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-phenylediamine) 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 chloroamines to react as well. The chloramines oxidise the iodide to iodine and then the iodine then reacts with the DPD.

Sampling and Sample Preparation:
Samples may be collected in 250 ml or 100ml amber glass bottles. They should be filled to the top with sample, with no headspace. 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 3±2°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.

Interferences
Bromine, Iodine and chlorine dioxide interfere at all levels with the test.
Strong oxidising reagents can interfere.
Extreme sample pH can interfere.
8.4Trace iodide from the Total Chlorine reagent can also interfere with the Free Chlorine test; this is avoided by proper rinsing of cells between analysis.
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 Method:

Range of Application:
LOQ – 2.00 mg/l Free Chlorine
LOQ – 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 Cl_2 should be diluted with deionised water and re-analysed.
Free Chlorine - Reporting Limit is 0.08 mg/l Cl_2
Total Chlorine **-** Reporting Limit is 0.08 mg/l Cl_2

Limit of Quantification:

Free Chlorine – 0.0707 mg/l Cl_2
Total Chlorine **-** 0.0500 mg/l Cl_2

Recoveries of Compounds, Bias and Uncertainty of measurement:

There is no performance data associated with this method.

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 5607-3-2018.