METHOD STATEMENT

Determinand:
Fluoride

Matrix:
Leachates, effluents, waste water's, surface water, ground water, trade and process water

Principle of Method:
The fluoride electrode is a chemical sensor in which the detector is a crystal of lanthanum fluoride across which a potential is developed in the presence of fluoride ions. It is used with a calomel reference electrode and a pH meter with an expanded millivolt scale.
The electrode responds to activity rather than concentration of the fluoride ions and to ensure a constant relationship between activity and concentration, samples and calibration standards must be adjusted to a constant ionic strength. They must also be buffered at a suitable pH value to prevent interference by hydroxide ions and also the formation of HF under acid conditions. The buffer contains metal-complexing agents to release free fluoride from certain metal complexes. Simple fluoro-silicates are rapidly hydrolysed in water and are detected as fluoride by the electrode.

Sampling and Sample Preparation:
Samples should not be stored in glass due to the formation of silica fluoride, which will not be detected by the method.
Samples should be stored at room temperature and analysed as soon as possible. If samples have been refrigerated, analysis must not be started until a stable room temperature is attained.

Should the sample be deemed cloudy, have a large amount of particulates or oil, the solution is filtered through a 0.45µm cellulose membrane. If it is not possible to filter through the cellulose membrane due to high number of particulates then a filter paper may be used prior. Leachate samples will have been filtered in the preparation of the Leachate and thus will not require filtering.

Samples are stable for 28 days (ISO 5667:3) from sampling.

Interferences:
The method is temperature sensitive. All standards, checks, samples and AQC solutions should be at room temperature to ensure a rapid stabilisation of the millivolt reading.

Hydroxide ions would contribute to the fluoride concentration that is measured, but this is compensated for by the TISAB reagent.

Aluminium greater than 5mg/l can be a source of interference as the TISAB can no longer complex the interferences out, a negative result will be observed.

If standards and samples containing fluoride are stored in glass, then there is the potential for the fluoride to react with the glass to form silica fluoride, which is not measured by this method. Plastic / PET containers are used to prevent this from occurring.

METHOD STATEMENT

Performance of Method:

Range of Application:	0.10 – 10 mg/l
Limit of Detection:	0.035 mg/l
Normal Reporting Level:	<0.1 mg/l

Determinand	Low standard		High standard	
	Tot. RSD %	Bias %	Tot. RSD %	Bias %
Fluoride	1.37	5.95	0.99	1.59

Determinand		Final Effluent	Crude sewage	Surface Water
		High	High	High
Fluoride	%RSD	1.36	1.14	1.50
	%Rec.	93.90	94.25	95.58

Determinand		Ground Water	Landfill Leachate	Soil Leachate
		High	High	High
Fluoride	%RSD	1.07	1.40	0.65
	%Rec.	99.36	94.25	94.23

Determinand		Trade	Process Water
		High	High
Fluoride	%RSD	0.83	0.89
	%Rec.	97.79	98.16

Uncertainty of Measurement:

The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

Determinand	Uncertainty of Measurement %
Fluoride	9.458

References:

Fluoride in waters, Effluents, Sludges, Plants and Soils 1982 Method for the Determination of Fluoride Potentiometric Method ISBN 0 11 751662 7.

ISO 5667-3 2003 - Water quality Sampling Part 3: Guidance on the preservation and handling of water samples

User guide for fluoride ion selective electrode, Thermo Scientific