METHOD STATEMENT

Determinand:

Free and Total Available Chlorine By DPD Spectrophotometric Method

Matrix:

Surface water, recreational water and process water.

Principle of Method:

Free chlorine reacts with diethyl-p-phenylenediamine to produce a pink colour. The intensity of the colour is proportional to the concentration of the chlorine present. The reaction is pH dependant; hence, the free chlorine powder pillows contain a buffer as well as DPD.

Potassium iodide is present in total chlorine pillows along with DPD and buffer. 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. The intensity of the colour is proportional to the concentration of the total chlorine.

Sampling and Sample Preparation:

Samples are normally collected in 250 ml amber glass bottles. They should be filled to the top with sample. Other size amber glass bottles are also suitable.
No special preservation is required
If analysis cannot be immediately undertaken, samples should be stored at a temperature of 2 - 8°C until the day of analysis. If samples have been refrigerated, they should be warmed up to room temperature prior to analysis and analysed within 1 working day.
Sample Stability Data

Chlorine should preferably be analysed as a field determinand due to the short stability period. Samples analysed in the laboratory give results that are indicative of the sample at the time of analysis. These results may be lower than if the sample was analysed within the 5 minute stability period quoted in ISO 5667:3 2003. Analysis of chlorine should be carried out as soon as possible.

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. 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

Performance of Method:

Determinand	Range of Application (mg/l)	LOD (mg/l)	High Standard	
			% RSD	% Bias
Total Chlorine	0.04- 2.00	0.04	1.66	5.31
Free Chlorine	0.05- 2.00	0.05	1.77	4.32

Determinand	Surface Water		Recreational Water		Dirty Process Water		Clean Process Water	
	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias
Total Chlorine 80% of Range	2.05	-2.19	0.85	3.15	1.75	-8.3	1.28	3.47
Free Chlorine 80% of Range	1.02	-4.83	0.99	0.37	1.63	-8.07	1.89	0.6

Uncertainty of Measurement

Determinand	Uncertainty of Measurement (%)
Total Chlorine	21.78
Free Chlorine	22.39

References

Based on Chemical Disinfecting Agents in Water and Effluents and Chlorine Demand 1980 (HMSO) ISBN 0117514934.
HACH Lange Free Chlorine and Total Chlorine Methods 8021 & 8167