

METHOD STATEMENT

Determinand:

Manual determination of Free and Total Chlorine

Matrix:

Sample Types: Raw, Potable, Surface and Ground waters.

Principle of Method:

For free chlorine, the reaction is a direct measurement. Chlorine reacts with p-aminodiethylaniline (diethyl-p-phenyldiamine) to produce a magenta colour. The intensity of the colour is proportional to the amount of chlorine present. The reaction is pH dependent, hence the free chlorine powder pillows contain a buffer as well as DPD

For total chlorine, potassium iodide is present as well as DPD and buffer in the total chlorine powder pillows. The iodide causes chlorine derivatives such as chloramines to react as well. The chloramines oxidise the iodide to iodine and then the iodine then reacts with the DPD.

Interferences:

Bromine, Iodine and chlorine dioxide interfere at all levels with the test.

Strong oxidising reagents can interfere.

Extreme sample pH can interfere.

Trace iodide from the Total Chlorine reagent can also interfere with the Free Chlorine test; this is avoided by using separate cells.

Cold samples can also cause condensation to form on the cell; this will give false results with a high bias. This is avoided by allowing the sample to rise in temperature.

For conventional free chlorine disinfection (beyond the breakpoint), monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test varies with the temperature, the relative amount of monochloramine to free ammonia, and the time required to do the analysis.

High levels of chlorine may give a false negative reading by 'bleaching' the colour formed during the reaction. An intense colour will initially form, but then it will rapidly fade to a colourless solution. Appropriate sample dilution should remove this interference. A strong chlorine odour should be noticeable.

Other chemicals not found in drinking water can also have a bleaching effect. Samples containing these chemicals may not be suitable for this test.

Performance of the Method:

Range of Application:

LOD – 2.00 mg/l Free Chlorine

LOD – 2.00 mg/l Total Chlorine

The analytical range may be extended by sample dilution.

Samples with a concentration higher than that of the top standard of 2.00 mg/l Cl₂ should be diluted with deionised water and re-analysed.

Free Chlorine - Reporting Limit is 0.02 mg/l Cl₂

Total Chlorine - Reporting Limit is 0.03 mg/l Cl₂

Limit of Detection

Free Chlorine - 0.0107 mg/l Cl₂

Total Chlorine - 0.0261 mg/l Cl₂



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Recoveries of Compounds and Uncertainty of measurement:

Free Chlorine

Sample type	Mean sample result (mg/l)	Mean sample spike result (mg/l)	Spike recovery (%)	Bias (%)	% Uncertainty
Soft	0.020	1.541	95.27	-	±8.44
Medium	0.019	1.545	95.57	-	± 8.31
Hard	0.021	1.568	96.93	-	±7.95
Borehole	0.025	1.300	79.89	-	±29.58
0.4 mg/l Std	0.400	-	-	0.11	± 8.95
1.6 mg/l Std	1.573	-	-	-1.68	± 5.69

Total Chlorine

Sample type	Mean sample result (mg/l)	Mean sample spike result (mg/l)	Spike recovery (%)	Bias (%)	% Uncertainty
Soft	0.010	1.548	98.94	-	± 3.94
Medium	0.012	1.549	98.89	-	± 3.92
Hard	0.018	1.552	98.75	-	±3.66
Borehole	0.023	1.559	98.86	-	±5.62
0.4 mg/l Std	0.0393	-	-	-1.70	± 8.20
1.6 mg/l Std	1.555	-	-	-2.81	± 6.22

References:

Based on Chemical Disinfecting Agents in Water and Effluents and Chlorine Demand 1980 (HMSO) ISBN 0117514934.

The Drinking Water Inspectorate – Guidance on Calibration and Analytical Quality Control for Residual Chlorine Measurements 2005

Hach Lange Free Chlorine and Total Chlorine Methods 8021 & 8167

Water Quality-Sampling-Part 3: Guidance on the Preservation and Handling of Water Samples. BS EN ISO 5607-3-2003, Page 14.

