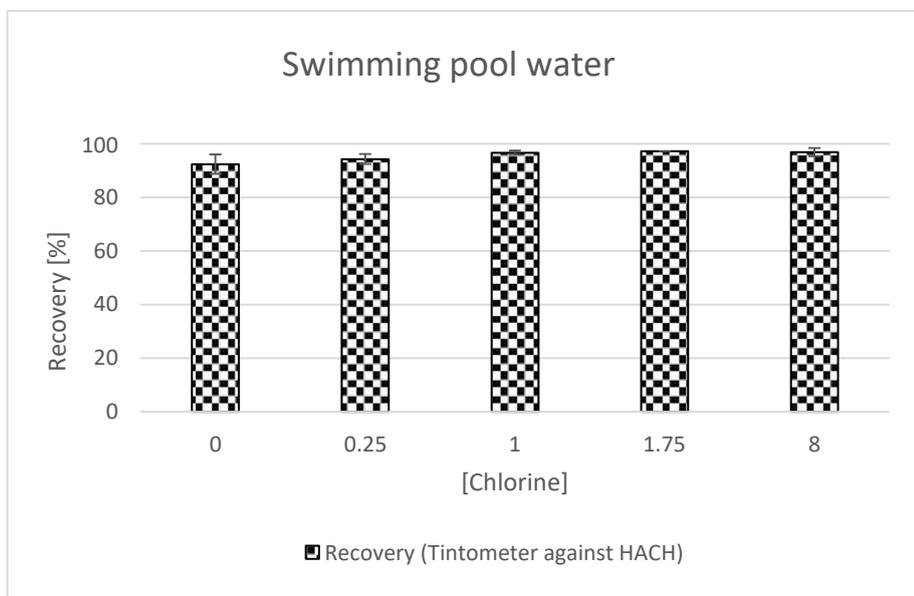


Figure 18: Recovery rates of the total chlorine in swimming pool water with different chlorine concentrations measured with “Tintometer total chlorine DPD/F10 and F25” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL and 25 mL”

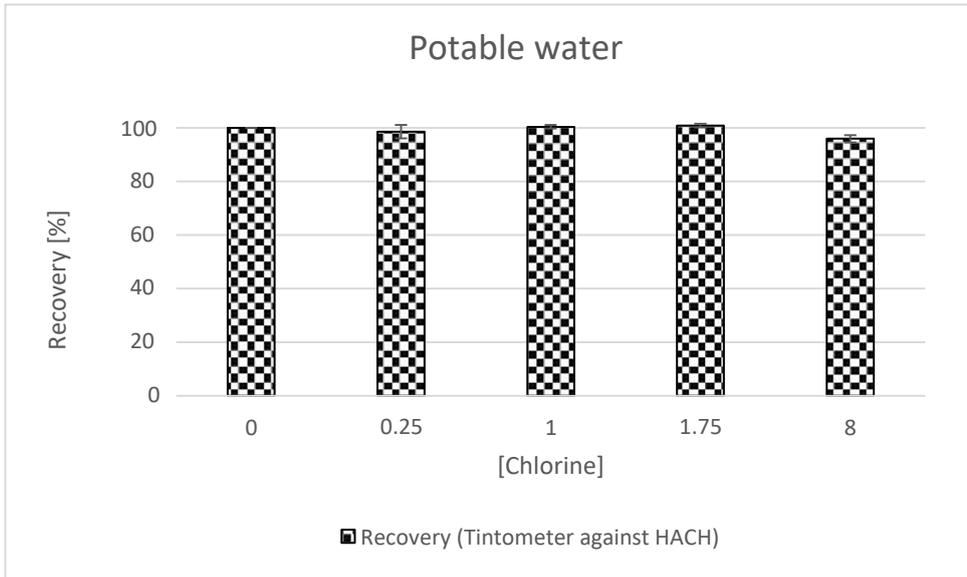


Figure 19: Recovery rates of the total chlorine in potable water with different chlorine concentrations measured with “Tintometer total chlorine DPD/F10 and F25” / “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL and 25 mL”

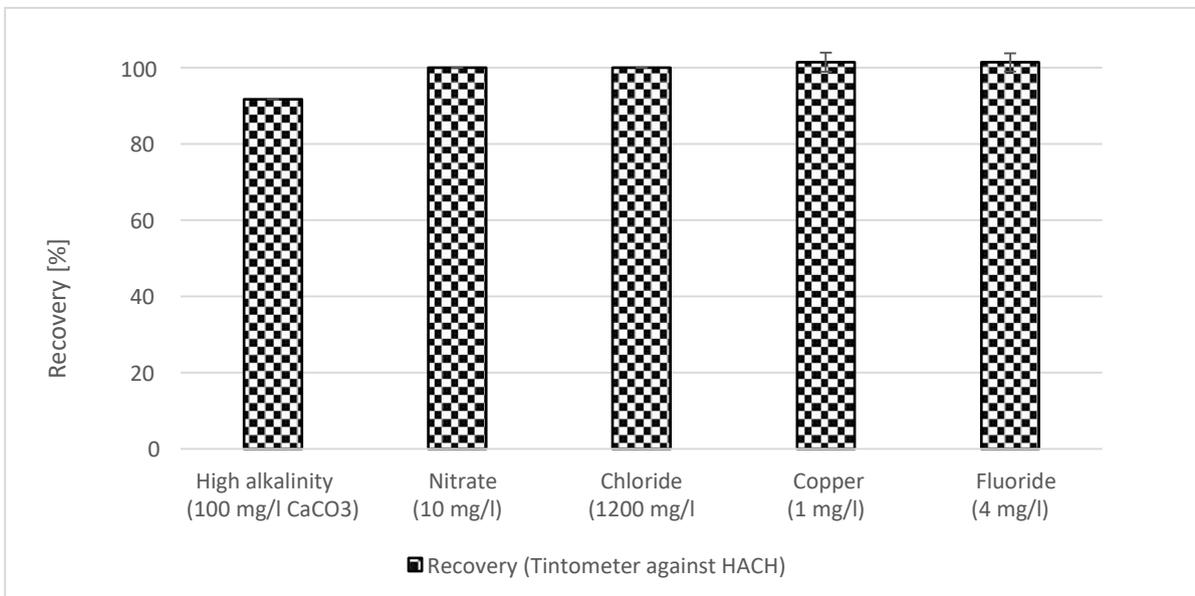


Figure 20: Recovery rates of total chlorine in waters with select contents measured with “Tintometer total chlorine DPD/F10” in comparison to “HACH DPD Total Chlorine Reagent Powder Pillows, 10 mL” with a free chlorine concentration of 0.25 mg/L

Assessment of the standard deviation of the measured values

The relative standard deviations of the total chlorine concentrations determined with the Tintometer GmbH reagents are between 0 and 6.0% for the low concentration range (0.02–2 mg/L total chlorine) and between 0 and 3.0% for the high concentration range (0.1–10 mg/L total chlorine). The relative standard deviations averaged over the respective fields of application and examined matrices are at 0.8% for the low concentration range (0.02–2 mg/L total chlorine) and at 1.0% for the high concentration range (0.1–10 mg/L total chlorine).

The relative standard deviations of the total chlorine concentrations determined with the Hach Lange GmbH reagents are between 0 and 2.5% for the low concentration range (0.02–2 mg/L total chlorine) and between 0 and 1.1% for the high concentration range (0.1–10 mg/L total chlorine). The relative standard deviations averaged over the respective fields of application and examined matrices are at 0.4 % for the low concentration range (0.02–2 mg/L total chlorine) and at 0.5 % for the high concentration range (0.1–10 mg/L total chlorine).

The standard deviations are illustrated in the overview in Table 4.

Table 4: Overview of the relative standard deviations (N = 3) while determining the total chlorine concentration

	Tintometer	HACH
Range of the relative standard deviations ([Cl ₂] = 0.02–2 mg/L)	0–6.0%	0–3.0%
Average relative standard deviation ([Cl ₂] = 0.02–2 mg/L)	0.8%	1.0%
Range of the relative standard deviations ([Cl ₂] = 0.1–10 mg/L)	0–2.5%	0–1.1%
Average relative standard deviation ([Cl ₂] = 0.1–10 mg/L)	0.4%	0.5%

Result

The average relative standard deviations (N = 3) determined with the reagents of Tintometer GmbH / Hach Lange GmbH are at a similar level when determining the total chlorine concentration (measurement range 0.02–2.0 mg/L: 0.8–1.0%; measurement range 0.1–10 mg/L: 0.4–0.5%).

The data regarding the relative standard deviations relates to the concentration ranges and aqueous matrices examined within the scope of the comparative study.

Assessment of the recovery

When **compared with those according to DIN EN ISO 7393-2**, the recoveries of the total chlorine concentrations determined with the **Tintometer GmbH** reagents are between 88 and 100% for the low concentration range (0.02–2 mg/L total chlorine) with standard deviations between 0 and 5%, and between 92 and 100% for the high concentration range (0.1–10 mg/L total chlorine) with standard deviations between 0 and 5.2%. Averaged over the respective fields of application, the recovery is at 96%.

When **compared with the reference concentrations according to DIN EN ISO 7393-2**, the recoveries of the total chlorine concentrations determined with the **Hach Lange GmbH** reagents are between 90 and 106% for the low concentration range (0.02–2 mg/L total chlorine) with standard deviations between 0 and 2.3%, and between 95 and 102% for the high concentration range (0.1–10 mg/L total chlorine) with standard deviations between 0 and 1.0%. Averaged over the respective fields of application, the recovery is at 97% in the low concentration range (0.02–2 mg/L total chlorine) and at 99% for the high concentration range (0.1–10 mg/L total chlorine).

When compared to the free chlorine concentrations determined with the **Hach Lange GmbH** reagents, the recoveries of the total chlorine concentrations determined with the **Tintometer GmbH** reagents are **between** 92 and 102% for the low concentration range (0.02–2 mg/L total chlorine) with standard deviations between 0 and 5.8%, and between 95 and 100% for the high concentration range (0.1–10 mg/L total chlorine) with standard deviations between 0 and 2.9%. Averaged over the respective fields of application, the recovery is at 99 % in the low concentration range (0.02–2 mg/L total chlorine) and at 97 % for the high concentration range (0.1–10 mg/L total chlorine).

The results of the recoveries are illustrated in the overview in Table 5.

Table 5: Overview of the recoveries while determining the total chlorine concentration

	Tintometer against reference	HACH against reference	Tintometer against HACH
Range of the recovery ([Cl ₂] = 0.02–2 mg/L)	88–100%	90–106%	92–102%
Average recovery ([Cl ₂] = 0.02–2 mg/L)	96%	97%	99%
Range of the recovery ([Cl ₂] = 0.1–10 mg/L)	92–100%	95–102%	95–100%
Average recovery ([Cl ₂] = 0.1–10 mg/L)	96%	99%	97%

Result

The differences between the recoveries of total chlorine determined with the Tintometer GmbH reagents in comparison to the Hach Lange GmbH method are coincidental and thus, not probable and not significant (P = 99%) (average recoveries 97–99%).

The data regarding the average recoveries relates to the concentration ranges and aqueous matrices examined within the scope of the comparative study.

4 Annex

List of annexes

Annex 1: Material and methods

Annex 2: Free chlorine raw data

Annex 3: Total chlorine raw data

Annex 1: Material and methods

Chemicals used

The chemicals used within this study are listed in Table 6. Table 6: Chemicals used

Chemicals	Purity	Manufacturer	Batch
Vario Chlorine Free – DPD F 10 mL		Lovibond	S09E
Vario Chlorine Free – DPD F 25 mL		Lovibond	S08G
Vario Chlorine Total – DPD F 10 mL		Lovibond	T04E
Vario Chlorine Total – DPD F 25 mL		Lovibond	S03C
DPD Free Chlorine Reagent for 10 mL Sample		HACH	A8087
DPD Free Chlorine Reagent for 25 mL Sample		HACH	A8088
DPD Total Chlorine Reagent for 10 mL Sample		HACH	A8093
DPD Total Chlorine Reagent for 25 mL Sample		HACH	A8064
Ammonium chloride (NH ₄ Cl)	99.99%	Merck	B1038943533
IC standard solution (1000 mg/L fluoride)		Roth	242625
Copper nitrate (Cu(NO ₃) ₂)	for analysis	Merck	A0963053606
Sodium chloride (NaCl)	99.99%	Merck	B1414006708
Sodium nitrate (NaNO ₃)	99.99%	Merck	B0905546 438
Sodium bicarbonate (NaHCO ₃)	for analysis	Merck	K48060929
Sodium hypochlorite solution (NaOCl solution)	approx. 13% free chlorine	Merck	K49914014 804

Characteristics of the potable and swimming pool water used as a matrix

Table 7 shows the contents of the potable and swimming pool water used as a matrix.

Table 7: Contents of the potable and swimming pool water used as a matrix

	Unit	Potable water	Swimming pool water
Conductivity (25°C)	µS/cm	591	544
pH value	-	7.93	7.10
Acid capacity	mmol/L	2.93	0.21
Chloride	mg/L	64.1	136
Nitrate	mg/L	7.48	20.5
Sulphate	mg/L	46.3	9.90
TOC	mg/L	0.77	-
Fluoride	mg/L	<0.1	<0.1
Calcium	mg/L	48.5	26.1
Magnesium	mg/L	8.23	3.08
Sodium	mg/L	55.6	70.0
Potassium	mg/L	5.29	4.09
Iron	mg/L	<0.010	<0.010
Manganese	mg/L	<0.010	<0.010
Copper	mg/L	0.013	<0.0020
Phosphorus, total	mg/L	0.11	<0.10
Lead	mg/L	<0.002	<0.002
Nickel	mg/L	<0.0020	<0.002
Chromium	mg/L	<0.00050	0.00073
Cadmium	mg/L	<0.0002	<0.0002
Silicon	mg/L	3.07	8.08
Oxidizability	mg/L O ₂	-	0.34

Estimate of the synthetic matrices

The synthetic matrices were estimated according to the schema in

Table 8. The acid capacity (K_s) was determined with the automatic titration system Robotic Titrosampler 855 (Metrohm). The concentration of anions chloride, nitrate and fluoride was determined using the ion chromatograph DX 500 (Dionex). The copper concentration was determined with the ICP-OES Agilent 5110 (Agilent).

Table 8: Estimate schema for the synthetic matrices (chemicals Table 6)

	Target concentration	Volume	Sample weight	Measured concentration
High alkalinity (CaCO₃)	100 mg/L (\cong 2 mmol/L K_s)	2 L	0.336 g NaHCO ₃	$K_s = 2.09$ mmol/L
Chloride	1200 mg/L	1 L	1.9782 g NaCl	1211 mg/L
Nitrate	10 mg/L	1 L	1.368 g NaNO ₃	10.4 mg/L
Copper	1 mg/L	1 L	3.802g (Cu(NO ₃) ₂)	1.06 mg/L
Fluoride	4 mg/L	1 L	4 mL fluoride solution	4.1 mg/L

Preparing the “free chlorine” test solutions

Two stock solutions (one containing 0.1% free chlorine and the other containing 100 mg/L free chlorine) were prepared every measurement day by dissolution of a commercially available approx. 13% hypochlorite solution. The concentration of the 100 mg/L stock solution was determined through a measurement of the solution in a 1:100 dilution with a method accredited at IWW according to DIN EN ISO 7393-2 (DPD method). The required test solutions were prepared under consideration of the actual concentration in stock solution 2 determined in this manner.

All glassware used had to be free of chlorine. It is stored in a 0.1% hypochlorite solution for approx. 24 hours for this purpose.

Preparing the “total chlorine” test solutions

Stock solutions containing 2.7-3.3 mg/L (stock solution 1) and 27-33 mg/L (stock solution 2) of total chlorine were prepared every measurement day. Therefore, at first the pH value of 2 L of potable water was adjusted to 9 +/- 0.25 by means of NaOH. After the addition of 2 mL (for stock solution 1) and 20 mL (for stock solution 2) of a 2 g/L NH₄Cl solution and 6.64 mL (for stock solution 1) and 66.4 mL (for stock solution 2) of a 0.1% sodium hypochlorite solution, the mixtures were stirred for one hour. The total chlorine concentration of the stock solutions was determined in a suitable dilution with the IWW-accredited method according to DIN EN ISO 7393-2 (DPD method), and the required test solutions were prepared in the corresponding matrices based on these actual concentrations.

All glassware used was rendered chlorine-free before use by storing it in a 0.1% hypochlorite solution for approx. 24 hours.

Performing the measurements

The vials to be used were rendered chlorine-free before use by storing them in a 0.1% hypochlorite solution for approx. 24 hours. Separate vials are used for the measurement of free chlorine and total chlorine.

The samples were measured using the Hach DR 900. The following methods were used:

- Chlorine, Free 0.02 to 2.00 mg/L Cl₂; Method 8021, Programme 80 Chlorine F&T PP (DOC316.53.01023)
- Chlorine, Free 0.1 to 10.0 mg/L Cl₂; Method 10069, Programme 88 Chlorine F&T HR (DOC316.53.01025)
- Chlorine, Total 0.02 to 2.00 mg/L Cl₂; Method 8167, Programme 80 Chlorine F&T PP (DOC316.53.01027)
- Chlorine, Total 0.1 to 10.0 mg/L Cl₂; Method 10070, Programme 88 Chlorine F&T HR, (DOC316.53.01029)

Statistical evaluation

The statistical evaluation of the data was carried out via the average t test (see formulae A1 and A2)

$$TV = \left| \frac{\bar{x}_1 - \bar{x}_2}{s_d} \right| \times \sqrt{\frac{N_1 \times N_2}{N_1 + N_2}} \quad (A1)$$

With TV = test value, \bar{x} average of the multiple determination, N = number of multiple determinations per concentration, matrix and reagent (N = 3), s_d = average standard deviation of two series of analyses.

$$s_d = \sqrt{\frac{(N_1 - 1) \times s_1^2 + (N_2 - 1) \times s_2^2}{N_1 + N_2 - 2}}$$

With s = standard deviation.

Decision:

$TV \leq t(f, P = 95\%)$: coincidental difference

$t(f, P = 95\%) < TV \leq t(f, P = 99\%)$: probable difference

$TV > t(f, P = 99\%)$: significant difference

Annex 2: Free chlorine raw data

Table 9: Raw data ultrapure water, measurement range 0.02–2 mg/L, Tintometer

Matrix: Ultrapure water	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T10	0	0	0	0	0	0	0	0	-0.02	-0.01	-0.01	-0.01	0.010	-43.3
	T10	0.1	0.11	0.07	0.08	0.08	0.08	0.01	7.5	0.039	0.047	0.049	0.045	0.005	11.8
	T10	0.5	0.51	0.47	0.48	0.48	0.48	0.01	1.2	0.274	0.281	0.280	0.278	0.004	1.4
	T10	1.0	1.03	0.97	0.96	0.96	0.96	0.01	0.6	0.563	0.560	0.559	0.561	0.002	0.4
	T10	1.5	1.53	1.47	1.47	1.46	1.47	0.01	0.4	0.853	0.857	0.850	0.853	0.004	0.4
	T10	2.0	2.10	1.94	1.92	1.93	1.93	0.01	0.5	1.126	1.107	1.120	1.118	0.010	0.9

Table 10: Raw data ultrapure water, measurement range 0.1–10 mg/L, Tintometer

Matrix: Ultrapure water	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T25	0	-	0	0	0	0	0	0	0.012	0.016	0.004	0.011	0.006	57.3
	T25	2.0	-	2.1	2.1	2.1	2.1	0	0	0.531	0.530	0.535	0.532	0.003	0.5
	T25	4.0	-	4.0	4.0	4.1	4.03	0.06	1.4	1.019	0.999	1.040	1.019	0.021	2.0
	T25	6.0	-	6.0	5.9	6.0	5.97	0.06	1.0	1.484	1.465	1.482	1.477	0.010	0.7
	T25	8.0	-	7.9	7.8	7.8	7.83	0.06	0.7	1.908	1.886	1.899	1.898	0.011	0.6
	T25	10.0	-	9.3	9.5	9.5	9.43	0.12	1.2	2.229	2.267	2.279	2.258	0.026	1.2

Table 11: Raw data swimming pool water, Tintometer

Matrix: Swimming pool water	Reagent	Target conc. Free chlorine	Reference conc.	[CI] 1	[CI] 2	[CI] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[CI] 1	[CI] 2	[CI] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T10	0	0.12	0.10	0.11	0.13	0.11	0.02	13.5	0.056	0.066	0.078	0.067	0.011	16.5
	T10	0.25	0.36	0.34	0.35	0.37	0.35	0.02	4.3	0.200	0.204	0.213	0.206	0.007	3.2
	T10	1.0	0.98	0.94	0.93	0.94	0.94	0.01	0.6	0.546	0.542	0.544	0.544	0.002	0.4
	T10	1.75	1.60	1.54	1.54	1.55	1.54	0.01	0.4	0.893	0.893	0.899	0.895	0.003	0.4
	T25	8.0	7.70	7.5	7.4	7.4	7.43	0.06	0.8	1.831	1.810	1.797	1.813	0.017	0.9

Table 12: Raw data potable water, Tintometer

Matrix: Potable water	Reagent	Target conc. Free chlorine	Reference conc.	[CI] 1	[CI] 2	[CI] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[CI] 1	[CI] 2	[CI] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T10	0	0	0	0	0	0	0	0.0	-0.002	-0.007	-0.008	-0.006	0.003	-56.7
	T10	0.25	0.24	0.18	0.17	0.17	0.017	0.01	3.3	0.106	0.097	0.102	0.102	0.005	4.4
	T10	1.0	1.05	0.98	0.96	0.97	0.97	0.01	1.0	0.569	0.555	0.563	0.562	0.007	1.2
	T10	1.75	1.79	1.70	1.67	1.69	1.69	0.02	0.9	0.990	0.971	0.981	0.981	0.010	1.0
	T25	8.0	8.1	7.9	7.7	7.9	7.83	0.12	1.5	1.923	1.872	1.917	1.904	0.028	1.5

Table 13: Raw data synthetic matrices, Tintometer

Matrix	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
High alkalinity	T10	0	<0.03	0	0	0	0	0	0	-0.013	-0.002	0.000	-0.005	0.007	-140.0
High alkalinity	T10	0.25	0.24	0.20	0.21	0.21	0.21	0.01	2.8	0.116	0.122	0.121	0.120	0.003	2.7
Nitrate	T10	0	<0.03	0	0	0	0	0	0	0.004	0.003	0.002	0.003	0.001	33.3
Nitrate	T10	0.25	0.22	0.19	0.19	0.17	0.18	0.01	6.3	0.112	0.113	0.100	0.108	0.007	6.7
Chloride	T10	0	<0.03	0	0	0	0	0	0	-0.009	-0.010	-0.005	-0.008	0.003	-33.1
Chloride	T10	0.25	0.24	0.21	0.21	0.20	0.21	0.01	2.8	0.121	0.120	0.116	0.119	0.003	2.2
Copper	T10	0	<0.03	0	0	0	0	0	0	-0.010	-0.007	-0.007	-0.008	0.002	-21.7
Copper	T10	0.25	0.26	0.22	0.21	0.22	0.22	0.01	2.7	0.130	0.122	0.130	0.127	0.005	3.6
Fluoride	T10	0	<0.03	0	0	0	0	0	0	-0.007	-0.019	-0.009	-0.012	0.006	-55.1
Fluoride	T10	0.25	0.25	0.22	0.21	0.22	0.22	0.01	2.7	0.126	0.122	0.125	0.124	0.002	1.7

Table 14: Raw data ultrapure water, measurement range 0.02–2 mg/L, HACH

Matrix: Ultrapure water	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H10	0	0	0	0	0	0	0	0	-0.005	-0.008	-0.007	-0.007	0.002	-22.9
	H10	0.1	0.11	0.09	0.09	0.09	0.09	0	0	0.053	0.054	0.054	0.054	0.001	1.1
	H10	0.5	0.51	0.50	0.50	0.50	0.50	0	0	0.289	0.289	0.290	0.289	0.001	0.2
	H10	1.0	1.03	0.98	0.97	0.97	0.97	0.01	0.6	0.570	0.566	0.566	0.567	0.002	0.4
	H10	1.5	1.53	1.45	1.47	1.48	1.47	0.02	1.0	0.842	0.857	0.862	0.854	0.010	1.2
	H10	2.0	2.1	1.98	1.98	1.98	1.98	0	0	1.150	1.151	1.149	1.150	0.001	0.1

Table 15: Raw data ultrapure water, measurement range 0.1–10 mg/L, HACH

Matrix: Ultrapure water	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H25	0	-	0	0	0	0	0	0	0.019	0.015	0.009	0.014	0.005	35.1
	H25	2.0	-	2.1	2.1	2.1	2.1	0	0	0.547	0.537	0.541	0.542	0.005	0.9
	H25	4.0	-	4.0	4.1	4.1	4.1	0.1	1.4	1.008	1.037	1.026	1.024	0.015	1.4
	H25	6.0	-	6.0	6.0	6.0	6.0	0	0	1.491	1.489	1.487	1.489	0.002	0.1
	H25	8.0	-	8.1	8.1	8.1	8.1	0	0	1.957	1.953	1.966	1.959	0.007	0.3
	H25	10.0	-	10.2	10.1	10.0	10.1	0.1	1.0	2.421	2.393	2.383	2.399	0.020	0.8

Table 16: Raw data swimming pool water, HACH

Matrix: Swimming pool water	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H10	0	0.12	0.09	0.11	0.12	0.11	0.02	14.3	0.054	0.062	0.070	0.062	0.008	12.9
	H10	0.25	0.37	0.34	0.36	0.36	0.35	0.01	3.3	0.196	0.209	0.210	0.205	0.008	3.8
	H10	1.0	0.96	0.95	0.94	0.94	0.94	0.01	0.6	0.550	0.546	0.546	0.547	0.008	0.4
	H10	1.75	1.60	1.55	1.56	1.55	1.55	0.01	0.4	0.898	0.908	0.900	0.902	0.005	0.6
	H25	8.0	7.7	7.7	7.6	7.6	7.63	0.06	0.8	1.875	1.848	1.859	1.861	0.014	0.7

Table 17: Raw data potable water, HACH

Matrix: Potable water	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H10	0	0	0	0	0	0	0	0	-0.010	-0.006	-0.012	-0.009	0.003	-32.7
	H10	0.25	0.22	0.16	0.22	0.20	0.19	0.03	15.8	0.093	0.128	0.119	0.113	0.018	16.0
	H10	1.0	0.98	0.91	0.89	0.84	0.88	0.04	4.1	0.530	0.571	0.485	0.529	0.043	8.1
	H10	1.75	1.76	1.48	1.62	1.59	1.56	0.07	4.7	0.859	0.940	0.922	0.907	0.043	4.7
	H25	8.0	8.2	8.1	8.2	8.2	8.17	0.06	0.7	1.963	1.984	1.977	1.975	0.011	0.5

Table 18: Raw data synthetic matrices, HACH

Matrix	Reagent	Target conc. Free chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
High alkalinity	H10	0	<0.03	0	0	0	0	0	0	-0.018	-0.009	-0.006	-0.011	0.006	-56.8
High alkalinity	H10	0.25	0.23	0.20	0.21	0.21	0.21	0.01	2.8	0.114	0.123	0.122	0.120	0.005	4.1
Nitrate	H10	0	<0.03	0	0	0	0	0	0	0.001	0.001	0.000	0.001	0.001	86.6
Nitrate	H10	0.25	0.20	0.18	0.18	0.17	0.18	0.01	3.3	0.105	0.107	0.098	0.103	0.005	4.6
Chloride	H10	0	<0.03	0	0	0	0	0	0	-0.010	-0.007	-0.014	-0.010	0.004	-34.0
Chloride	H10	0.25	0.24	0.21	0.20	0.17	0.19	0.02	10.8	0.120	0.119	0.100	0.113	0.011	10.0
Copper	H10	0	<0.03	0	0	0	0	0	0	-0.008	0.009	-0.016	-0.011	0.004	39.6
Copper	H10	0.25	0.25	0.22	0.21	0.23	0.22	0.01	4.6	0.129	0.123	0.133	0.128	0.005	3.9
Fluoride	H10	0	<0.03	0	0	0	0	0	0	-0.010	-0.019	-0.009	-0.013	0.006	-43.5
Fluoride	H10	0.25	0.23	0.21	0.20	0.21	0.21	0.01	2.8	0.123	0.117	0.124	0.121	0.004	3.1

Annex 3: Total chlorine raw data

Table 19: Raw data ultrapure water, measurement range 0.02–2 mg/L, Tintometer

Matrix: Ultrapur e water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avrg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avrg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T10	0	0	0	0	0	0	0	0	0.000	-0.001	0.000	0.000	0.001	-173.2
	T10	0.1	0.11	0.10	0.09	0.10	0.10	0.01	6.0	0.059	0.055	0.057	0.057	0.002	3.5
	T10	0.5	0.51	0.49	0.49	0.49	0.49	0	0	0.287	0.284	0.286	0.286	0.002	0.5
	T10	1.0	0.99	0.98	0.97	0.97	0.97	0.01	0.6	0.570	0.565	0.562	0.566	0.004	0.7
	T10	1.5	1.48	1.43	1.43	1.43	1.43	0	0	0.832	0.830	0.832	0.831	0.001	0.1
	T10	2.0	1.96	1.87	1.83	1.84	1.85	0.02	1.1	1.089	1.063	1.071	1.074	0.013	1.2

Table 20: Raw data ultrapure water, measurement range 0.1–10 mg/L, Tintometer

Matrix: Ultrapur e water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avrg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avrg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T25	0	0	0	0	0	0	0	0	0.014	0.012	0.014	0.013	0.001	8.7
	T25	2.0	2.0	1.9	1.9	2.0	1.93	0.06	3.0	0.503	0.504	0.505	0.504	0.001	0.2
	T25	4.0	3.92	3.8	3.8	3.8	3.80	0	0	0.965	0.969	0.968	0.967	0.002	0.2
	T25	6.0	6.0	5.8	5.7	5.7	5.73	0.06	1.0	1.429	1.422	1.418	1.423	0.006	0.4
	T25	8.0	8.0	7.7	7.6	7.6	7.63	0.06	0.8	1.860	1.851	1.838	1.850	0.011	0.6
	T25	10.0	10.0	9.4	9.4	9.2	9.33	0.12	1.2	2.254	2.253	2.207	2.238	0.027	1.2

Table 21: Raw data swimming pool water, Tintometer

Matrix: Swimming pool water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T10	0	0.29	0.29	0.28	0.28	0.28	0.01	2.0	0.167	0.166	0.164	0.166	0.002	0.9
	T10	0.25	0.51	0.50	0.50	0.49	0.50	0.01	1.2	0.291	0.292	0.287	0.290	0.003	0.9
	T10	1.0	1.19	1.17	1.17	1.17	1.17	0	0	0.680	0.682	0.682	0.681	0.001	0.2
	T10	1.75	2.08	1.99	2.00	1.98	1.99	0.01	0.5	1.157	1.163	1.154	1.158	0.005	0.4
	T25	8.0	7.9	7.3	7.4	7.2	7.3	0.10	1.4	1.788	1.796	1.755	1.780	0.022	1.2

Table 22: Raw data potable water, Tintometer

Matrix: Potable water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	T10	0	0	0	0	0	0	0	0	-0.002	0.001	-0.002	-0.001	0.002	-173.2
	T10	0.25	0.24	0.23	0.22	0.23	0.23	0.01	2.6	0.135	0.130	0.131	0.132	0.003	2
	T10	1.0	0.94	0.82	0.91	0.92	0.92	0.01	0.6	0.535	0.531	0.534	0.533	0.002	0.4
	T10	1.75	1.78	1.68	1.68	1.68	1.68	0	0	0.979	0.978	0.978	0.978	0.001	0.1
	T25	8.0	8.1	7.8	7.7	7.7	7.73	0.06	0.8	1.886	1.873	1.882	1.880	0.007	0.4

Table 23: Raw data synthetic matrices, Tintometer

Matrix	Reagent	Target conc. Total chlorine	Reference conc.	[C] 1	[C] 2	[C] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[C] 1	[C] 2	[C] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
High alkalinity	T10	0	0	0	0	0	0	0	0	0.005	0.005	0.004	0.005	0.001	12.4
High alkalinity	T10	0.25	0.24	0.22	0.22	0.22	0.22	0	0	0.126	0.126	0.128	0.127	0.001	0.9
Nitrate	T10	0	0	0	0	0	0	0	0	-0.002	-0.006	0.000	-0.003	0.003	-114.6
Nitrate	T10	0.25	0.25	0.23	0.23	0.23	0.23	0	0	0.134	0.132	0.135	0.134	0.002	1.1
Chloride	T10	0	0	0	0	0	0	0	0	-0.006	0.003	0.001	-0.001	0.005	-708.9
Chloride	T10	0.25	0.26	0.24	0.24	0.24	0.24	0	0	0.142	0.140	0.138	0.140	0.002	1.4
Copper	T10	0	0	0	0	0	0	0	0	0.000	0.001	0.002	0.001	0.001	100
Copper	T10	0.25	0.26	0.24	0.24	0.23	0.24	0.01	2.4	0.138	0.138	0.135	0.137	0.002	1.26
Fluoride	T10	0	0	0	0	0	0	0	0	0.002	0.002	0.002	0.002	0.000	0
Fluoride	T10	0.25	0.26	0.25	0.24	0.24	0.24	0.01	0.4	0.143	0.141	0.139	0.141	0.002	1.4

Table 24: Raw data ultrapure water, measurement range 0.02–2 mg/L, HACH

Matrix: Ultrapure water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H10	0	0	0	0	0	0	0	0	-0.001	0.000	-0.002	-0.001	0.001	-100.0
	H10	0.1	0.11	0.10	0.10	0.10	0.1	0	0	0.056	0.061	0.056	0.058	0.003	5.0
	H10	0.5	0.51	0.49	0.49	0.49	0.49	0	0	0.287	0.284	0.287	0.286	0.002	0.6
	H10	1.0	0.99	0.96	0.96	0.95	0.96	0.01	0.6	0.561	0.557	0.555	0.558	0.003	0.6
	H10	1.5	1.48	1.43	1.41	1.40	1.41	0.02	1.1	0.831	0.818	0.813	0.821	0.009	1.1
	H10	2.0	1.96	1.88	1.82	1.79	1.83	0.05	2.5	1.094	1.057	1.042	1.064	0.027	2.5

Table 25: Raw data ultrapure water, measurement range 0.1–10 mg/L, HACH

Matrix: Ultrapure water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H25	0	0	0	0	0	0	0	0	0.014	0.015	0.015	0.015	0.001	3.9
	H25	2.0	2.0	2.0	2.0	2.0	2.0	0	0	0.524	0.527	0.525	0.525	0.002	0.3
	H25	4.0	4.0	4.0	4.0	4.0	4.0	0	0	1.014	1.004	1.002	1.007	0.006	0.6
	H25	6.0	6.0	6.0	5.9	5.9	5.93	0.06	1.0	1.484	1.471	1.465	1.473	0.010	0.7
	H25	8.0	8.0	7.9	8.0	7.9	7.93	0.06	0.7	1.921	1.928	1.925	1.925	0.004	0.2
	H25	10.0	10.0	9.8	9.8	9.7	9.77	0.06	0.6	2.337	2.344	2.310	2.330	0.018	0.8

Table 26: Raw data swimming pool water, HACH

Matrix: Swimming pool water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H10	0	0.29	0.30	0.31	0.31	0.31	0.01	1.9	0.177	0.180	0.180	0.179	0.002	1.0
	H10	0.25	0.52	0.52	0.53	0.53	0.53	0.01	1.1	0.305	0.308	0.3077	0.307	0.002	0.5
	H10	1.0	1.19	1.21	1.22	1.20	1.21	0.01	0.8	0.701	0.707	0.700	0.703	0.004	0.5
	H10	1.75	2.08	2.05	2.05	2.04	2.05	0.01	0.3	1.190	1.194	1.187	1.190	0.004	0.3
	H25	8.0	7.9	7.6	7.5	7.5	7.53	0.06	0.8	1.850	1.836	1.835	1.840	0.008	0.5

Table 27: Raw data potable water, HACH

Matrix: Potable water	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	[%]
	H10	0	0	0	0	0	0	0	0	0.001	-0.002	-0.002	-0.001	0.002	-173.2
	H10	0.25	0.24	0.23	0.23	0.23	0.23	0	0	0.135	0.132	0.132	0.133	0.002	1.3
	H10	1.0	0.96	0.91	0.91	0.92	0.91	0.01	0.6	0.527	0.529	0.535	0.530	0.004	0.8
	H10	1.75	1.78	1.66	1.66	1.68	1.67	0.01	0.7	0.964	0.965	0.975	0.968	0.006	0.6
	H25	8.0	8.1	8.0	8.1	8.1	8.07	0.06	0.7	1.946	1.964	1.960	1.957	0.009	0.5

Table 28: Raw data synthetic matrices, HACH

Matrix	Reagent	Target conc. Total chlorine	Reference conc.	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation	[Cl] 1	[Cl] 2	[Cl] 3	Avg.	Abs. standard deviation	Rel. standard deviation
		[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[%]	Ext.	Ext.	Ext.	Ext.	Ext.	Ext.
High alkalinity	H10	0	0	0	0	0	0	0	0	0.005	0.005	0.004	0.005	0.001	12.4
High alkalinity	H10	0.25	0.24	0.24	0.24	0.24	0.24	0	0	0.137	0.141	0.139	0.139	0.002	1.4
Nitrate	H10	0	0	0	0	0	0	0	0	-0.008	-0.005	-0.004	-0.006	0.002	-36.7
Nitrate	H10	0.25	0.25	0.23	0.23	0.23	0.23	0	0	0.135	0.133	0.134	0.134	0.001	0.8
Chloride	H10	0	0	0	0	0	0	0	0	-0.006	0.000	0.000	-0.002	0.003	-173.2
Chloride	H10	0.25	0.26	0.24	0.24	0.24	0.24	0	0	0.138	0.139	0.138	0.138	0.001	0.4
Copper	H10	0	0	0	0	0	0	0	0	0.003	0.004	0.001	0.003	0.002	57.3
Copper	H10	0.25	0.26	0.24	0.23	0.23	0.23	0.01	2.5	0.139	0.136	0.134	0.136	0.003	1.9
Fluoride	H10	0	0	0	0	0	0	0	0	0.002	0.001	0.001	0.001	0.001	43.3
Fluoride	H10	0.25	0.26	0.24	0.24	0.24	0.24	0	0	0.139	0.138	0.138	0.138	0.001	0.4

Table 29: statistical evaluation of free chlorine ($t_{f=4, P=95\%} = 2.776$; $t_{f=4, P=99\%} = 4.604$)

Matrix	Target concentration	\bar{x} (Tintometer) (N = 3)	s(Tintometer)	\bar{x} (HACH) (N = 3)	s(HACH)	TV
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	
Ultrapure water	0	0.00	0.00	0.00	0.00	-
Ultrapure water	0.1	0.08	0.01	0.09	0.00	0.304
Ultrapure water	0.5	0.48	0.01	0.50	0.00	0.512
Ultrapure water	1.0	0.96	0.01	0.97	0.01	0.161
Ultrapure water	1.5	1.47	0.01	1.47	0.02	0.00
Ultrapure water	2.0	1.93	0.01	1.98	0.00	0.866
Ultrapure water	0	0.00	0.00	0.00	0.00	-
Ultrapure water	2.0	2.10	0.00	2.10	0.00	-
Ultrapure water	4.0	4.03	0.06	4.07	0.06	0.170
Ultrapure water	6.0	5.97	0.06	6.00	0.00	0.240
Ultrapure water	8.0	7.83	0.06	8.10	0.00	1.922
Ultrapure water	10.0	9.43	0.12	10.10	0.10	2.488
Swimming pool water	0	0.11	0.02	0.11	0.02	0.066
Swimming pool water	0.25	0.3	0.01	0.35	0.01	0
Swimming pool water	1.0	0.94	0.01	0.94	0.01	0.107
Swimming pool water	1.75	1.54	0.01	1.55	0.01	0.161
Swimming pool water	8.0	7.43	0.06	7.63	0.06	1.019
Potable water	0	0.00	0.00	0.00	0.00	-

Matrix	Target concentration	\bar{x} (Tintometer) (N = 3)	s(Tintometer)	\bar{x} (HACH) (N = 3)	s(HACH)	TV
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	
Potable water	0.25	0.17	0.01	0.19	0.03	0.182
Potable water	1.0	0.97	0.01	0.88	0.04	0.726
Potable water	1.75	1.69	0.02	1.56	0.07	0.716
Potable water	8.0	7.83	0.12	8.17	0.06	1.387
High alkalinity	0	0.00	0.00	0.00	0.00	-
High alkalinity	0.25	0.21	0.01	0.21	0.01	0.00
Nitrate	0	0.00	0.00	0.00	0.00	-
Nitrate	0.25	0.18	0.01	0.18	0.01	0.088
Chloride	0	0.00	0.00	0.00	0.00	-
Chloride	0.25	0.21	0.01	0.19	0.02	0.142
Copper	0	0.00	0.00	0.00	0.00	-
Copper	0.25	0.22	0.01	0.22	0.01	0.046
Fluoride	0	0.00	0.00	0.00	0.00	-
Fluoride	0.25	0.22	0.01	0.21	0.01	0.161

Table 30: statistical evaluation of total chlorine ($t_{f=4, P=95\%} = 2.776$; $t_{f=4, P=99\%} = 4.604$)

Matrix	Target concentration	\bar{x} (Tintometer) (N = 3)	s(Tintometer)	\bar{x} (HACH) (N = 3)	s(HACH)	TV
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	
Ultrapure water	0	0.00	0.00	0.00	0.00	-
Ultrapure water	0.1	0.10	0.01	0.10	0.00	0.076
Ultrapure water	0.5	0.49	0.00	0.49	0.00	-
Ultrapure water	1.0	0.97	0.01	0.96	0.01	0.269
Ultrapure water	1.5	1.43	0.00	1.41	0.02	0.234
Ultrapure water	2.0	1.85	0.02	1.83	0.05	0.112
Ultrapure water	0	0.00	0.00	0.00	0.00	-
Ultrapure water	2.0	1.93	0.06	2.00	0.00	0.481
Ultrapure water	4.0	3.80	0.00	4.00	0.00	-
Ultrapure water	6.0	5.73	0.06	5.93	0.06	1.019
Ultrapure water	8.0	7.63	0.06	7.93	0.06	1.529
Ultrapure water	10.0	9.33	0.12	9.77	0.06	1.803
Swimming pool water	0	0.28	0.01	0.31	0.01	0.376
Swimming pool water	0.25	0.50	0.01	0.53	0.01	0.484
Swimming pool water	1.0	1.17	0.00	1.21	0.01	0.693
Swimming pool water	1.75	1.99	0.01	2.05	0.01	0.781
Swimming pool water	8.0	7.30	0.10	7.53	0.06	1.018
Potable water	0	0.00	0.00	0.00	0.00	-

Matrix	Target concentration	\bar{x} (Tintometer) (N = 3)	s(Tintometer)	\bar{x} (HACH) (N = 3)	s(HACH)	TV
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	
Potable water	0.25	0.23	0.01	0.23	0.00	0.076
Potable water	1.0	0.92	0.01	0.91	0.01	0.054
Potable water	1.75	1.68	0.00	1.67	0.01	0.215
Potable water	8.0	7.73	0.06	8.07	0.06	1.699
High alkalinity	0	0.00	0.00	0.00	0.00	-
High alkalinity	0.25	0.22	0.00	0.24	0.00	-
Nitrate	0	0.00	0.00	0.00	0.00	-
Nitrate	0.25	0.23	0.00	0.23	0.00	-
Chloride	0	0.00	0.00	0.00	0.00	-
Chloride	0.25	0.24	0.00	0.24	0.00	-
Copper	0	0.00	0.00	0.00	0.00	-
Copper	0.25	0.24	0.01	0.23	0.01	0.054
Fluoride	0	0.00	0.00	0.00	0.00	-
Fluoride	0.25	0.24	0.01	0.24	0.00	0.076