

METHOD STATEMENT



Determinand:

Determination of Fluoride

Matrix:

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

Principle of Method:

This method uses the Thermo Scientific Orion Star meter in mV mode of operation.

After the addition of the reagent TISAB to adjust the pH value and release fluoride ions from certain complexes eg:- Simple fluoro-silicates are rapidly hydrolysed in water and are detected as fluoride by the fluoride ion selective electrode.

The electrode responds to the activity of fluoride ions and not their concentration, samples and standards must be adjusted to the same ionic strength and buffered to prevent interferences.

Fluoride is determined potentiometrically. All readings obtained are in mV. The obtained mV readings are converted to concentration units using the appropriate excel spreadsheet.

Sampling and Sample Preparation:

Samples are normally collected in 500 ml PET bottles. Other size PET bottles are also suitable.

No special preservation is required.

If analysis cannot be immediately undertaken, samples should be stored at a temperature of 1-5°C until the day of analysis. Samples should be warmed up to room temperature prior to analysis and analysed within 28 days of Sampling.

Interferences

Of the commonly occurring ionic species (other than fluoride) the electrode responds directly only to hydroxide ions. This effect causes serious error if the hydroxide ion concentration exceeds one tenth of the fluoride ion concentration. The total ionic strength adjustment buffer TISAB is designed to avoid these interferences with all but strongly acid or alkaline samples by maintaining the pH of the sample between pH 5.0 and 6.0.

Under acidic conditions the formation of HF reduces the concentration of fluoride ions. The total ionic strength adjustment buffer TISAB is designed to avoid these interferences with all but strongly acid or alkaline samples by maintaining the pH of the sample between pH 5.0 and 6.0.

Polyvalent cations e.g. Ca, Fe and Al alone or in combination with other species form complexes with fluoride to which the electrode does not respond. The total ionic strength adjustment buffer TISAB also contains complexing agents which release fluoride ions from these and some other metal-fluoride complexes.

Performance of Method:

Range of Application:

LOQ - 2.0 mg/l F

The analytical range may be extended by sample dilution. Samples with a concentration higher than that of the top standard of 2.0 mg/l F should be diluted with deionised water and reanalysed.

Reporting Limit is 0.04 mg/l F (40µg/l F).

Limit of Quantification:

0.04 mg/l F (40µg/l F).



Recoveries of Compounds, Bias and Uncertainty of measurement:

Sample type	Mean sample result (mg/l)	Mean sample spike result (mg/l)	Conc. of spike (mg/l)	Spike recovery (%)	Bias (%)	% uncertainty
Soft- Langsett	0.063	1.541	1.50	98.52	-	7.48
Medium- Wakefield	0.063	1.536	1.50	98.18	-	9.64
Hard- Bristol	0.078	1.547	1.50	97.91	-	8.65
Surface-Derwent / Elvington	0.108	1.581	1.50	98.21	-	7.28
Borehole-Nutwell	0.065	1.548	1.50	98.85	-	7.72
0.4 mg/l Std	0.37	-	-	-	-7.50	15.21
1.6 mg/lStd	1.58	-	-	-	-1.22	8.39

References:

Fluoride in Waters, Effluents, Sludges, Plants and Soils 1982. Methods for the Examination of Waters and Associated Materials. HMSO, 1982, ISBN 0 11 751662 7

Thermo Scientific Orion Star meter instruction manual.

261. Methods for the Examination of Waters and Associated Materials, November 2018, The Stability and Preservation of Drinking, Ground and Surface Water Samples, Appendix 1: Table of stability periods (Excel), 261.2, Standing Committee of Analysts (SCA).