

DEVELOPMENTS IN THE ANALYSIS OF FLUORIDE 1997-1999

F Yin, Y Yao, CC Liu, ML Wen^a
Kunming, China

This biennial review is a continuation of the previous survey¹ and covers primarily the critical literature of the analysis of fluoride from July 1997 to December 1999.

ELECTROANALYSIS

A new membrane material for fluoride selective, chemically modified field effect transistors (CHEMFETs) was developed by incorporation of a uranyl salophen derivative as the anion receptor into a polysiloxane membrane doped with acetylphenoxypropyl or phenylsulfonylpropyl substitutes.² The sensitivity and selectivity of the fluoride selective CHEMFETs was better with a polysiloxane membrane than with plasticized PVC membranes. Even in the presence of 0.1 M of the more lipophilic chloride, bromide, or nitrite ions, an almost Nernstian response and a detection limit of 0.25 mM was obtained for fluoride ($\log K_{F,j}^{pot} = -2.5$). A simple Si/LaF₃/Pt structure with a thin layer of the ionic conductor LaF₃ in direct contact with the semiconductor without an intermediate insulator provides a sensor for the determination of fluorine gas.³ The field effect in the semiconductor led to much steeper capacitance-voltage curves than is usually found for conventional multiple ion selective structures; potential formation took place at the three-phase LaF₃/Pt/gas boundary. The lower detection limit of the optimized sensor was <0.1 ppm.

A similar SiC/SiO₂/LaF₃/Pt structure was used to fabricate a chemical semiconductor sensor for high-temperature measurements of fluorine up to 350°C.⁴ The influence of temperature on the sensor response time was smaller than expected, but the increased desorption rate and a high signal-to-noise ratio (S/N) improved the detection limit.

Different decomposition methods in aqueous solutions were evaluated for their accuracy and reproducibility for determining the constituents of bioactive fluoride-containing glasses used in dental glass ionomer cements. Fluoride could be determined with an ISE after degrading the samples in 0.5M HCl; however, higher HCl concentrations enhanced the risk of HF release.⁵ A complex of Zr(IV) with a hydrophilic resin having an iminodiacetic acid group rapidly and selectively absorbed fluoride from acidic media, which was reversibly expelled on increase in pH.⁶

A flow system consisting of a mini-column packed with this polymer complex was used for separation and preconcentration of fluoride. An ion-selective electrode for detection gave the same peak height for the same

^aFor correspondence: Dr M L Wen, Department of Chemistry, Yunnan University, Kunming, Yunnan 650091, China. Fax: +86 871 515 3832. E-mail: mlwen@ynu.edu.cn

amount of fluoride, irrespective of the sample concentration and volume. Thus calibration could be based on the amount of F chemical. The detection limit defined by $S/N = 3$ was 0.1 nmol. Use of the flow system decreased the lower limit for quantitative adsorption of fluoride down to 5×10^{-8} M (compared with 1×10^{-4} M by batch adsorption). At the same time, tolerance limits for interfering cations and anions were greatly increased; even a 4-fold weight ratio of Al^{3+} to F^{-} was tolerated with cyclohexanedaminetetraacetic acid as the masking reagent. This system was applied to the determination of fluoride in drinking water and concentrated brine. Group 13 metal species Ga(III), In(III), and Tl(III), when inserted into either octaethyl- or tetraphenyl-porphyrin derivatives and subsequently incorporated into plasticized PVC membranes, serve as anion ionophores with selectivity patterns that deviate significantly from the classical Hofmeister series for anions.⁷ The Ga(III) porphyrin-based electrode exhibited significantly enhanced response toward fluoride, whereas the In(III) and Tl(III) porphyrins displayed some preference for chloride and also effectively discriminated among less hydrated anions such as perchlorate and nitrate.

The concentrations of diffusible and total fluoride in cow's milk samples from areas with widely different fluoride levels in drinking water were determined using a fluoride electrode.⁸ The diffusible fluoride was determined by direct hexamethyldisiloxane microdiffusion; for total fluoride, samples were subjected to either open ashing or digestion with proteolytic enzymes before microdiffusion. Diffusible fluoride ranged from 0.024 to 0.28 $\mu\text{g/mL}$ while total fluoride ranged from 0.05 to 0.31 $\mu\text{g/mL}$. The use of proteolytic enzymes before microdiffusion resulted in measurement of total fluoride. The study concluded that all fluoride in milk is inorganic in nature with the bound fluoride being physically or chemically sequestered in the milk proteins.

Drawing on the principle that enzymatic conversion of catechol is inhibited by a variety of organic and inorganic inhibitors, a substrate regenerating bienzyme sensor has been developed to measure, with high selectivity, such inhibitors as carboxylic acids, kojic acids, thiourea derivatives, and inorganic ions including fluoride.⁹ Two cooperating enzymes, cytosolic quinoprotein glucose dehydrogenase and mushroom tyrosinase, were immobilized in polyvinyl alcohol coupled to a Clark-type oxygen electrode; the oxygen consumption, which was related to inhibitor concentration, was monitored during catechol conversion.

Electroanalysis methods for fluoride are shown in Table 1.

Table 1. Determination of fluoride by electroanalysis

Method	Application	References
Amperometry using conducting polymer electrodes	F ⁻	Electroanalysis 1997;9(6):461-7
Hexamethyldisiloxane volatilization followed by F-ISE detection	F ⁻	Anal Lett 1997;30(4):673-81
F-ISE based on Tin (IV) organometallic compounds as ion carriers	F ⁻	Quim Anal 1997;16 (Suppl 1):S105-9
Array of sensors based on chalcogenide glass electrodes & artificial neural net works	F ⁻ in mixed solution	J Anal Chem 1997;52(11):1087-92
FIA-F-ISE	F ⁻ in tap water, river water and well water	Quim Anal 1997;16(3):197-204
Isolation by pyrohydrolysis and determination by FIA-F-ISE	F ⁻ in human hair	Environ Sci 1997;5(1):49-56
Hexamethyldisiloxane microdiffusion followed by F-ISE detection	F ⁻ in soil and plant containing high concentration of Al ³⁺	Talanta 1997;44(10):1729-33
F-ISE	F ⁻ impurities in calcium ascorbate	Arch Pharm 1997;330(11):348-52
FIA-F-ISE	F ⁻ in chromium electroplating baths	Fresenius' J Anal Chem 1998; 362(2):230-3
Decomplexation of Al-F complexes by citrate-based buffers as a function of pH, Al ³⁺ and F ⁻ concentrations	F ⁻	Anal Chim Acta 1998;368(3):265-73
FIA-F-ISE	Speciation of F ⁻ and Ca ²⁺ in natural water	Anal Chim Acta 1998;366(1-3):23-33
F-ISE with ultrasonic sample preparation	F ⁻ in waters, brines, and common salt	J Anal Chem 1998;53(5):461-5
A continuous flow-system equipped with a F-ISE	Free and total amount of F ⁻ in rainwater	Anal Chim Acta 1998;364(1-3):117-23
F-ISE	F ⁻ in microvolume sample (20 µL)	Arch Oral Biol 1998;43(10):819-23
Potentiometric titration with AlCl ₃ solution combined with oxygen flask combustion	Fluorine in organic compounds	Anal Sci 1998;14(6):1145-7
F-ISE with Gran's plot	F ⁻ in wine	Food Addit Contam 1998;15(8):893-7
F-ISE	F content in high purity fluorapatite	Talanta 1998;46(6):1273-7
F-ISE	F ⁻ in bovine urine	J AOAC Int 1998;81(4):839-43
Preconcentration with chromato-membrane cell and adsorptive polarography	F in air	Talanta 1998;47(1):25-32
A PVC membrane electrode containing naphthyl-boronic acid as an ionophore and tridodecylmethylammonium chloride as an additive	F ⁻	Anal Chim Acta 1999;387(2):189-95
FIA-F-ISE	F ⁻ in water	Lab Rob Autom 1999;11(2):105-9
Polarography	Trace F ⁻ in food	Food Chem 1999;66(4):519-23

SPECTRAL ANALYSIS

Threshold ionization mass spectrometry (MS) has been applied to the study of the neutral radicals present in a microwave-generated CF_4 plasma.¹⁰ Calibration of the MS signals by comparison with ion signals produced by the dissociative ionization of CF_4 allowed estimation of the absolute concentration of the radicals in a 15-mtorr plasma, with emphasis on atomic fluorine and CF_X ($X = 1-3$) radicals. Fluorescence measurements of the beads formed by fusing UO_2^{2+} with F^- in the presence of a mixture of sodium and potassium carbonates at $700 \pm 30^\circ\text{C}$ offers a novel fluorometric method for the rapid determination of fluoride in fluoride-bearing minerals and compounds.¹¹ The fluorescence intensity of the species formed was directly proportional to the amount of fluoride ion (80-2000 μg) and a fixed amount of UO_2^{2+} , e.g., 10 μg of U(VI). To eliminate interference by potential quenchers, metal ions are separated by fluoride distillation or by precipitation in matrix ions as hydrous oxides. With the use of time-resolved laser-induced breakdown spectroscopy (TRELIBS), low concentrations of main-group heteroatoms such as fluorine, chlorine, sulfur, and carbon in pollutants and chemical agents have been rapidly detected in atomic condition.¹² The detection limits are close to 10-50 ppm for F, Cl, and C atoms. With boronic acids as receptor units, fluorescent photoinduced electron transfer (PET) sensors exhibit F^- selective fluorescent quenching in aqueous solution at pH 5.5.¹³ Decrease in the color intensity of the thorium-bromocresol orange complex with F^- ion provides a direct spectrophotometric method for the determination of F^- ion in water from 0.02 to 3.00 $\mu\text{g}/\text{mL}$ (S.D. $\pm 0.9\%$).¹⁴

Determination of fluoride by spectral analysis is summarised in Table 2.

Table 2. Determination of fluoride by spectral analysis

Method	Application	References
Infrared laser adsorption spectroscopy (IRLAS)	Behavior of F species and FC_X radical species in etching plasma	Optronics 1997;190:145-9
Actinometry and vacuum ultraviolet absorption spectroscopy	F atom density	Jpn J Appl Phys 1997; Part 2;36 (9A/B):L1261-4
Pyrohydrolytic decomposition followed by spectrophotometric determination based on the reaction of F^- -La-alizarin ternary complex formation at pH 4.6	F content in soil	Zavod Lab 1997;63(3):11-2
Spectrophotometry	F compounds in air	Zavod Lab 1997;63(10):13-6
Atomic emission spectrometry with computer processing of spectra	F	J Anal Chem 1997; 52(12):1118-27

Table 2. continued

Method	Application	References
Spectrophotometry based on the reaction of F ⁻ with thorium-arsenazo complex	F ⁻ in natural water and sea water	Izv Vyssh Uchebn Zaved Khim Khim Tekhnol 1997;40(3):52-4
Negative ion electrospray mass spectroscopy (ES-MS)	F ⁻ in mouthwash samples	J Anal At Spectrom 1997;12(5):497-501
Extraction/ Spectrophotometry with a long capillary cell	Trace F ⁻ in water	Fenxi Huaxue 1997;25(2):201-4
Spectrophotometry based on the reaction of F ⁻ with zirconium-arsenazo complex	F in welding- aerosol-type complex multi-component systems	Izv Vyssh Uchebn Zaved Khim Khim Tekhnol 1997;40(3):49-52
Molecular absorption spectroscopy	Determination of F as AlF	J Anal Chem 1998;53(2):100-8
Adsorption-spectrophotometry	F ⁻	J Anal Chem 1998;53(2):117-20
Atomic emission spectrometry with algorithms of searching for molecular band edges of CaF	F in rocks	J Anal Chem 1998;53(2):125-32
Indicator paper impregnated with zirconium-alizarin complex	F ⁻ in environmental samples	J Anal Chem 1998;53(8):762-7
Ion scattering spectroscopy (ISS)	F in the speckled area of Al-Li alloys	Mater Lett 1998; 37(6):366-70
Visual colorimetry based on the reaction of F ⁻ with alizarin complexone	F ⁻ in water	Kogyo Yosui 1998;481:37-44
Diffuse reflectance near infrared spectroscopy	Organic fluoride compounds	J Near Infrared Spectrosc 1998; 6(1-4):A239-41
Fluorophotometric titration based on the reaction of F ⁻ with Al-CNDA (3-carboxy-2-naphthyl-N, N-diacetic acid) complex	Organic fluoride compounds	Yakugaku Zasshi 1998;118(8):301-9
Colorimetry based on the reaction of F ⁻ with cerium-alizarin complexone or with sodium-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate	F ⁻ in drinking water	Field Anal Chem Technol 1998; 2(1):51-8
Spectrophotometry following pyrohydrolytic distillation	F ⁻ in fluoro-phosphate glasses	Glass Technol 1998;39(3):100-4
Spectrophotometry based on the reaction of F ⁻ with lanthanum-alizarin complexone	F ⁻ in plant samples	Talanta 1999;48(1):57-62

CHROMATOGRAPHY

A commercial micromembrane suppressor, usually used to chemically suppress eluent conductance in ion chromatography, was successfully used to effect ion replacement reactions in suppressed eluent streams.¹⁵ For 10 mM fluoride and 10 μ M acetate, there were net decreases in conductance

upon conversion of the acids into their sodium salts, thus showing that these concentrations were below their critical point concentrations (CPCs).

For simultaneous determination of small cations and anions, a capillary electrophoresis system was developed with only one capillary and just one detector.¹⁶ The sample was injected into the front end of the separation capillary and subsequently into the back end. When high voltage was applied, the cations and anions in the two injected sample portions started to migrate toward the center of the capillary, where a detection window was located. A background electrolyte, composed of 6 mM 4-aminopyridine, 2.7 mM H_2CrO_4 , and 30 μM cetyltrimethylammonium bromide at pH 8, provided excellent separation of 22 small inorganic and organic anions and group 1A and 2A cations within 5 min. The overall deviation of migration times was less than 0.3%. Reproducibility of peak areas ranged from 1.7 to 5.5% ($n = 9$), based on manual hydrodynamic injections with a duration of 40 s.

A contactless capacitively-coupled conductivity detector for capillary electrophoresis has been introduced.¹⁷ The detector consists of two electrodes that are placed cylindrically around the outer polyimide coating of the fused-silica capillary with a detection gap of 2 mm. The electrodes form a cylindrical capacitor, and the electric conductivity of the solution in the gap between the electrodes is measured. For an improved version of the detector, two syringe cannulas are used as the electrodes, and the capillary is assembled into the tubing, allowing easy placement of the detector at various positions along the capillary.

Using an online 2D isotachophoretic system, potential impurities such as F^- , NO_3^- , SO_4^{2-} , NO_2^- , PO_4^{3-} , formate, and oxalate were detected up to an analyte-to-excess ratio of $1:(3 \times 10^5)$.¹⁸ With an electrolyte system consisting of two different leading electrolytes, limits of detection in the nmol/L range were realized by conductivity detection. These optimized conditions were applied to the determination of these anionic impurities in different types of acetic acid and acetate salts to evaluate and verify their quality. Without sample preparation and/or preconcentration, it was possible to determine the above-mentioned analytes in the range of 0.00032 to 0.001% within 20 min. Based on the ternary M-F^- -(5-Br-PADAP) complexes [$\text{M} = \text{Zr}^{\text{IV}}$ or Hf^{IV} and 5-Br-PADAP = 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol], optimum conditions for the direct reverse-phase LC determination of fluoride were reported.¹⁹ Chromatographic separation was performed with a C_{18} end-capped column with an eluent consisting of MeCN- H_2O (85:15 vol./vol.) mixture of pH 4.0 ± 0.3 (flow rate 1 mL/min), the eluent was monitored spectrophotometrically at $\lambda_{\text{max}} = 585$ nm. Calibration curves were linear over a wide range of fluoride concentrations: from 1 to 110 and 150 ng/mL for the $\text{Zr}^{\text{IV}}\text{-F}^-$ -(5-Br-PADAP) and $\text{Hf}^{\text{IV}}\text{-F}^-$ -(5-Br-PADAP) systems, respectively (using a 20 μL loop). The detection limits were 0.8 and 0.7 ng/mL,

and the quantification limit was 1.0 ng/mL for both methods. With this technique, fluoride was determined directly in tap water, saliva, and Leuprolid, an anti-cancer agent for prostatic cancer.

Capillary GC-coupled with microplasma MS provides a method for simultaneous element-selective detection of halogens and carbon.²⁰ The microplasma ion source was a radio frequency plasma contained inside the last 4-5 cm of a 0.32-mm i.d. fused silica capillary column. Atomic ions were detected in the positive mode. Detection limits were in the low picogram area, and the selectivity ranged from 8×10^2 for C and F to $>10^4$ for the other halogens. By introducing both H₂ and O₂ as reagent gases, peak tailing was avoided by suppression of analyte reactions with the silica walls of the ion source. With a chromate-based electrolyte, the analytical performance characteristics of the separation of fluoride in toothpaste by capillary zone electrophoresis (CZE) were investigated.²¹ High precision was recorded for absolute migration time (1.7% relative standard deviation, RSD), peak area (0.8% RSD), and peak height (0.4% RSD). Fluoride was separated in less than 4 min without matrix interference or co-migration with phosphate (resolution *ca* 8). The peak area calibration curve was linear between 5 to 120 µgF/mL. Using this curve, one toothpaste sample was detected to have about 12 µgF/mL ($\approx 0.1\%$ m/m undried basis). The detection limit was 0.5 µg/mL and mean recovery was 106%.

Fluoride analysis by chromatography is summarised in Table 3.

Table 3. Analysis of fluoride by chromatography

Method	Application	References
Capillary electrophoresis (CE) using pyridine-2,6-dicarboxylic acid as electrolyte and tetra-decyltrimethyl-ammonium bromide as electroosmotic flow modifier	F ⁻ in waste water	Chemosphere 1997;35(7):1509-18
CE using ATP as UV chromophore for indirect photometric detection and cetyl-trimethylammonium bromide as modifier	F ⁻ in toothpaste	J Chromtogr A 1997;781(1+2):457-66
IC following sample preparation by combustion	F in oil and sewage sludge	Oesterr Chem Z 1997;98(4):88-92
IC with preconcentration	F ⁻ and other common anions	J Anal Chem 1997;52(7):666-9
Kinetic differentiation-mode CE using three cationic polymer as electroosmotic flow and selectivity modifiers	Co ²⁺ , Ni ²⁺ , Fe ²⁺ , and 11 inorganic anions including F ⁻	J Chromtogr A 1997;776(2):329-36
Capillary zone electrophoresis (CZE) with indirect ultraviolet detection	F ⁻ in an anions mixture	Anal Sci 1997;13 (Suppl Asianalysis IV):243-6
Hyphenated ion chromatography-ion-exclusion chromatography	Anions including F ⁻ in nutrient broths	J Anal Chem 1997;52(7):661-5

Table 3. continued

Method	Application	References
IC with post column deviation equipped with reagent preparation device	Bromate and anions including F ⁻ in drinking water	Anal Chim Acta 1997;346(3):299-305
IC using alkanesulfonate homologous series as eluent components	Common inorganic anions including F ⁻	J Chromtogr A 1997;771(1+2):23-33
Calculation of detection limits for a single-laboratory IC	F ⁻ and other anions in ultrapure water	J Chromtogr A 1997;770(1+2): 105-14
CE with conductivity detection	F ⁻ and other anions in pharmaceutical drug substances	J Pharm Biomed Anal 1997;16(3):469-79
Gas chromatography (GC) used a metal column and FID detection	Ultra-micro-trace F ⁻ in human femur bones	Herba Pol 1997;43(4):417-20
IC employed a new methacrylate-based anion stationary phase	Common inorganic anions including F ⁻	J Chromtogr A 1997;789(1+2):127-34
CE with electrokinetic sample introduction	Anions including F ⁻	Chromatographia 1997;45:301-11
CZE with indirect UV detection	Anions including F ⁻ in cooling lubricants	GIT Labor-Fachz 1997;41(7):742-4
IC	Anions including F ⁻ in Al salt cake	Light Met 1997;1135-40
GC following the conversion of F to its corresponding trimethylsilane derivative using trimethylchlorosilane	F ⁻ impurities in pharmaceutical grade Ca ascorbate	Arch Pharm 1997;330(11):348-52
IC	F ⁻ and Cl ⁻ in high purity water	J Anal Chem 1998;53(2):173-7
Ion Chromatography (IC)	F ⁻ in atmospheric particulate	Sci Total Environ 1998;215(1,2):123-34
CE	F ⁻ and other anions in rainwater	Talanta 1998;45(4):641-56
Suppressed ion-interaction chromatography using a graphitized carbon column	Common anions including F ⁻	J Chromtogr A 1998;800(2):239-45
Reversed phased high performance chromatography (HPLC)	F ⁻ in mineral water and table salt	Fenxi Huaxue 1998;26(3):369
CZE used fluorescein Na salt for indirect fluoremetric detection	Anions including F ⁻	Analisis 1998;26(3):107-15
Enhanced ion chromatography with sequential flow injection analysis	Inorganic anions including F ⁻ in various water	Am Environ Lab 1998;10(2):16-7
IC	SO ₄ ²⁻ , F ⁻ , and other anions on damaged stones and mortars	Atmos Environ 1998;32(4):783-9
Capillary ion electrophoresis	4 anions including F ⁻ and 4 cations in drinking water	Food Chem 1998;61(1-2):249-54

Table 3. continued

Method	Application	References
IC following HPLC-grade water extraction of plant tissues	Anions including F ⁻ and cations in plant tissues	Commun Soil Sci Plant Anal 1998;29(3&4):245-53
IC following absorption with silica gel and extraction with carbonate-hydrogen carbonate solutions	HF and HCl in air of clean-rooms	J Chromtogr A 1998;804(1+2):273-8
Capillary isotachopheresis with enlarged sample load	Anionic trace impurities including F ⁻ in glycerol	J Chromtogr A 1998;810(1+2):201-8
IC using a Dionex AS14 column	Quantitation of F ⁻ and CH ₃ COO ⁻	J Chromtogr A 1998;804(1+2):123-9
CE with a chelating agent	Anions including F ⁻ and cations in mineral water	J Liq Chromatogr Relat Technol 1998;21(10):1445-56
CZE with indirect UV detection	F ⁻ in a synthetic mixture of anions	Anal Sci Technol 1998;11(3):213-21
IC	Anions including F ⁻ in certified ref. materials	J Chromtogr A 1998;813(1):85-90
CZE with electrokinetic injection and indirect UV detection	Anions including F ⁻ in the secondary circuit water of a nuclear power plant	Chromatographia 1998;47(11/12):630-6
IC using alternate eluents	F ⁻ in lead-acid battery electrolyte	Analyst 1998;123(5):1109-13
CZE with indirect UV detection using dual UV-absorbing background electrolytes	Small cations and anions including F ⁻	Electrophoresis 1998;19(12):2243-51
Anion-exchange chromatography using a anion-exchange resin containing three amine groups	Anions including F ⁻	J Chromtogr A 1998;793(2):231-8
CZE with indirect photometric detection	F ⁻ and other anions in soil extracts and atmospheric deposition	Commun Soil Sci Plant Anal 1998;29(11-14):1585-92
CZE and IC	F ⁻ and other anions in H ₂ O ₂	J Chromtogr A 1998;829(1+2):351-7
IC following membrane filtration and conjunction with solution absorption	F ⁻ and other anions in high-purity gases	J Chromtogr Sci 1998;36(12):579-82
IC	F ⁻ in a 60 year-old core from Antarctica	Ann Glaciol 1998;27:391-7
IC with online post-column fluorimetric detection	Trace F ⁻ in natural water	Analyst 1999;124(1):27-31

MISCELLANEOUS

Taking advantage of the specific interaction of fluoride with hydroxyapatite, a thermometric method for detection of fluoride has been developed.²²

Table 4. continued

Method	Application	References
The $^{19}\text{F}(\alpha, \rho)^{22}\text{Ne}$ resonant nuclear reaction at a 2313 KeV	Detection and depth profiling of ^{19}F	Nucl Instrum Methods Phys Res Sect B 1998;136-138:528-32
X-ray photoelectron spectrometry	Depth profile of implanted F ions in SiO_2/Si	Nucl Instrum Methods Phys Res Sect B 1998;140(1, 2):124-8
Instrumental neutron activation analysis equipped with a new raid pneumatic tube irradiation facility	Determination of activation products including F	J Radioanal Nuc Chem 1998;233(1-2):155-9
Neutron activation analysis equipped with a fast pneumatic irradiation system	Ultra-micro F	Bunseki Kagaku 1998;47(9):613-20
Thermogravimetric analysis and differential scanning calorimetry	Characterization of a polymer surface	Proc Conf North Am Therm Anal Soc 26th 1998;15-20
Instrumental photon activation analysis and neutron activation analysis	Analysis of halogens in various Matrixes	Fresenius' J Anal Chem 1998;362(4):382-6
Instrumental neutron activation analysis	Trace F in silicon nitride	Bunseki Kagaku 1998;47(11):829-34

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the Natural Science Fund of Yunnan and the Science Fund of Yunnan Education Department.

REFERENCES

- 1 Wen ML, Shi NH, Qin Y, Wang CY. Developments in the analysis of fluoride 1995-1997. *Fluoride* 1998;31(2):74-80.
- 2 Antonisse MMG, Snellink-Ruel BHM, Reinhoudt DN. Chemically modified field effect transistors with nitrite or fluoride selectivity. *J Chem Soc Perkin Trans* 1998;2(4):773-7.
- 3 Moritz W, Krause S, Bartholomaus L, Gabusjan T, Vasiliev AA, Godovski DY, et al.. Silicon-based sensor for fluorine gas. *ACS Symp Ser* 1998;690 (Polymers in Sensors):119-29.
- 4 Vasiliev A, Moritz W, Fillipov V, Bartholomoaus L, Terentjev A, Gabusjan T. High temperature semiconductor sensor for the detection of fluorine. *Sens Actuators* 1998;B49(1-2):133-8.
- 5 De Maeyer EAP, Verbeeck RMH. Analysis of bioactive fluoride-containing calcium aluminosilicate glasses. *Anal Chim Acta* 1998;358(1):79-83.
- 6 Yuchi A, Matsunaga K, Niwa T, Terao H, Wada H. Separation and preconcentration of fluoride at the ng/mL level with a polymer complex of Zirconium(IV) followed by potentiometric determination in a flow system. *Anal Chim Acta* 1999;388(1-2):201-8.

- 7 Steinle ED, Schaller U, Meyerhoff ME. Response characteristics of anion-selective polymer membrane electrodes based on gallium(III), indium(III) and thallium(III) porphyrins. *Anal Sci* 1998;14(1):79-84.
- 8 Kahama RW, Damen JJM, Bob JM, Cate C. Enzymic release of sequestered cow's milk fluoride for analysis by the hexamethyldisiloxane microdiffusion method. *Analyst* 1997;122(8):855-8.
- 9 Streffer K, Kaatz H, Bauer CG. Application of a sensitive catechol detector for determination of tyrosinase inhibitors. *Anal Chim Acta* 1998;362(1):81-90.
- 10 Schwarzenbach W, Tserepi A, Derouard J, Sadeghi N. MS detection of F atoms and CF_x radicals in CF₄ plasmas. *Jpn J Appl Phys* 1997;Part 1;36(7B):4644-7.
- 11 Tarafder PK, Khorge CR, Saran R. Fluorometric determination of fluoride. *Chem Anal* 1997;42(3):391-6.
- 12 Dudragne L, Adam PH, Amouroux J. Time-resolved laser-induced breakdown spectroscopy: application for qualitative and quantitative detection of fluorine, chlorine, sulfur and carbon in air. *Appl Spectrosc* 1998;52(10):1321-7.
- 13 Cooper Christopher R. Selective fluorescence detection of fluoride using boronic acids. *Chem Commun* 1998;(13):1365-6.
- 14 Khalifa ME, Hafez MAH. Spectrophotometric and complexometric methods for the determination of thorium and fluoride using bromocresol orange reagent. *Talanta* 1998;47(3):547-59.
- 15 Caliamanis A, McCormick MJ, Carpenter PD. Conductometric detection of anions of weak acids in chemically suppressed ion chromatography. *Anal Chem* 1997;69(16):3272-6.
- 16 Kuban P, Karlberg B. Simultaneous determination of small cations and anions by capillary electrophoresis. *Anal Chem* 1998;70(2):360-5.
- 17 Zemann AJ, Schnell E, Volgger D, Bonn GK. Contactless conductivity detection for capillary electrophoresis. *Anal Chem* 1998;70(3):563-7.
- 18 Meissner, T, Eisenbeiss F, Jastroff B. Determination of anionic trace impurities in acetic acid by two-dimensional capillary isotachopheresis. *Fresenius' J Anal Chem* 1998;361(5):459-64.
- 19 Oszwaldowski S, Lipka R, Jarosz M, Majewski T. Sensitive reversed-phase liquid chromatographic determination of fluoride based on its ternary systems with zirconium(IV) or hafnium(IV) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. *Analyst* 1998;123(7):1529-33.
- 20 Brede C, Lundanes E, Greibrokk T, Pederson-Bjergaard S. Simultaneous element-selective detection of C, F, Cl, Br and I by capillary gas chromatography coupled with microplasma MS. *J High Resolut Chromatogr* 1998;21(12):633-9.
- 21 Harakuwe AH, Haddad PR. Analytical performance characteristics of the separation of fluoride in toothpaste by capillary zone electrophoresis. *Anal Commun* 1997;34(2):67-8.
- 22 Salman S, Haupt K, Ramanathan K, Danielsson B. Thermometric sensing of fluoride by adsorption on ceramic hydroxyapatite using flow injection analysis. *Analyst* 1997;122(11):329-32.