METHOD STATEMENT

Determinand:
Determination of Mercury

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

Principle of Method:
This method uses the Agilent 7800 and 7900 ICPMS and Agilent Technologies SPS4 Autosampler.
The method describes a technique for the determination of mercury in solution. The basis of the method is the measurement of ions produced by an Inductively Coupled Plasma and detected using a mass spectrometer. Acidified samples preserved with gold solution are nebulised and the aerosol that is produced is transported to the plasma torch where excitation of the metal atoms occur. Excitation is due to the high temperatures (up to 6,000°C) produced by the radio frequency inductively coupled plasma. The metal ions thus produced pass through an interface region into the mass spectrometer. There the ions are separated by a quadropole and fall on to the mass detector. The intensities of the currents produced are processed and controlled by a computer system.
Internal standardisation is used to correct for transport and matrix effects.
A table of the isotopes measured and the internal standards used is given below.

Agilent ICP-MS			
Element	**Mass**	**Internal Standard used**	**Mass**
Hg	200	Bi	209

Sampling and Sample Preparation:
Samples are normally collected in 125 ml polyethylene bottles
The 125 ml HDPE sampling bottles contain1.25 ml of concentrated nitric acid and 0.6 ml of 1000 mg/l Gold Standard. The gold is present as a preservative. It forms an amalgam with mercury and will readily stop the loss of mercury
If analysis cannot be immediately undertaken, samples can be stored at room temperature until the day of analysis. Samples should be analysed within 30 days of the sampling date.

Interferences
Due to the large mass of the mercury isotopes, there are few interferences within potable water that could cause interferences. However, interference correction equations are available from the instrument's pre-loaded library.

Performance of Method:

Range of Application:
LOQ – 1.25 µg/l Hg
The analytical range may be extended by sample dilution. The final concentration of acid / gold in the diluted solution should remain the same.
Agilent
The reporting limit is <0.04 µg/l Hg for both 7800 & 7900

Limit of Quantification:
Agilent 7800: Statistically obtained limit of quantification < 0.0346 µg/l Hg.
Agilent 7900: Statistically obtained limit of quantification < 0.0179 µg/l Hg.

Recoveries of Compounds, Bias and Uncertainty of measurement:
Agilent 7800

Sample type	Mean sample result (µg/l)	Mean sample spike result (µg/l)	Spike recovery (%)	Bias (%)	% uncertainty
Soft	0.007	0.986	98.07	-	± 3.96
Medium	0.009	0.996	98.84	-	± 3.16
Hard	0.009	1.009	100.05	-	± 2.70
Raw Surface	0.010	1.008	99.92	-	± 2.71
Borehole	0.010	1.018	100.97	-	± 3.07
Hard filtered	0.011	1.005	99.57	-	± 3.15
0.25 µg/l Std	0.258	-	-	3.04	± 10.71
1.00 µg/l Std	1.010	-	-	1.00	± 4.55

Agilent 7900

Sample type	Mean sample result (µg/l)	Mean sample spike result (µg/l)	Spike recovery (%)	Bias (%)	Combined Uncertainty (k=2) %
Soft	0.004	1.007	100.35	-	12.01
Medium	0.005	0.988	95.35	-	
Hard	0.005	1.011	100.68	-	
Raw Surface	0.004	1.042	103.80	-	
Borehole	0.004	1.019	101.48	-	
Hard filtered	0.006	1.028	102.27	-	
0.25 µg/l Std	0.252	-	-	0.95	
1.00 µg/l Std	1.000	-	-	0.02	

References:

In house method based on SCA bluebook 163 inductively Coupled Plasma Spectrometry 1996 and DWI Guidance note Sample Preservation and Preparation for Metals Analysis of Drinking Water.