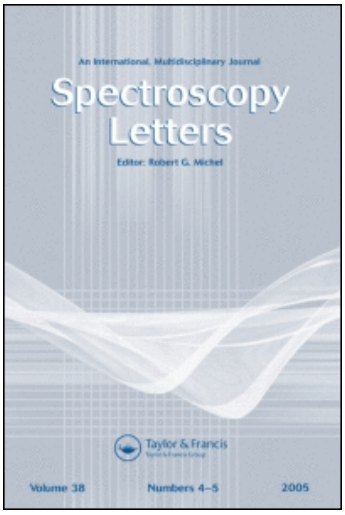

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 17 March 2010

To cite this Article Jankowski, Krzysztof , Jackowska, Adrianna and Tyburska, Anna(2010) 'Determination of Aqueous Fluoride by Continuous Powder Introduction Microwave-Induced Plasma Optical Emission Spectrometry after Preconcentration on Various Sorbents', Spectroscopy Letters, 43: 2, 91 — 100
To link to this Article: DOI: 10.1080/00387010903278291
URL: http://dx.doi.org/10.1080/00387010903278291

Spectroscopy Letters, 43:91–100, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903278291

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ABSTRACT A spectrometric determination of aqueous fluoride has been improved by coupling of continuous powder introduction microwave-induced plasma optical emission spectrometry with separation of the analyte onto powdered sorbents. A selective solid phase extraction method for preconcentrating trace fluoride from aqueous environmental samples on calcium hydrogenphosphate dihydrate in batch operation was employed while, for flow operation, the zirconium modified activated carbon method was adopted. The fluoride could be readily excited in helium plasma at 685.6 nm. Using a 1-L sample volume and a preconcentration factor of 1000, practical detection limit with respect to water sample is in the range 4.0–4.7 ng mL^{-1}, depending on the sorbent used. External calibration was done using standards obtained by the dropping of standard fluoride solution on the powdered sorbent covering fluoride content from 50 to 5000 μg g^{-1}. The procedure was applied to the determination of fluoride in mineral waters and certified reference material (CRM) drinking water.

KEYWORDS continuous powder introduction, fluoride, microwave-induced plasma, mineral water analysis, optical emission spectrometry, solid phase extraction

INTRODUCTION

The determination of trace inorganic fluoride in aqueous solutions is of great environmental importance. However, most of the spectrometric as well as potentiometric methods with ion selective electrodes for determining fluoride at sub-mg L^{-1} levels suffer from lack of sensitivity or selectivity sufficient for the direct determination.[1–5] Optical emission spectrometry (OES) with helium plasma offers a relatively low detection limits for fluoride. Additionally, using spectoscopic methods of the determination total

Received 21 November 2008; accepted 30 May 2009.

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fluoride content is possible even in the presence of fluoride complexing metals. Conventional plasma emission spectrometry is not applicable to the determination of fluoride at a concentration lower than 150 ng mL^{-1}, as reported by Okamoto et al.[2] Hence, for the determination of fluoride at the ng mL^{-1} level, the use of a preconcentration procedure is required. Interests have been directed toward the use of solid phase extraction (SPE) as an effective separation technique for fluoride[6–9]; however, up to now, it was not used in combination with plasma spectrometry techniques. The main advantages of the SPE preconcentration procedures are the availability of a relatively high preconcentration factor, a reduction of wastes, and the possibility of on-line operation.

Plasma spectrometry is generally known as a useful technique for determining elements in water samples. However, some limitations with respect to fluorine detection exist, including lack of energy for efficient ionization and excitation of fluorine atom. Resonance lines of fluorine useful for optical detection are out of the conventional UV-VIs region, and then the less intense emission line at 685.6 nm is usually used. Mass spectrometric detection of aqueous fluoride is restricted by the spectral interference from the matrix elements. However, the use of helium gas, in particular, a helium microwave-induced plasma (MIP), provides fluoride determination at trace levels. Numerous approaches were developed to improve aqueous fluoride determination by OES. Some authors proposed indirect methods based on the formation of fluoride complexes with calcium, aluminum, or silicon and detection of molecular or atomic emission related to the fluoride content.[10–12] Gehlhausen and Carnahan[1] and Okamoto et al.[2] applied desolvation of aqueous aerosol before determination of fluoride by He-MIP-OES to prevent the decrease in the ionization efficiency of a fluorine atom caused by introduction of water and obtained the detection limit for fluoride of 4 and 0.15 μg mL^{-1}, respectively. The separation of fluoride from the solvent by electrothermal vaporization was developed by Okamoto et al. before determination of fluoride by both optical[3] and mass spectrometry.[5]

In this article, SPE has been coupled with the continuous powder introduction (CPI) technique and He-MIP-OES, taking advantage of an extremely high preconcentration factor, matrix separation, and effective excitation of fluorine by He-MIP. A successful extension of the calcium hydrogenphosphate dihydrate (CaHPDH) method is described to the environmental samples in combination with plasma spectrometry. In the other approach, fluoride in water was continuously enriched from a large volume samples (up to 10 L) using zirconium-impregnated activated carbon (ZrIAC) and determined by CPI-MIP-OES.

MATERIALS AND METHODS

Instrumentation

A model MIP 750 MV MIP (Analab Ltd., Warsaw, Poland) sequential spectrometer was used. The reciprocal linear dispersion of the spectrometer was 0.40 nm mm^{-1} in the VIS region. A Hamamatsu Photonics (Toyooka, Japan) Model R446 photomultiplier tube was used as a detector. The spectrometer incorporated a Plazmatronika (Wrocław, Poland) microwave plasma excitation source based on a TE_{101}-integrated microwave resonator. For sample introduction, a previously described homemade CPI system was used.[13] A diagram of the device is shown in Fig. 1. The plasma gas flow is passing through the outer tube of the injector while the sampling gas transports the powdered material from the sample chamber through the inner tube to the MIP torch.

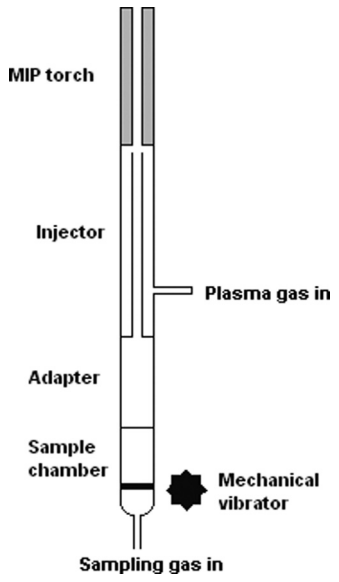

FIGURE 1 Schematic diagram of the CPI device.

TABLE 1 Measurement Conditions for CPI-MIP-OES System with Helium Plasma

Microwave frequency (MHz)	2450
Microwave power (W)	350
Plasma viewing mode	Axial
Plasma gas flow rate (mL min$^{-1)}$	200
Sampling gas flow rate (mL min^{-1})	400–500
Integration time (s)	0.5
Wavelength (nm)	F(I) 685.6

The experimental conditions of spectrometric measurements are collected in Table 1. Potentiometric measurements were made using digital ion meter equipped with a fluoride selective electrode (model 94-09, Orion, Beverly, USA).

Reagents

Analytical reagent-grade chemicals were employed in the preparation of all solutions. Fluoride standard solution (5000 mg L^{-1}) was prepared by dissolving of ammonium fluoride (Merck, Darmstadt, Germany) with 0.25% ammonia solution and stored in a polyethylene bottle.

CaHPDH (POCh, Gliwice, Poland) was powdered, sieved, and the 45–63 μm fraction was retained. Finally, it was dried for 5 h in an electric oven at 80°C and kept in a dry environment. Activated carbon (AC) Darco G-60, −100 mesh (Aldrich, Steinheim, Germany) was sieved and the 45–63 μm fraction was used without any pretreatment.

Zirconyl nitrate solution (1-g Zr, pH 1.6) was prepared by dilution with water from 35%$_{w/w}$ zirconyl nitrate solution in dilute nitric acid, 99+% (Sigma-Aldrich, Steinheim, Germany) directly before use.

The ZrIAC was prepared according to Hashitani et al.[7] by mixing 200-mL zirconyl nitrate solution with 20 g of AC at room temperature for three days, filtering and drying the powder in air. The only difference was in the kind of AC used, including the particle size range. Ten grams of ZrIAC included about 0.56 g of zirconium.

A 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) buffer solution (Aldrich, Steinheim, Germany) of pH 5.5 was used for potentiometric determination of fluoride in some mineral water samples.

Procedures

Batch Preconcentration Procedure Using CaHPDH

A 0.2- to 1-L volume of sample solution containing 20–5000 μg of fluoride was placed in a polypropylene beaker. The pH was adjusted to 8.5 ± 0.2 with ammonia, and the solution was heated to 60°C. Then, the 1.00 g weight of 45–63 μm fraction of CaHPDH was added. After the sorption process with the aid of magnetic stirring, the mixture was filtered through a filter paper, and the powdered sorbent with retained analyte was washed with a small amount of deionized water and dried at 110°C for 1 h before fluoride determination by CPI-MIP-OES.

Flow Procedure Using ZrIAC

A ZrIAC bed was formed on a Millipore filter paper 45 mm in diameter by filtering an aqueous ZrIAC suspension with suction (1.00 g of 45–63 μm fraction of ZrIAC in 50-mL distilled water) through the filter. An aqueous sample, containing 20–5000 μg of fluoride, with the pH adjusted to 3.8 ± 0.3 with diluted hydrochloric acid was passed with suction through the ZrIAC bed to collect the fluoride. Then, the sorbent was washed with a small amount of water at pH of 3.8 and dried at 70°C for 2 h.

Measurement Procedure

A dried material obtained during the preconcentration procedure, containing analyte-on-sorbent particles, was placed in the sample chamber of the CPI system. The helium plasma was ignited, and the microwave power was adjusted to 350 W. Then, both the sampling gas flow and the plasma gas flow were adjusted to 400 (or 500) mL min^{-1} and 200 mL min^{-1}, respectively. The 5-min delay time before readings was used to allow the stabilization of the sample delivery and plasma conditions. The fluorine emission was measured at 685.6 nm and corrected for background by off-peak measurements.

Direct potentiometric measurements with a fluoride selective electrode were conducted after the addition of 10 mL of the HEPES buffer solution to 15 mL of the aqueous sample to attain the adequate ionic strength for improving the precision of the measurements at lower F^- concentrations. Then,

the calibration range of the electrode (nominal 1.9–1900 mg L^{-1}) could be extended to about 0.3 mg L^{-1}.

RESULTS AND DISCUSSION

Optimization of SPE Procedures

In conventional SPE procedure, when applying sorption of the trace elements and a subsequent elution into an aqueous phase for sample preparation before determination, contamination or losses of analyte, as well as a dilution during the latter step, may occur. These problems may be omitted by solid sampling of analyte-on-sorbent particles and analyzing by the direct plasma spectrometric technique. For the overall analytical performance of the method, the quantitative recovery of the analyte is desirable rather than the selectivity of sorption. The limitation of the method is that it is impractical for recovering sorbent after use because it is destroyed in the plasma. For this reason, low-cost materials are preferred. Fortunately, numerous types of low-cost materials have been proposed as a sorbent for fluoride. Tafu et al.[6] used CaHPDH as a collector for fluoride in water. Yuchi et al.[9] used preconcentrated fluoride at the ng mL^{-1} level using polymer complex of zirconium followed by analyte elution and potentiometric determination in a flow system. AC loaded with zirconium has been used by Hashitani et al.[7] as a collector for fluoride preconcentration before its colorimetric determination.

Although the natural background emission near the fluoride line at 685.6 nm is low, the sorbent selected for the sorption of fluoride should not contribute an appreciable background; the use of CaHPDH, alumina, and AC offers good possibilities. Fluoride was retained on the 1-g portion of the individual sorbent. The weighed amount of the sorbent was added to 500 mL volume of solution containing 500 µg of fluoride after pH adjustment. The optimum pH values for fluoride sorption by CaHPDH, alumina, and AC were 8.5, 5.5, and 3.8, respectively. The quantitative recovery of fluoride was determined for CaHPDH and alumina, while the sorption efficiency of the fluoride on the AC was only 68%. In order to improve fluoride recovery for AC, the sorbent was modified according to the procedure proposed by Hashitani et al.[7] This improvement is due to the chemical interaction between zirconyl groups and fluoride (as F^- or HF) to form mixed-ligand complexes. The use of ZrIAC allows quantitative sorption of fluoride, and the results obtained using this sorbent are described in this article in more detail.

Comparing the fluoride emission signals obtained for all sorbents used in this study, it was stated that the signal obtained for CaHPHD is about two times higher than that for other sorbents. This corresponds to the results obtained by Sugimae and Skogerboe,[10] who proposed the addition of calcium carbonate to improve the spectrographic determination of fluoride in a number of geological materials. However, the use of CaHPDH provides appreciable background emission in comparison with AC. Nevertheless, CaHPDH was chosen for further investigation.

CaHPDH Method

Calcium phosphate quantitatively reacts with fluoride in the solution to form sparingly soluble fluorapatite. Tafu et al.[6] used 10 mg of CaHPDH for the enrichment of fluoride before its microdetermination with the fluoride selective electrode after dissolution of the sorbent with nitric acid. This SPE technique was adopted to the CPI-MIP-OES approach. The amount of sorbent used was enlarged to 1.0 g, suitable for CPI technique, and the dissolution step of fluoride containing sorbent was omitted. The optimum conditions of the batch operation were verified with respect to the pH, contact time, and temperature of sorption, as well as the particle size of the sorbent and the effect of metal ions concentration in the solution.

The pH value of the solutions does not appear to be critical for the overall performance of the SPE method. However, the pH adjustment of the solution above 7.0 is required because of the solubility of CaHPDH and resulting fluorapatite.[6] It was found experimentally that the sorption of fluoride higher than 90% occurs in the pH range 7.5–10. Finally, a pH of 8.5 was chosen, as some mineral water samples showed slightly low recovery at lower pH.

In the experiments designed to study the effects of contact time and temperature of sorption of fluoride on CaHPDH, 500 mL of a solution containing 500 µg fluoride was stirred continuously with 1.0 g of CaHPDH for periods ranging from 0.5 to 6 h and at

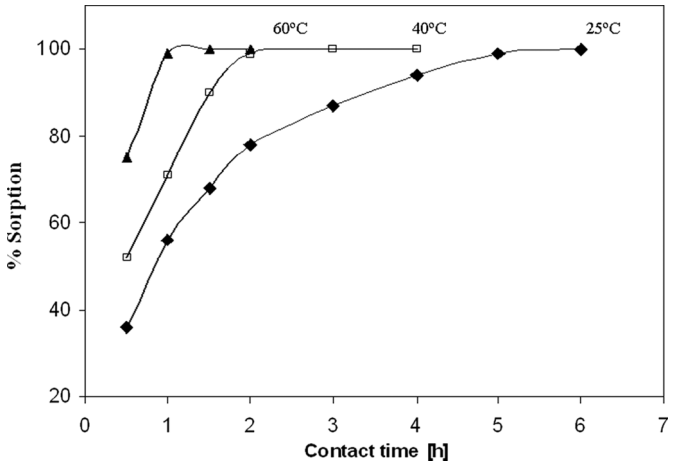

FIGURE 2 Effect of time and temperature on sorption of fluoride (500 μg in 0.5 L) on CaHPDH (1.0 g).

temperatures 25°C, 40°C, and 60°C. The results are shown in Fig. 2. A 100% retention of fluoride on CaHPDH was achieved at each temperature; however, the sorption rate increased with temperature. The marked effect of temperature on the sorption of fluoride on calcium phosphate was also observed by Venkateswarlu and Sita.[8] A 1-h batch sorption at 60°C was therefore followed in the procedure described above for the determination of fluoride by the SPE-CPI-MIP-OES technique. The amount of the sorbent used, ranging from 0.5 to 2.0 g, did not influence fluoride recovery. However, the mass of 1.0 g was selected as suitable for the CPI system operation.

For sorption efficiency measurement, powdered standards were prepared by dropping the aliquot of the fluoride standard solution containing 500 μg of fluoride on a 1-g portion of the individual sorbent. After drying, fluoride emission was measured and compared with the results obtained with batch sorption procedure. The maximum sorption capacity, ca. 7 mg of fluoride on 1.0 g CaHPDH, was obtained under experimental conditions.

ZrIAC Method

CaHPDH is not applicable in the flow sorption procedure due to the drastically low column permeability. In contrast, AC-loaded columns exhibit good permeability; however, the sorption efficiency for fluoride is low. These drawbacks have been overcome by the use of ZrIAC. ZrIAC was prepared with the use of 45–63 mm fraction of AC as described in the experimental section. Gravimetric analysis reveals 5.56% of zirconium for synthesized ZrIAC, which corresponds well with the result obtained by Hashitani et al.[7]

The effect of pH, contact time, and temperature on the sorption of fluoride on ZrIAC was examined in the batch method and compared to AC. Each solution (500 mL) contained both 500 μg of fluoride and 1.0 g of ZrIAC. The suspended solution was stirred, and then the solid material was filtered and dried. The amount of fluoride retained on the ZrIAC was determined by measuring the fluoride signal with CPI-MIP-OES from the analyte-on-sorbent particles. The effect of varying the pH from 1 to 7 on the sorption efficiency is shown in Fig. 3. Fluoride is adsorbed quantitatively on ZrIAC at a pH below 4.5; a plateau does form below 4.0. Considering these results, the selected pH was 3.8 ± 0.3. The recovery of fluoride is not quantitative when AC is used as a sorbent with maximum sorption efficiency at a pH of about 3.5. Figure 4 shows the change in the amount of fluoride retained on ZrIAC and AC with contact time up to 12 h. For ZrIAC, complete retention occurred after more than 2 h; whereas for AC, the recoveries were below 70% even after 12 h of sorption process. No effect of temperature was found in the range of 15°C to 40°C. However, comparing with the sorption on CaHPDH at 60°C, the sorption rate of fluoride on AC, or even on ZrIAC, is much lower.

Optimum conditions for the quantitative recovery of fluoride were determined in flow procedure by

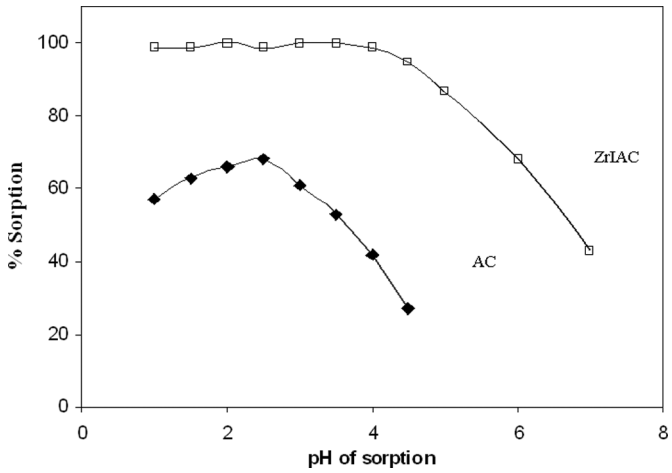

FIGURE 3 Effect of pH on sorption of fluoride (500 μg in 0.5 L) on ZrIAC and AC (1.0 g each).

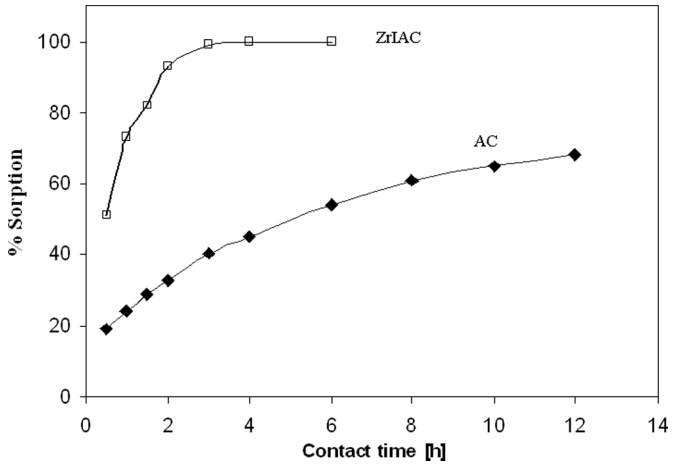

FIGURE 4 Effect of time on sorption of fluoride (500 μg in 0.5 L) on ZrIAC and AC (1.0 g each).

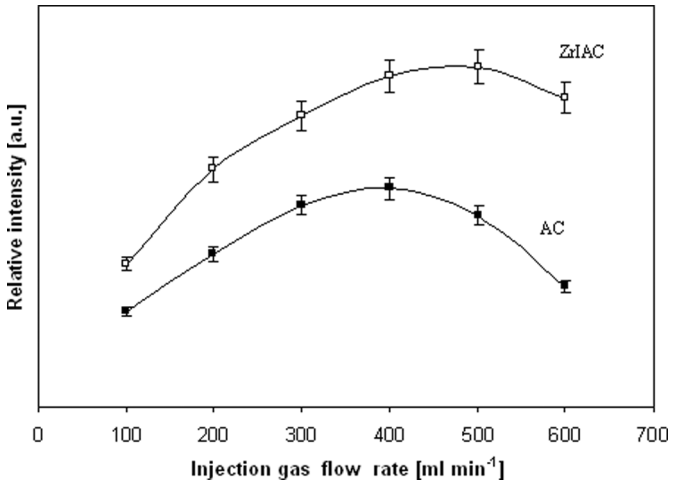

FIGURE 5 The effect of injection gas flow rate on emission intensity of fluorine on CaHPDH and ZrIAC by CPI-MIP-OES (plasma gas flow rate of 200 mL min^{-1}; microwave power of 350 W).

studying the effect of mass of sorbent and sample volume. An aqueous solution with the pH adjusted to 3.8 ± 0.3 is passed with suction through the ZrIAC bed to collect the fluoride. The fluorine signal was monitored by measuring with CPI-MIP-OES. Fluoride was recovered quantitatively from 0.1 to 1 L of solutions containing 50 to 5000 μg of fluoride with the proposed method. Moreover, by the following procedure, 10 L of aqueous solution containing 100 μg of fluoride was preconcentrated on a 1-g ZrIAC bed with a recovery higher than 95% within 3 h. The maximum sorption capacity, ca. 6.0 mg of fluoride on 1.0 g ZrIAC, was obtained at pH below 4.0.

Optimization of CPI-MIP-OES Conditions

Optimization experiments were performed with the aid of the fluoride powdered standard obtained by the dropping of 500 μg of the analyte on the 1-g amount of both CaHPDH and ZrIAC, respectively. The emission intensities for fluorine were measured as a function of microwave power as well as sampling and plasma gas flow rates. The sample feed rate was controlled with sampling gas flow rate value and determined by weighing the sample chamber before and after the measurement period.

Effects of the plasma and sampling gas flow rate on the emission intensity under the constant microwave power are shown in Figs. 5 and 6, respectively. These effects are similar to those observed previously for AC- and silica-based fluoride standards.[4] For the fixed plasma gas flow rate of 200 mL min^{-1}, the sampling gas flow rate was varied between 100 to 1000 mL min^{-1}. Initially, with the increasing sampling gas flow rate, the intensity increases gradually and then decreases, as seen in Fig. 5. The decrease of the signal could be explained in terms of plasma overloading with the sample rather than the reduction of the residence time of analyte in the plasma. An optimum sampling gas flow rate for both CaHPDH- and ZrIAC-based standards is 400 and 500 mL min^{-1}, which corresponds to sample feed rate of 12 and 20 mg per minute, respectively. The effect of plasma gas flow rate observed under constant sampling gas flow rate is similar to that

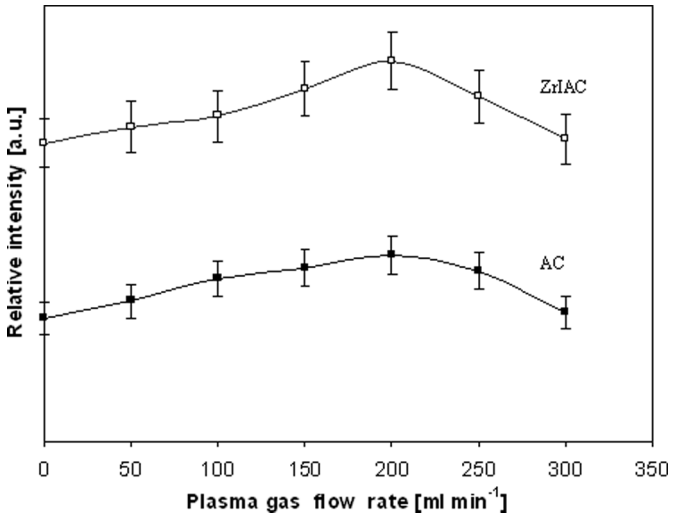

FIGURE 6 The effect of plasma gas flow rate on emission intensity of fluorine on CaHPDH and ZrIAC by CPI-MIP-OES (injection gas flow rate of 500 and 400 mL min^{-1}, respectively; microwave power of 350 W).

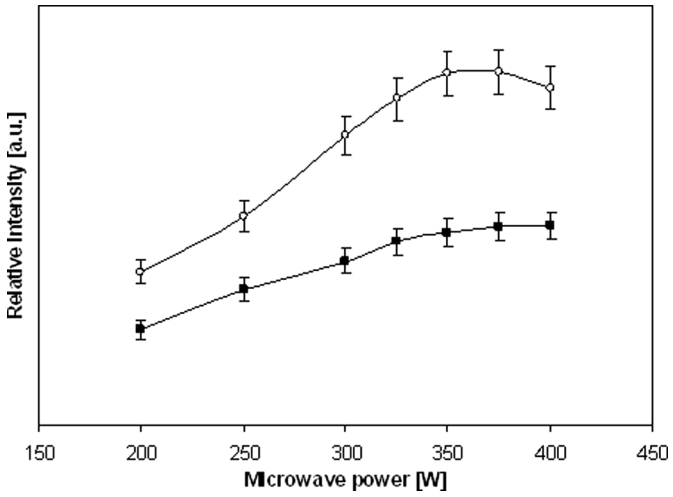

FIGURE 7 The effect of microwave power on emission intensity of fluorine on CaHPDH and ZrIAC by CPI-MIP-OES (total gas flow rate of 600 mL min^{-1}).

observed for the sampling gas flow rate. The emission intensity increased initially, reaching maximum at about 200 mL min^{-1} for both standards, as shown in Fig. 6. The increase of plasma gas flow rate from 50 to 200 mL min^{-1} improves vaporization conditions in the plasma as a result of increasing helium to sample load ratio. The signal decrease observed for higher plasma gas flow rates could be explained, considering the decrease of the particle residence time in the plasma.

The influence of microwave power on the analytical signal was examined, while the total gas flow was held constant at 600 mL min^{-1}. As shown in Fig. 7, fluorine emission increased by a factor of almost two when the microwave power is raised from 200 W to 350 W and then stabilized.

Calibration Strategy

For calibration of the analytical system, two sets of five calibration standards each (50–5000 μg of fluorine per 1 g of CaHPDH or ZrIAC) was prepared by dropping the aliquot of fluoride standard solution under the experimental conditions described above. The calibration graphs were linear over about two orders of magnitude (see Table 3 below). The correlation coefficients (R^2) of the analytical curves by the CPI-MIP-OES for fluoride on CaHPDH or ZrIAC are 0.9973 and 0.9990, respectively, up to at least 5000 μg g^{-1}. These values are comparable with those obtained previously for AC- and silica-based standards.[4] However, the slope of the calibration function for CaHPDH-based standards is more than two times higher than those for other sorbents, indicating the matrix effect caused by calcium. Probably, fluorine is readily volatilized from the fluorapatite particles as a CaF_2 molecule (boiling point about 2500°C) with subsequent dissociation to form a CaF molecule and fluorine atom or to directly form fluorine molecule. This was concluded previously by Sugimae and Skogerboe[10] for their improved DC arc spectrographic method of fluorine determination.

TABLE 2 Comparison of Detection Limits for Fluoride by Various Atomic and Mass Spectrometric Techniques

Analytical technique	Sample form	Detection limit (ng mL^{-1})	Reference
DC arc-OES[a]	Powder	20,000	10
CPI-MIP-OES	Powder	3200–5600	4
USN-MIP-OES	Solution	150	2
USN-MIP-OES	Solution	4000	1
FIA-MIP-OES	Solution	35,000	1
ETV-MIP-OES	Solution	71,000	3
ETV-MIP-MS	Solution	3200	5
SPE-CPI-MIP-OES	Powder	4.0–4.7	This work
IC-ICP-MS[a]	Solution	0.1	12
VG-DCP-OES[a]	Gaseous	0.9	11
Potentiometric with ISE[b]	Solution	750	6

[a]Indirect method.
[b]Direct method (for comparison).
Abbreviations: USN, ultrasonic solution nebulization; FIA, flow injection analysis; ETV, electrothermel vaporization; IC, ion chromatography; VG, vapor generation; DCP, direct current plasma; ISE, ion selective electrode.

Analytical Performance of the Method

The experimental detection limits in the developed methods were calculated according to

TABLE 3 Analytical Figures of Merit of Fluorine Determination at 685.6 nm by SPE-CPI-MIP-OES Method

Calibration standards	Linear range (μg g^{-1})	RSD (%)	Tolerance limit for interfering ions (mg L^{-1})
CaHDPH-based	20–5000	4.6	Ca, 200 Mg, 200 Al, 10
ZrIAC-based	25–5000	3.2	Ca, 200 Mg, 200 Al, 1

TABLE 4 Determination of Fluoride in Mineral and Drinking Water Samples by SPE-CPI-MIP-OES (n = 5)

Sample	Determined by SPE-CPI-MIP-OES with CaHDPH (mg L^{-1})	Determined by SPE-CPI-MIP-OES with ZrIAC (mg L^{-1})	Determined by potentiometry (mg L^{-1})	Certified value (mg L^{-1})
Mineral water 1	0.31 ± 0.019	0.30 ± 0.020	0.32 ± 0.014	
Mineral water 2	0.25 ± 0.013	0.26 ± 0.014	0.26 ± 0.015	
Mineral water 3	0.12 ± 0.007	0.13 ± 0.008	0.12 ± 0.038	
Mineral water 4	0.08 ± 0.005	0.08 ± 0.006	n.d.	
ERM-CA016A drinking water	1.49 ± 0.08	1.47 ± 0.08		1.5 ± 0.1

The uncertainty is based on a 95% confidence interval for the mean.

Boumans, using the SBR-RSDB approach based on the 3σ criterion.[14] The values obtained by CPI-MIP-OES are 4.0 and 4.7 μg g^{-1} when fluoride is collected on CaHPDH and ZrIAC, respectively. Using SPE, the enrichment factor of 1000 (for a sample volume of 1.0 L and sorbent mass of 1.0 g) was obtained with respect to the determination by CPI-MIP-OES without preconcentration. The resulting detection limits were 4.0 and 4.7 ng mL^{-1} with respect to initial fluoride concentration in a water sample. However, the detection limit for the flow procedure with ZrIAC is probably lower than 1 ng mL^{-1} for 10 L of initial sample volume. The detection limits achieved for fluoride by the SPE-CPI-MIP-OES method are compared with some results from the literature, as shown in Table 2. Compared with the direct spectrometric methods for fluorine determination in solid and aqueous samples,[1–5] the detection limit for fluorine was improved by a factor of 50–1000 using the proposed method. Considerably lower detection limits were reported by Bayon et al.[12] and Barnett et al.[11] for indirect methods; however, silicon or aluminum emission was measured instead of fluorine emission. Moreover, they employed separation and preconcentration of the analyte before determination and performed transient peak measurements.

Other analytical figures of merit of the CPI-MIP-OES method in combination with the preconcentration of fluoride are summarized in Table 3. The relative standard deviation for 10 replicate determinations was below 5.0% for 100 μg of the fluoride per 1.0 g of the sorbent. The linear dynamic ranges cover about two orders of magnitude, which is sufficient for fluoride determination in environmental water samples.

In order to evaluate the fluoride recovery of the proposed SPE methods, 1.0 L of water samples containing 50, 500, and 5000 μg of fluoride were subjected to the analytical procedures. The recoveries obtained were between 95.0% and 101.0% for 50 and 500 μg of fluoride, while for 5000 μg of fluoride sorbed on CaHPDH and ZrIAC, they were 93% and 90%, respectively.

As shown in Table 3, fluoride (50–500 μg) is quantitatively recovered in the presence of up to 200 mg L^{-1} of calcium and magnesium by both SPE techniques. However, aluminum interfered with the sorption of fluoride on ZrIAC, even with nearly stoichiometric amounts. The tolerance limit toward aluminum ions is higher for the CaHDPH method. Aluminum could be coprecipitated with CaHPDH and does not interfere with determination of fluoride by CPI-MIP-OES.

TABLE 5 Content of Major Constituents in the Mineral Water Samples Examined and CRM (ERM-CA016a)

	Anions (mg · L^{-1})					Cations (mg · L^{-1})				
Sample	HCO_3^-	SO_4^{2-}	Cl^-	F^-	SiO_3^{2-}	Mg^{2+}	Ca^{2+}	Na^+	K^+	Total ions, mg · L^{-1}
Mineral water 1	495.80	—	8.50	0.30	36.00	23.10	114.50	12.70	5.40	709.00
Mineral water 2	309.60	39.59	23.80	0.26	—	22.48	91.18	5.00	1.00	508.95
Mineral water 3	143.40	17.50	8.50	0.12	—	4.25	51.10	2.00	0.90	260.84
Mineral water 4	109.00	—	4.60	0.07	—	8.18	27.73	8.00	—	185.84
ERM-CA016a	—	25.4[a]	25.00[a]	0.15[a]	—	—	—	—	—	—

[a]The concentration under experimental conditions.

Sample Analysis

The proposed methods are applicable to the determination of fluoride in mineral water and drinking water. The results are presented in Table 4. In mineral water, the predominant anions are hydrogencarbonates, chlorides, and sulfates. Alkali and alkaline earth metal ions also exist in wide varieties (see Table 5).

For mineral water, the fluoride preconcentration was performed in filtered samples of 1.0-L volume. In the batch procedure, the pH of sample was adjusted to 8.5 and stirred with 1.0 g of CaHPDH at 60°C for 1 h. In the flow procedure, water samples were adjusted to the desired pH and passed through a ZrIAC bed. An amount of sorbent of 1.0 g had ample capacity for complete sorption of fluoride in the presence of competing species in a wide variety of mineral waters with both CaHDPH and ZrIAC methods. The recoveries of fluoride spiked to some water samples were found to be 93–102%. The results obtained for samples containing more than $0.1\,mg\,L^{-1}$ of fluoride agreed exactly with the result obtained by direct potentiometry. For fluoride concentrations lower than $0.15\,mg\,L^{-1}$, the accuracy of potentiometric determination is insufficient.

Finally, in order to validate the reliability of the proposed SPE-CPI-MIP-OES methods, the drinking water CRM was analyzed. The aliquots of water samples (50 mL of ERM-CA016a) were diluted with deionized water to 0.5 L, adjusted to the desired pH depending on the sorbent use, and treated with 1 g of powdered sorbent. The result shown in Table 4 is in agreement with the certified value.

CONCLUSIONS

Two SPE techniques using different sorbent materials for CPI-MIP-OES has been evaluated and demonstrated to be promising for routine determination of fluoride at low levels in mineral and drinking water samples. An effective batch method for preconcentration of fluoride in aqueous solution has been adopted using CaHPDH. ZrIAC proved to be very attractive as a collector for trace fluoride in flow operation. The proposed preconcentration procedures for fluoride involving sorption but not requiring elution lead to high enrichment factors and provide trace fluoride determination in natural water samples at the $ng\,mL^{-1}$ level when coupled with the CPI-MIP-OES technique. Since the analyte was separated from the solvent prior to CPI introduction into the MIP, effective excitation for atomic fluorine emission was achieved. Considering the effect of fluoride complexing ions, a large excess of Ca, Mg, and less of Al concentrations does not have any effect on the recovery of fluoride at sub-$\mu g\,mL^{-1}$ levels. The sensitivity of direct fluoride determination was substantially improved compared with the other spectrometric techniques previously described.

ACKNOWLEDGMENTS

This work was financially supported by the Warsaw University of Technology.

REFERENCES

1. Gehlhausen, J. M.; Carnahan, J. W. Determination of aqueous fluoride with a helium microwave-induced plasma and flow injection analysis. *Anal. Chem.* **1989**, *61*(7), 674–677.
2. Okamoto, Y.; Murohashi, H.; Wake, S. Detection of aqueous fluoride with a high-power microwave-induced helium plasma at atmospheric pressure. *Anal. Sci.* **2001**, *17*(Supplement), i967–i970.
3. Okamoto, Y.; Yasukawa, N.; Fujiwara, T.; Iwamoto, E. Determination of fluoride ion in aqueous samples by inductively coupled plasma atomic emission spectrometry with tungsten boat furnace vaporiser. *J. Anal. At. Spectrom.* **2000**, *15*(7), 809–811.
4. Jankowski, K.; Jackowska, A.; Mrugalska, M. Direct spectrometric determination of total fluorine in geological materials by continuous powder introduction into helium microwave induced plasma. *J. Anal. At. Spectrom.* **2007**, *22*(4), 386–391.
5. Okamoto, Y. Determination of fluorine in aqueous samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). *J. Anal. At. Spectrom.* **2001**, *16*(6), 539–541.
6. Tafu, M.; Kagaya, S.; Chohji, T. A separation method for simplified determination of fluoride by using calcium phosphate. *Anal. Sci.* **2001**, *17*(Supplement), i753–i756.
7. Hashitani, H.; Okumura, M.; Fujinaga, K. Effective preconcentration method for fluoride ions from dilute aqueous solution by activated carbon loaded with zirconium. *Fresenius Z. Anal. Chem.* **1985**, *320*, 774.
8. Venkateswarlu, P.; Sita, P. A new approach to the microdetermination of fluoride. Adsorption-diffusion technique. *Anal. Chem.* **1971**, *43*(6), 758–760.
9. Yuchi, A.; Matsunaga, K.; Niwa, T.; Terao, H.; Wada, H. Separation and preconcentration of fluoride at the $ng\,mL^{-1}$ level with a polymer complex of zirconium(IV) followed by potentiometric determination in a flow system. *Anal. Chim. Acta* **1999**, *388*, 201–208.
10. Sugimae, A.; Skogerboe, R. K. Direct emission spectrographic determination of fluoride in geological materials by formation and excitation of calcium fluoride in a direct current arc. *Anal. Chem.* **1979**, *51*(7), 884–888.
11. Barnett, N.; Beere, H.; Ebdon, L.; Fairman, B. Chemical generation of silicon tetrafluoride with direct current plasma atomic emission spectrometry for the determination of fluorine. *J. Anal. At. Spectrom.* **1989**, *4*(8), 805–806.

12. Bayon, M. M.; Garcia, A. R.; Alonso, J. I. G.; Sanz-Medel, A. Indirect determination of trace amounts of fluoride in natural waters by ion chromatography: A comparison of on-line post-column fluorimetry and ICP-MS detectors. *Analyst* **1999**, *124*(1), 27–31.
13. Jankowski, K.; Jackowska, A.; Łukasiak, P. Determination of precious metals in geological samples by continuous powder introduction microwave induced plasma atomic emission spectrometry after preconcentration on activated carbon. *Anal. Chim. Acta* **2005**, *540*, 197–205.
14. Boumans, P. W. J. M. Detection limits and spectral interferences in atomic emission spectrometry. *Anal. Chem.* **1994**, *66*(8), 459A–467A.