

# METHOD STATEMENT



## Determinand:

Determination of acid extractable fluoride

## Matrix:

Sample Type: soil and sludges

## Principle of Method:

A sample of soil (dried and ground) or sewage sludge (liquid or cake) is extracted using  $110 \pm 5^\circ\text{C}$  dilute sulphuric acid. A citrate buffer is used to adjust the final pH to  $5.4 \pm 0.2$ , release any complexed fluoride ions and to maintain the provision of constant high ionic strength. A fluoride selective electrode is used to measure the activity of fluoride in the prepared extract by means of standard addition technique, since the samples analysed contain substances likely to interfere.

## Sampling and Sample Preparation:

Samples are normally taken in sludge pots or sealable plastic bags with ground soils being stored at room temperature, sludges and wet soils are refrigerated at  $3 \pm 2^\circ\text{C}$

Soil samples are dried and ground according to method WSC15 prior to analysis.

Sludge samples are usually analysed on an 'as received' basis and are mixed to obtain as near a homogeneous sample as possible.

Samples are stable for 30 days (BS ISO 18512: 2007) from sampling.

## Interferences

Fluoride ions readily form complexes with polyvalent cations such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$  and making them undetectable by ion selective electrode. Citrate buffer contains complexing agents, which release fluoride ions from metal-fluoride complexes that form. Hydroxyl ions ( $\text{OH}^-$ ) cause interference when the pH is 8 or more, this is overcome by the buffer.  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  can also increase the  $\text{OH}^-$  interference. Under acidic conditions the formation of HF reduces the concentration of fluoride ions. The citrate buffer is designed to mitigate these interferences by maintaining the pH of the sample between 5.2 and 5.6.

## Performance of Method:

### Range of Application:

Reporting limit: 10mg/kg as F

### Limit of Detection:

2.7mg/kg as F

### Recoveries of Compounds and Bias:

Sample type	Mean sample result (mg/kg)	Bias (%)	RSD (%)	Spike recovery (%)
Soil	60.45	-	4.98	88.55
Liquid sludge	106.30	-	5.43	96.05

Sample type	RSD (%)	Prediction interval, mg/kg	Mean result, mg/kg
Sandy loam CRM	7.71	45.5 - 193	148.20
Clay CRM	7.51	77.9 - 412	291.80

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## References:

Fluoride in waters, effluents, sludges, plants and soils 1982; Methods for the Examination of Waters and Associated Materials; HMSO 1983 (ISBN 011 751662 7).

4500-F- Fluoride analysis by ion selective electrode; Standard Methods for the Examination of Water and Wastewater; 18th Ed. 1992; Arnold E. Greenberg et al. (ISBN 0-87553-201-1).