METHOD STATEMENT

Determinand:
Mercury

Matrix:
Sample Type: Waste & trade effluents, final effluent and crude sewage samples

Principle of Method:
Samples are preserved with hydrochloric acid and potassium bromate/bromide reagent, on site at the point of sampling. All organomercury, inorganic mercury and any insoluble mercury species are oxidised to mercury (II) by the liberated elemental bromine. The treated samples, after removal of the excess bromine with a single drop of 12% m/v hydoxylammonium chloride, are reacted with acidic tin (II) chloride to convert the mercury (II) present into mercury (0) vapour. The mercury vapour is then transported to the fluorescence detector by a stream of argon gas and is detected by atomic fluorescence spectrometry. Argon is used as a carrier gas as both air and nitrogen cause significant quenching of the fluorescence and significantly reduce the sensitivity.

Interferences:
The bromination digestion procedure coupled to atomic fluorescence spectrometry overcomes many interferences including interferences caused by the formation of mercury complexes with organic material (e.g. fulvic and humic acids) and will oxidise sulphide. It will also breakdown all organomercury compounds.

For waste water samples, no significant interference effects have been observed other than iodide, to a much lesser extent bromide, silver and gold. These anion interferences are due to the iodide or bromide forming a complex with any mercury present, therefore a reduced result would be obtained. Silver and gold interference is due to the amalgam formed with elemental mercury, after the reduction stage with the addition of tin (II) chloride. However, these two elements should not be present in significant quantities in waste waters.

The presence of water vapour in the fluorescence cell may cause suppression due to quenching. This is normally overcome by using a hygroscopic membrane or dessicant to remove water from the carrier gas stream prior to it entering the detector.

This method utilises a bromide matrix and the mercury response is significantly dependent upon the final bromide concentration. It is essential that the final bromide concentration is kept constant in all samples, standards and AQCs especially with respect to any over range sample dilution steps.

Performance of Method:
Range of Application:

LOD to 2.00 µg/l Hg. This range may be extended by sample dilution.

The reporting limit is 0.05 µg/l Hg

Limit of Detection:

0.031 µg/l Hg

Recoveries of Compounds and Bias:

Sample type	Mean sample result (µg/l)	Bias (%)	Rsd (%)	Spike recovery (%)
Low Standard	0.397	-0.69	4.86	-
High Standard	1.598	-0.14	4.03	-
Final Effluent	0.086	-	5.62	99.95
Crude Sewage	0.002	-	3.56	94.41
Trade Effluent	0.044	-	5.56	98.63

References:

PS Analytical Technical Information file. Method - Total mercury in drinking, surface, ground and saline waters, January 2001

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