INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON MICROCHEMICAL TECHNIQUES AND TRACE ANALYSIS*

DETERMINATION OF FLUORIDE IN VARIOUS MATRICES†

Prepared for publication by

A. D. CAMPBELL

Department of Chemistry, University of Otago,
Box 56, Dunedin, New Zealand

Determination of fluoride in various matrices

Abstract - Methods for the determination of fluorine in a variety of
matrices are reviewed with particular attention to those techniques which
are widely adopted as routine methods.   The fluoride ion-sensitive electrode
is a very successful potentiometric technique for the determination of
fluoride in aqueous solution and it has largely replaced the various
colorimetric methods formerly used.   However it is apparent that the rapid
development of ion chromatography with its advantage of simultaneous multi
anion determination is introducing a new phase into fluoride analysis.

INTRODUCTION

The element fluorine occurs very widely as fluoride.   It is present in water, minerals,
most foods and many plant and animal tissues.   It is of particular interest because of its
inclusion in the list of elements believed to be essential for animal life and also because
of its toxic effects at higher concentrations.   In many parts of the world there is an
inverse relationship between the fluoride content of drinking water and the amount of dental
caries in the population and the fluoridation of public water supplies to a level of about
1 mg dm^{-3} is now relatively common (ref. 1).   However careful control of fluoride levels
is required because high concentrations are known to cause mottling of the teeth and various
bone disorders.   The presence of fluoride in industrial effluents must also be monitored
because many plants are quite sensitive to fluoride while others are fluoride accumulators.

DISSOLUTION OF FLUORIDE

The literature contains numerous examples of methods used to obtain fluoride from plant
materials.   They range from extraction with hot water to complete digestion or ashing and
fusion of the ash with alkali.   Each is probably relevant for a particular type of material
but it would be unwise to consider that each is in anyway universal in application.
Jacobson, and his collaborators, who have organised many investigations into the deter-
mination of fluoride in plant materials report (ref. 2) "Despite improvement in speed and
simplicity of fluoride analysis during the last decade, agreement between laboratories has
not improved because of the variety of methods and techniques in use, the inherent differ-
ences between methods, and, apparently, poor laboratory quality control".   For large
numbers of samples, as in monitoring work, it is essential to have rapid methods which show
trends under particular circumstances but these must be checked against recognised standard
methods where the absolute level must be known with certainty.

McElfresh (ref. 3) extracted finely pulverised (passing 180 μm screen) potato tops with hot
water and obtained fluoride levels consistent with those obtained by a standard method
while Villa (ref. 4) reports a rapid dilute perchloric acid extraction method which has
been modified by Vijan and Alder (ref. 5).   However one of the more reliable and
relatively widely used direct extraction procedures is that of Jacobson and Heller (ref. 6)
who extracted fluoride from plant material by successive reaction with 0.05 mol dm^{-3} nitric
acid and then 0.05 mol dm^{-3} potassium hydroxide.   This method is the basis of the Official
First Action AOAC method (ref. 7) for fluoride in plant material.   A rapid direct
extraction method has also been used for the determination of fluoride in deboned meat.
This method (ref. 8), which correlates well with alternative ashing procedures, involves
defatting the meat with hexane, homogenising the sample and decomplexing the fluoride with
ethylenediaminetetraacetic acid.   Citric acid at pH 3.3 releases the fluoride in milk
(ref. 9) and coagulates the protein to provide the solution suitable for analysis.
Minerals such as phosphate which are soluble in acid are readily solubilised for fluoride
determination (ref. 10).   The determination of fluoride in tablets by direct solubilisation
in aqueous solution has been the subject of a collaborative study (ref. 11).

Ashing techniques, particularly those involving fusion with alkali, are less likely to give
low results than direct extraction methods for plant materials but they are much more time
consuming.   Bock (ref. 12) reports that an ashing aid is not required providing the ash is
alkaline as is the case with a wide range of plant materials, but fluoride is likely to be
lost at ashing temperatures much above 550°C.   Also contamination can be a greater problem
with ashing techniques due to the release of fluoride from ceramic furnace materials by

pyrohydrolysis. In a comparison of several analytical techniques (ref. 13) low temperature ashing with radiofrequency excited oxygen at 50-60°C was found to give the highest sensitivity and reproducibility. In this case the ash was solubilised with dilute hydrochloric acid for analysis by an ion sensitive electrode procedure, but others using higher temperature ashing procedures find it necessary to fuse the ash with alkali (ref. 14) to effect the solubilisation of the fluoride.

Fusion techniques are necessary for silicate rocks, coal and for plant materials which have a high silica ash content. Hall (ref. 15) found better reproducibility for fluoride in soil and silicate containing plant ashes when the sample was fused with potassium hydroxide although lithium hydroxide and sodium hydroxide were satisfactory for other plant ashes. Others fuse with sodium hydroxide (ref. 16), sodium carbonate (ref. 17), a mixture of sodium carbonate and potassium nitrate (ref. 18), calcium oxide followed by sodium hydroxide (ref. 14), zinc oxide (ref. 8) and mixtures of sodium carbonate and zinc oxide (ref. 19). Both platinum and nickel crucibles are used to contain the sample. A fairly wide range of fusion temperatures is reported but most involve a pro-longed period at a relatively low temperature followed by a short period at a higher temperature. For minerals Fabbri and Donati (ref. 16) report good recoveries in the temperature range of 450-600°C but greater variability outside this. For fluoride estimation the reaction mixture may be dissolved in water (ref. 18, 19) or acid (ref. 17). In order to minimise the iron and aluminium content McQuaker and Gurney (ref. 20) filtered the sample solution while it was only slightly alkaline. Careful fusion with magnesium acetate is a satisfactory method for samples of blood (ref. 21).

The oxygen-filled flask combustion technique is a well established method for the determination of fluorine in organic compounds. Satisfactory decomposition of perfluorinated compounds may be accomplished if the sample is wrapped in a piece of polyurethane foam plastic. Organic compounds in dilute aqueous solution have been combusted using an oxy-hydrogen torch (ref. 22).

SEPARATION OF FLUORIDE

Diffusion

Separation of fluoride by diffusion from a perchloric acid acidified solution is effective though normally rather slow (ref. 23,24), but Taves (ref. 25) noted that the rate of diffusion is greatly accelerated through contact with the silicone greases frequently used as sealants for the diffusion dishes. This finding was exploited by Hall (ref. 26) who saturated the perchloric acid with hexamethyldisiloxane. The method has been further developed by Sara and Wänninen (ref. 27) with a novel diffusion dish which enables the hexamethyldisiloxane saturated perchloric acid to be mixed with the sample solution after the dish is sealed. However, although they recommend the addition of ethanol to the per-chloric acid to increase the solubility of hexamethyldisiloxane when analysing compounds of higher fluoride content, this solution would seem to be potentially explosive. The diffusion method has the added advantage that it will hydrolyse monofluorophosphate. The hexamethyldisiloxane aided transferrence of fluoride has also been applied to large volumes of solution (ref. 28). The fluoride is reacted with hexamethyldisiloxane in a distillation apparatus to form volatile fluorosilanes which are transferred at room temperature in a stream of nitrogen to an absorption vessel containing dilute alkali. The fluorosilanes undergo rapid hydrolysis in alkali and estimation may be effected by any of the conventional methods. Interference due to aluminium was effectively suppressed by adding phosphoric acid to the sample solution.

Distillation

The classical method for the separation of fluoride from interfering substances is the steam distillation method of Willard and Winter (ref. 29). However the method is slow, it requires extreme care and experience to keep the blank acceptably low and it is virtually impractical for very large numbers of samples. Many variations of this method will be noted. The basic equipment is a Pyrex Claisen flask with the auxiliary neck sealed off close above the side arm (ref. 30), but other more elaborate distillation units (ref. 31) are very effective. Both sulfuric acid and perchloric acid are used to promote distillation of the fluoride as hydrogen fluoride (ref. 32) and silver perchlorate is added to prevent the co-distillation of other halogens and sulphide. The distillation has been automated (ref. 14).

Pyrohydrolysis

A procedure which is satisfactory for the displacement of fluoride from refractory matrices is pyrohydrolysis. Most procedures involve heating the sample, with or without various materials as fluxes, to a temperature of 800-1200°C in a flow of steam although moist oxygen or moist air are sometimes used. The method is reviewed by Berns and Van der Zwaan (ref. 33). A variation (ref. 34) which is applicable to a very wide range of refractory materials, fluorides of alkaline earths, organic compounds and organometallics and coal and alumina-based catalysts involves heating the sample to 1120°C in a stream of superheated steam. Tungsten trioxide is mixed with samples which resist decomposition. A high frequency induction furnace (ref. 35) has been used to obtain excellent recoveries of fluoride from environmental standard reference materials including coal and coal fly ash.

MEASUREMENT OF FLUORIDE

Fluoride ion-sensitive electrode

The most significant advance in the determination of fluoride was the development of the fluoride ion-sensitive electrode by Frant and Ross (ref. 36). This is the most successful of the ion sensitive electrodes and it has received wide acceptance to the stage where it is now uncommon to see alternative methods reported. The electrode is available both as a single electrode to be used in conjunction with a calomel reference electrode or as a combination electrode with the reference electrode incorporated in an outer sheath of the electrode body. Both designs give similar results.

The equation for the potential developed at the electrode in a solution of fluoride is given by the equation $E = E^O - RT/F \ln[F^-]$ where R is the gas constant and T is the absolute temperature. The electrode is sensitive to changes in temperature and most electrodes appear to stabilise more rapidly at higher temperatures. However this may cause some reduction in the life of the electrode and Nicholson and Duff (ref. 37) found reproducibility at 50° inferior to that at 20°C. In practice the lower limit for analysis is around 1×10^{-6} mol dm^{-3} (0.019 mg dm^{-3}) fluoride. However this limitation would appear to be a function of the impurities in reagents because Nernstian response has been attained down to 1×10^{-9} mol dm^{-3} (ref. 38, 39). Errors and problems associated with the use of fluoride ion-sensitive electrodes are fully discussed a recent reviews (ref. 37, 40).

When using a fluoride ion-sensitive electrode it is normal to add a solution commonly called a Total Ionic Strength Adjustment Buffer (TISAB-solution). This reagent serves three functions, namely adjustment of the pH, the provision of a constant high ionic strength and release of fluoride from complexes. Adjustment of the pH to a constant value is required because the fluoride ion-sensitive electrode is responsive to changes in hydroxide ion concentration particularly at high pH. A pH of 5.5 appears to be optimum for the determination of fluoride (ref. 41). At this pH there is little association as HF or HF$_2^-$ and it is a value which is readily attained using an acetate or citrate buffer. However waters of a relatively unpolluted nature and with adequate buffering, as is the case with seawater, do not require buffering (ref. 42). A second function of TISAB-solution is to provide a relatively high ionic strength to ensure that liquid junction potentials are minimised and to provide a constant ionic strength background thus minimising variations between samples and standards.

Most of the TISAB-solutions commonly used incorporate a complexing reagent which will release fluoride from its complexes. Aluminium is the principal interferent although iron(III) and magnesium(II) may also be troublesome. Typical decomplexing reagents are citrate, CDTA (ref. 43) (trans-1,2-diaminocyclohexane-N,N,N',N'-tetra-acetic acid), tiron (ref. 44, 45) (pyrocatechol 3,5-disodium disulfonate), tris (tris(hydroxymethyl methylamine)), mannitol, triethanolamine and salicylate. There would appear to be considerable disagreement as to which is the most effective decomplexing reagent and the situation is made more confusing through the use of varying concentrations of TISAB-solutions and the adoption of ill-defined abbreviations for solution names.   The ability of a TISAB-solution to release fluoride will depend very much on the total composition of the analyte solution and what is best for relatively pure natural waters is not necessarily the best for complex effluent mixtures. Citrate at appropriate concentration (ref. 10, 44, 46, 47) is one of the most effective TISAB-solutions but where there is considerable supression of the fluoride due to aluminium it is important to ensure sufficient time lapses between addition and potential measurement to allow complexing to take place. Nicholson and Duff (ref. 47), who made a comprehensive study of eleven different systems, recommend a minimum of 20 min although in some cases a delay of 20-24 h is necessary. They also recommend that TISAB-solutions

should be prepared regularly every two weeks. Bagg (ref. 48) proposed the use of potassium salts rather than sodium because the former have less tendency for ion pair formation, but others have not been troubled in this way. The purity of reagents is another obvious though sometimes neglected factor which will affect the electrode response. In order to avoid an electrode memory effect it is advisable to arrange the work so that solutions are analysed in order of increasing concentration (ref. 49). To save time the tendency is to insert the fluoride ion-sensitive electrode direct into the analyte solution without purification in order to avoid the time consuming distillation procedure. Matrix effects are therefore extremely important. Interfering elements, such as aluminium, which form stable compounds with fluoride are the main cause for concern and various procedures other than distillation have been proposed to effect a clean up of the solution before analysis. Ion exchange is tedious for large numbers of solutions. The iron and aluminium content of analyte solutions from soil samples was minimised by filtration while slightly alkaline, and extraction of aluminium with oxine has been used by Nicholson and Duff (ref. 50).

The analysis of very small samples has been facilitated by the development of techniques which require only a few μL of analyte solution. Potentials which develop across a μL sample held between the face of the fluoride electrode and the salt bridge of a reference electrode have been measured (ref. 51). In an alternative procedure several μL samples of the analyte solution are placed on an inverted fluoride electrode and contacted in turn with a reference microelectrode while being observed under a microscope (ref. 52, 53).

In most analytical work the potential developed in the analyte solution is compared with that obtained for a series of standard solutions similarly treated with TISAB-solution. However potentiometric measurements are much more reliable if the matrix of the standard solutions is matched to the analyte solutions. For example when analysing sea water the standard solutions should be prepared in synthetic seawater (ref. 54). An alternative procedure to overcome matrix effects is standard addition. A single shot standard addition procedure is used with commercially available instruments and van Leuven (ref. 34) has described a procedure involving titration with standard fluoride to produce a calculated potential change. Of the various multiple addition procedures the method used by Rix, Bond and Smith (ref. 42) for unbuffered sea water, and modified by Campbell and Graham (ref. 55) for variable matrices, has considerable merit.

The fluoride sensitive electrode has been used as a sensor in the determination of fluoride by flow injection procedures (ref. 56-58). However under these conditions the electrode response is not Nernstian and reproducible results are obtained only with a procedure involving frequent calibration checks and active quality control. A cell with a rapid response is described by Van Oort and Van Eerd (ref. 88).

Detailed methods for the determination of total fluoride in a variety of environmentally relevant matrices such as in gaseous emissions, rain water and aqueous effluents, vegetation, human urine, factory air and environmental air are presented in a recent report compiled by the Analytical Working Group of the Comité Technique Européen du Fluor (ref. 89).

Photometric methods

Most of the photometric methods initially used for the determination of fluoride depended upon the bleaching action of fluoride on the intensity of the absorbance of the complex or "lake" formed between a dyestuff and a metal. For example the bleaching action of fluoride ions on the complex formed between sodium 2-(p-sulfo-phenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (SPADNS) and zirconium (ref. 59) follows Beers Law over the range of 0 - 1.4 mg dm^{-3} fluoride. This method was widely used for the determination of fluoride in potable waters. Other methods of this type are the bleaching action of fluoride on the complexes formed between Eriochrome cyanine R (ref. 60) or 3-alizarinsulfonic acid (ref. 61) and zirconium. However these methods are effective over limited concentration ranges and subject to many interferences particularly from phosphate, aluminium and iron.

In contrast to the above reagents where the colour intensity is decreased by fluoride ion the cerium or lanthanum complexes of alizarin fluorine blue (3-[N,N-di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone)of Belcher, Leonard and West (ref. 62, 63) are "positive" photometric reagents with the colour becoming more intense with increasing fluoride ion concentration. These reagents have been extensively studied and widely applied. Greenhalgh and Riley (ref. 64) found

increased stability and sensitivity of the lanthanum/alizarin complexone reagent
in 16% acetone and applied the method to the determination of fluoride in natural
waters including seawater.   The method has been automated for the determination
of fluoride in seawater (ref. 65), urine (ref. 66) and plant materials (ref. 67).
The alternative cerium III reagent favoured by others is also more sensitive and
stable when used in mixed solvents (ref. 68) and has been applied to the deter-
mination of fluoride in seawater (ref. 69).   However the properties of alizarin
fluorine blue have now been surpassed by sulfonated alizarin fluorine blue
(ref. 70), 3-[N,N-di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone-5-
sulfonic acid.   In a detailed comparison of the two reagents Deane, Leonard,
McKee and Svehla (ref. 71) report that although both reagents are broadly similar
the sulfonated derivative is more soluble, gives a more rapid development of
maximum absorbance, better sensitivity, improved adherence to Beer's Law and
comparable precision.   In comparison with fluoride ion-sensitive electrode
potentiometric methods these photometric reagents are in general more time
consuming and not so tolerant to interferences.   However in the absence of
serious interferences they tend to be more reproducible except at very low
concentrations.

Ion chromatography

In 1975 Small, Stevens and Bauman (ref. 72) used a strong base anion exchange
resin absorbed onto a surface sulfonated polymer to effect the separation of anions
and followed this with a supressor column of high capacity cation exchange resin
to strip sodium ions from the sodium phenate eluent and convert it to a slightly
dissociated weak acid of low conductivity.   This enabled a conductivity detector
to be used to measure the eluted anions.   The separation and measurement of anions
by ion chromatography is now a very rapidly developing field and many variations
of the original technique have been described.   Ion chromatography has particular
appeal in water analysis because it provides a measurement of a range of anions.

A sodium carbonate/sodium bicarbonate buffer is now widely used as the eluent and
fluoride ions are normally eluted first.   However, except where columns are
comparatively new, fluoride is unlikely to be separated from organic acids such as
acetic and formic acids (ref. 73) although the latter do have much smaller
conductivities than fluoride and alternative eluents such as disodium tetraborate
enable complete separation to be accomplished.   The method had been applied to
the determination of anions including fluoride in geological samples following
fusion with sodium carbonate (ref. 74), geothermal water (ref. 75) and organic
compounds after sodium fusion (ref. 76), but this technique is reported to be
unacceptable for the derermination of atmospheric fluoride because of lack of
correlation with recognised standard methods (ref. 77).   One of the problems of
ion chromatography is the wide variation in rates of elution for the anions.   A
combination of potentiometric and cundoctometric detectors with switching to change
the effective column length has been used to overcome this problem (ref. 78).

Gjerde, Fritz and Schmuckler (ref. 79,80) found that it is not necessary to use a
suppressor column when using a special anion-exchange resin of low capacity and an
eluent of very low conductivity such as dilute aqueous potassium benzoate or
potassium hydrogen phthalate, although the sensitivity is not as good as that of
the dual column system.   Separation of a range of anions including fluoride has
been accomplished using organic acids such as succinic and nicotinic acids, the
detection limits for fluoride being 26 and 5 μgL^{-1} respectively (ref. 81).   The
reduction in the conductivity of potassium hydroxide eluent caused by the presence
of eluted anions has been found to be more sensitive for the determination of
anions on a single column than was the increase in conductivity when using
potassium hydrogen phthalate as eluent (ref. 82).

Atomic and molecular spectroscopy

Although many anions may be conveniently determined by indirect atomic spectro-
scopy the published techniques for fluorine show no real advantage over direct
methods.   Methods involving the addition of calcium, lead or bismuth salts in
excess have been reviewed (ref. 83).   The calcium method is the most effective
but they all require careful technique.   Suppression of the magnesium signal by
fluoride is reported by Bond and O'Donnell (ref. 84) to be proportional to the
fluoride concentration but signal depression techniques are prone to matrix inter-
ferences and this would appear to be no exception.   The molecular absorption of
aluminium monofluoride at 227.5 nm as observed in a carbon furnace or nitrous
oxide - acetylene flame is a direct method for the determination of fluoride but
this method would also suffer from interference.   It has been applied to the
determination of fluoride in milk (ref. 85, 86).   Fluoride is determined as

silicon tetrafluoride in a molecular emission cavity analysis procedure (ref. 87), but boron and arsenic will interfere.

EQUIPMENT

There is unlikely to be any significant loss of fluoride onto good quality borosilicate glass equipment used to hold solutions for short periods.   This would include volumetric equipment used for preparing solutions and measurement cells. However fluoride solutions and reagents such as the TISAB-solution should be stored in high density polythene or polypropylene containers.

CONCLUSIONS

The fluoride ion-sensitive electrode is the preferred method for the determination of fluoride in aqueous solutions and it should be the method of choice for those with little experience in analytical chemistry.   It is easy to operate, relatively rapid and requires little technical skill.   However, although it is easy to make a measurement the conversion of the fluoride in the sample into a form suitable for analysis is a very critical operation.   When dealing with new matrices the analyst should check the results of simple extraction methods with those obtained by a reference procedure, such as distillation, to ensure that matrix effects are minimised.   The rapid methods which avoid distillation of the fluoride depend on very effective complexing of the interfering substances.   The photometric method using the SPADNS reagent is suitable for the determination of fluoride in most potable waters but in general the photometric methods are not so tolerant to interferences as the fluoride ion-sensitive electrode.   The more recently developed methods based on ion chromatography are of particular value where the concentrations of several anions as well as fluoride are required.

REFERENCES

1. Fluoride Teeth and Health, The Royal College of Physicians of London, Pitman Medical 1976.
2. J.S. Jacobson, J.J. Troiano, C.G. Cosentini and J. Evans, J. Assoc. Off. Anal. Chem., 65, 1150 (1982).
3. P.M. McElfresh, J. Agri. Food Chem., 26, 276 (1978).
4. A.E. Villa, Analyst, 104, 545 (1979).
5. P.H. Vijan and B. Alder, International Laboratory, 14(7), 94 (1984).
6. J.S. Jacobson and L.I. Hellier, J. Assoc. Off. Anal. Chem. 58, 1129 (1975).
7. W. Horwitz,Official Methods of Analysis of the Association of Analytical Chemists, Washington, D.C. p. 40 (1980).
8. T. Dolan, L. Legette, J. McNeal and A.J. Malanoski, J. Assoc. Off. Anal.Chem., 61, 982 (1978).
9. C.G. Beddows and D. Kirk, Analyst, 106, 1341 (1981).
10. C.R. Edmond, Analyt. Chem., 41, 1327 (1969).
11. J.R. Marzilli, J. Assoc. Off. Anal. Chem., 67, 682 (1984).
12. R. Bock, Decomposition Methods in Analytical Chemistry, trans. by I.L. Marr, International Text Book Co. Glasgow, p. 138 (1979).
13. M.A. Van Den Heede, A.M. Heyndrickx, C.H. Van Peteghem and W.A. Van Zele, J. Assoc. Off. Anal. Chem., 58, 1135 (1975).
14. W. Horwitz, Official Methods of Analysis of the Association of Analytical Chemists, Washington D.C. p. 41 (1980).
15. R.J Hall, Analyst, 93, 461 (1968).
16. B. Fabbri and F. Donati, Analyst, 106, 1338 (1981).
17. R.A. Nadkarni , Analyt. Chem., 52, 929 (1980).
18. S.J. Haynes, Talanta, 25, 85 (1978).
19. B.L. Ingram, Analyt. Chem., 42, 1825 (1970).
20. N.R. McQuaker and M. Gurney, Analyt. Chem., 49, 53 (1977).
21. J. Alary, P. Bourbon and C. Balsa, Analyt. Chim. Acta., 148, 311 (1983).
22. E. Kissa, Analyt. Chem., 55, 1445 (1983).
23. R.W. Dabeka, A.D. McKenzie and H.B.S. Conacher, J. Assoc. Off. Anal. Chem., 62, 1065 (1979).
24. R.D. Dabeka and A.D. McKenzie, J. Assoc. Off. Anal. Chem., 64, 1021 (1981).
25. D.R. Taves, Talanta, 15, 969 (1968).
26. R.J. Hall, Talanta, 16, 129 (1969).
27. R. Sara and Z. Wänninen, Talanta, 22, 1033 (1975).
28. M. Yoshida, M. Kitami, N. Murakami and T. Katsura, Analyt. Chim. Acta, 106, 95 (1979).
29. H.H. Willard and O.B. Winter, Ind. Eng. Chem., Analyt. Ed., 5, 7 (1933).

30. W. Horwitz, <u>Official Methods of Analysis of the Association of Analytical Chemists</u>, Washington D.C. p. 392 (1980).
31. T.S. Ma and J. Gwirtsman, Analyt. Chem., <u>29</u>, 141 (1957).
32. Z. Marczenko, L. Lenarczyk and E. Kowalczyk, Chemia Analytyczna, <u>21</u>, 1039 (1976).
33. E.G. Berns and P.W. Van der Zwan, Analyt. Chim. Acta. <u>59</u>, 293 (1972).
34. A.C.E. van Leuven, G.J. Rotscheid and W.J. Buis, Fresenius Z. Anal. Chem., <u>296</u>, 36 (1979).
35. M. Bettinelli, Analyst, <u>108</u>, 404 (1983).
36. M.S. Frant and J.W. Ross, Analyt. Chem., <u>40</u>, 1169 (1968).
37. K. Nicholson and L.J. Duff, Analyst, <u>106</u>, 985 (1981).
38. M. Trojanowicz, Talanta, <u>26</u>, 985 (1979).
39. J.F. Coetzee and M.W. Martin, Analyt. Chem., <u>52</u>, 2412 (1980).
40. K. Nicholson, Chem. Geol., <u>38</u>, 1, (1983).
41. J. Vesely and K. Stulik, Analyt. Chim. Acta, <u>73</u>, 157 (1974).
42. C.J. Rix, A.M. Bond, J.D. Smith, Analyt. Chem., <u>48</u>, 1236 (1976).
43. J.E. Harwood, Water Research, <u>3</u>, 273 (1967).
44. S. Tanikawa, H. Kirihara and S. Shiraishi, Analyt. Lett., <u>8</u>. 879 (1975).
45. H. Ballczo and M. Sager, Fresenius Z. Anal. Chem., <u>298</u>, 382 (1979).
46. P. Kauranen, Analyt. Lett., <u>10</u>, 451 (1977).
47. K. Nicholson and E.J. Duff, Analyt. Lett., <u>14</u>, 493 (1981).
48. J. Bagg, Analyt. Chem., <u>48</u>, 1811 (1976).
49. K. Toth, I. Gavaller and E. Pungor, Analyt. Chim. Acta, <u>57</u>, 131 (1971).
50. K. Nicholson and E.J. Duff, Analyst, <u>106</u>, 904 (1981).
51. A.S. Hallsworth, J.A. Weatherell and D. Deutsch, Analyt. Chem., <u>48</u>, 1660 (1976).
52. G.L. Vogel, L.C. Chow and W.E. Brown, Analyt. Chem. <u>52</u>, 375 (1980).
53. G.L. Vogel and W.E. Brown, Analyt. Chem., <u>52</u>, 377 (1980).
54. T.B. Warner, Deep Sea Res., <u>18</u>, 1255 (1971).
55. A.D. Campbell and P.B. Graham, N.Z. J. Sci., <u>26</u>, 433 (1983).
56. J. Slanina, W.A. Lingerak and F. Bakker, Analyt. Chim. Acta, <u>117</u>, 91 (1980).
57. M. Trojanowicz and Matuszewski, Analyt. Chim. Acta, <u>138</u>, 71 (1982).
58. P. Van Den Winkel, G. De Backer, M. Vandeputte, N. Mertens, L. Dryon and D.L. Massart, Analyt. Chim. Acta, <u>145</u>, 207 (1983).
59. E. Bellack and P. J. Schouboe, Analyt. Chem., <u>30</u>, 2032 (1958).
60. P.L. Sarma, Analyt. Chem., <u>36</u>, 1684 (1964).
61. <u>Standard Methods for the Examination of Water and Wastewater</u>, 15th Edition, American Public Health Association, Washington, 1981, p. 339.
62. R. Belcher, M.A. Leonard and T.S. West, J. Chem. Soc., <u>1959</u>, 3577.
63. R. Belcher and T.S. West, Talanta, <u>8</u>, 863 (1961).
64. R. Greenhalgh and J.P. Riley, Analyt. Chim. Acta, <u>25</u>, 179 (1961).
65. K.M. Chan and J.P. Riley, Analyt. Chim. Acta, <u>35</u>, 365 (1966).
66. J.A. Hargreaves, G.S. Ingram and D.L. Cox, Analyst, <u>95</u>, 177 (1970).
67. L.H. Weinstein, J.S. Jacobson and R.H. Mandl, J. Assoc. Off. Anal. Chem., <u>55</u>, 998 (1972).
68. S.S. Yamamura, M.A. Wade and J.H. Sikes, Analyt. Chem., <u>34</u>, 1308 (1962).
69. R.A. Kletsch and F.A. Richards, Analyt. Chem., <u>42</u>, 1435 (1970).
70. M.A. Leonard and G.T. Murray, Analyst, <u>99</u>, 645 (1974).
71. S.F. Deane, M.A. Leonard, V. McKee and G. Svehla, Analyst, <u>103</u>, 1134 (1978).
72. H. Small, T.S. Stevens and W.C. Bauman, Analyt. Chem., <u>47</u>, 1801 (1975).
73. C.E. Coggan, Analyt. Proc. Royal Soc. Chem., <u>19</u>, 567 (1982).
74. S.A. Wilson and C.A. Gent, Analyt. Lett. <u>15</u>, 851 (1982).
75. R.P. Lash and C.J. Hill, Analyt. Chim. Acta, <u>108</u>, 405 (1979).
76. C.Y. Wang and J.G. Tartar, Analyt. Chem., <u>55</u>, 1775 (1983).
77. J. Crowther and J. McBride, Analyst, <u>106</u>, 702 (1981).
78. Chung-Yu Wang, S.C. Bunday and J.G. Tartar, Analyt. Chem., <u>55</u>, 1617 (1983).
79. D.J. Gjerde, J.S. Fritz and G. Schmuckler, J. Chromatography, <u>186</u>, 509 (1979).
80. D.J. Gjerde, G. Schmuckler and J.S. Fritz, J. Chromatography, <u>187</u>, 35 (1980).
81. J.S. Fritz, D.L. DuVal and R.E. Barron, Analyt. Chem., <u>56</u>, 1177 (1984).
82. T. Okada and T. Kuwamoto, Analyt. Chem., <u>55</u>, 1001 (1983).
83. L. Campanella, G. de Angelis, R. Sbrilli and A. Marabini, Frezenius Z. Analyt. Chem., <u>307</u>, 411 (1981).
84. A.M. Bond and T.A. O'Donnell, Analyt. Chem., <u>40</u>, 560 (1968).
85. K. Tsanoda, K. Fujiwara and K. Fuwa, Analyt. Chem., <u>49</u>, 2035, (1977).
86. A. Takatsu, K. Chiba, M. Ozaki, K. Fuwa and H. Haraguchi, Spetrochim. Act, <u>39B</u>, 365 (1984).
87. M. Burguera, A. Townshend and S.L. Bogdanski, Analyt. Chim. Acta., <u>117</u>, 247 (1980).
88. W.J. Van Oort and E.J.J.M. Van Eerd, Analyt. Chim. Acta, <u>155</u>, 21 (1983).
89. The Analytical Working Group of the Comité Technique Européen du Fluor, Analyt. Chim. Acta, <u>182</u>, 1 (1986).